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Literature reviews of each research area in WP 1

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ABSTRACT

This document contains the Literature Reviews of the Early Stage Researchers active in Work Package 1 of the REFLOW European Training Network.

Phosphorous is an essential nutrient for all living organisms but in order to meet an ever-increasing demand for efficiency in modern industrial food systems it is administered at levels far in excess of biological requirements leading to very high P leakage, with downstream environmental consequences. The EU Circular Economy initiative along with the revised fertilizer regulations provide an opportunity for industrialised food production systems such as the dairy processing industry to play a key role in the recovery and recycling of phosphorous and enabling more sustainable, efficient food production by closing the P cycle while increasing EU resilience to future disruption to P supply chains. The waste sludge from the dairy processing industry is rich in P and represents a valuable source of recycled P, however due to the variety of dairy food products and production systems there is no single process that is going to recover and recycle P recycling from dairy processing waste (DPW).

What is required is the development of several technologies which can integrate and be adapted into processes which can be used to recover, concentrate and recycle P rich ingredients for incorporation into fertilizers. The first steps in any P recycling is to capture and concentrate the P from the dairy wastewater into a sludge using phosphate accumulating organism to avoid the use of heavy metals or other chemicals. This sludge can then be thermochemically treated using either combustion to produce an ash which can be transformed into phosphoric acid fertilizer products or into through hydrothermal carbonisation for the recovery of phosphate salts and a solid P-rich hydrochar which can be used as fertilizer ingredients.

INTRODUCTION

This document contains the Literature Reviews of the Early Stage Researcher Fellows active in Work Package 1 of the REFLOW European Training Network. The overall objectives for this work package in terms of scientific and technological objectives are:

1. To achieve removal of up to 90% of soluble P from dairy effluent streams using enhanced biological P removal rather than chemically using alum or iron salts, in order to concentrate the P-rich bio-solids.
2. To mineralise and release P from P-rich bio-solids as a sterile substrate using thermochemical processes such as fluidised bed mono-incineration (<850°C) or Hydrothermal Carbonisation (<350°C).
3. To extract and recover heavy-metal-free, water-soluble phosphate salts or phosphoric acid, from the mineralised phosphrous in order to create new REFLOW fertilizers.

The literature reviews cover the topics directly related to these objectives and provide the Fellows with the essential background knowledge and current scientific state-of-the-art in order to clearly define their individual research questions and hypotheses for testing. The Fellows will prepare technical reviews for publication from this review document.

Phosphorous (P) is essential for life, but it is a finite resource. The industrialization of food production in order to feed a rapidly expanding population is giving rise to serious leakage of P through the global agricultural food system. This is particularly the case in the dairy industry, where losses of P cause environmental damage and ultimately put food safety at risk. The production of dairy products such as cheese and yogurt gives rise to P-rich dairy processing waste (DPW). The dairy industry is the EU's largest industrial food wastewater contributor and one of the main sources of P-rich industrial effluent. The abolition of EU milk quotas (2015) resulted in a 2.8% annual growth in milk production with a corresponding increase in DPW. Since 2014, phosphorous has been included in the list of EU critical raw materials due to its importance to the EU agri-food sector. The EU has no significant phosphate mines and rock P is concentrated in geopolitically sensitive regions. The fertilizer industry is the largest user of P (1.1 million tonnes p.a) therefore alternative sources to rock phosphate are urgently needed. The EU, through its Circular Economy Package (2016), prioritized the recovery and safe reuse of plant bioavailable P from food and municipal waste streams in order to add resilience in the event of disruption of supply while simultaneously mitigating the environmental consequences of P leakage.

To date, finding a solution to reusing P from DPW, other than direct land spreading of dairy wastewater sludge, has been hampered by a lack of available technology, suitably trained personnel and a market for the products. To stimulate innovation in technologies for producing substitutes for mined phosphate rock from P-rich wastes, the EU has implemented changes to the Fertilizers Regulations, which permit CE labelling of waste-based fertilizers in order to ease their access to the single market. This opens opportunities for the dairy processing industry to innovate by adapting technologies and new waste management strategies to minimize P leakage while benefiting from emerging market opportunities. To ensure the long-term economic and environmental sustainability these non-mineral fertilizer products will need to provide plant crops with required nutrients and should not negatively impact on the environment or adversely affect the safety of food or animal feedstuff.

Approximately 0.6Mt per annum of recoverable P, equivalent to 43% of the rock P currently applied to EU crops, is not being recaptured. Each tonne of recovered and reused P means: (i) less aquatic and atmospheric pollution; (ii) less depletion of finite reserves (P); (iii) Reduced environmental pollution associated with mining, processing and transport of P; (iv) diversification of nutrient supply thereby reducing reliance on imported phosphate rock. The most promising substrates for recovery of P are animal manures, municipal sewage waste and food chain waste, with recovery of P from food chain waste especially dairy processing wastewater currently the least developed. The dairy industry generates 1-4m^3 of wastewater per tonne of milk processed, depending on the final product (e.g. milk, yogurt etc.). P content in DPW is up to 640 g/m^3 corresponding to 0.02 Mt of recoverable P from EU milk factories. After treatment the effluent water is returned to rivers and the sludge mostly applied to agricultural soils, but application rates are not well matched to crop nutrient requirements. Some EU Member States are reluctant to reuse sludge as (a) there is often insufficient knowledge and specification of the plant-available nutrients present when applied to land (b) there are concerns about possible pathogens, pharmaceuticals and complex organic compounds which could threaten plant and long-term soil health.

Due to its complexity, there is no single process that is going to transform P recycling from DPW. What is required is to push several activities to their potential, in line with the goal of the Circular Economy initiative. Several P recovery processes have been investigated over recent years, however, very few are operating at full-scale or even as pilot plants with only one for DPW. The first step in any P recycling is to capture and concentrate the P from the dairy waste water. Enhanced biological phosphorous removal (EBPR) is key to achieving this, using polyphosphate-accumulating organisms (POAs) to uptake P from the wastewater and concentrate it in a bio-solid. EBPR bio-solids have 5-7% P compared with 1-2% in non-EBPR sludges. Dairy waste is a suitable candidate for EPBR due to its high COD:P (Chemical Oxygen Demand: Phosphorous) ratio (>40). EBPR requires alternating anaerobic and aerobic/anoxic conditions with the amount of phosphate taken up by POAs exceeding that released anaerobically, giving net P accumulation in the bio-solids. A critical challenge for EBPR is to control the growth of glycogen accumulating organisms (GAOs), which can also thrive under alternating anaerobic and aerobic/anoxic conditions competing with POAs for the limited carbon in wastewater. The volatile fatty acid (VFA) composition of wastewater is a key influence on the PAO/GAO competition, as is temperature. Poor control of operational parameters is one of the most common causes of EBPR failure. The efficiency of EPBR depends on environmental and operational parameters e.g. temperature, internal recycling time mode, hydraulic (HRT) and solids (SRT) retention times. It is key to the application of EBPR to dairy wastewater that optimised process conditions are established and in order to limit GAO proliferation.

Anaerobic digestion (AD) facilitates the release of P from the biodegradable fraction of waste, with organic P hydrolyzed to soluble P. This can form insoluble salts or adsorbs onto the solid digestate. AD is not widespread in the dairy industry due to problems of slow reaction, which requires longer HRTs. Anaerobic microorganisms grow more slowly than aerobic ones, consequently biomass retention (BR) is critical for high-rate anaerobic treatment of wastewaters. Granule and biofilms are the traditional way of achieving BR, however, under the specific conditions found in DPW, such as high salinity typically found in dairy wastewaters they do not work well. Anaerobic membrane reactors (AnMBRs) can operate under these conditions, significantly improving anaerobic treatment. To date only bench scale investigations of AnMBRs have been undertaken for DPWs. Careful selection of operating conditions such as SRT and HRT, good control of the mixed-liquor temperature, and avoidance of pH shocks are important for stable long-term AnMBR performance, as is proper selection of membrane materials.

P-rich biosolids can be either applied directly to land or mineralized and the P recovered as struvite or phosphoric acid (H_3PO_4). There is evidence that P supplied as EBPR biosolids is as effective for crops as mineral P but biosolids are bulky to transport, require specialist spreading equipment and have low %P compared to mineral fertilizer. Some reports suggest that AD decreases P availability for plants. Direct application also carries the risk of contamination either from pathogens, heavy metals or persistent organic pollutants (POPs). Sterilization and POP destruction can be achieved thermochemically by hydrothermal carbonization or incineration with subsequent P recovery as H_3PO_4 or struvite. P is non-volatile and is preserved in the ash after incineration with lower temperature incineration (combustion) shown to improve the P plant availability of the ash. Fluidized bed combustion (FBC) has a bed temperature typically between 750°C and 850°C. Most of the P and K, and heavy metals are retained in the fly ash which contain up to 12% P. An assessment of the viability of P recycling from mono-incinerated sewage sludge ash found P-recovery from chemical-P wastewater treatment more challenging than from EBPR sludges due to Fe/Al-rich ashes. To enhance the release and transformation of P during FBC of dairy bio-solids it is important to understand the role of temperature and stoichiometric oxygen to P-ash chemistry.

Hydrothermal carbonization (HTC) is a low temperature (<250^{o}C) alternative thermochemical process typically used for treating wet wastes producing a hydrochar (HC) and a liquor (HCL). Understanding of the effects of HTC processing conditions on P transformation within DPW streams opens the potential of two P recovery product streams (i) a P rich solid hydrochar and (ii) the liquor (HCL) from which P rich mineral salts such as struvite can be recovered.

Bioaccumulation of P from organic rich wastewater and drying to a P-rich biosolid fertilizer (ESR1)

A systematic literature review was performed to identify papers which describe the experience in applying enhanced biological phosphorus removal and biodrying technologies on wastewater, both municipal and agro industrial. Major research trends were highlighted, and knowledge gaps were revealed and emphasized as much needed research lines in order to optimize and bring up the opportunity of scaling up the processes. The focus was set at phosphorus discharges from dairy processing wastewater and the sludge produced as a result of its treatment aiming to a further valorization of the obtained bio product. Particularly for phosphorus, circular economy framework establishes a significant chance for optimizing its recovery from wastewater. Although originally considered a residue, produced sludge can be used as a source of energy or resources, thus replacing an equivalent amount of materials/energy that would otherwise need to be produced from non-renewable resources with considerable environmental impacts. This review will analyze the opportunity of reusing these products as biofertilizers as the main objective.

Results show that even though the proposed technologies have literature records for the last years, the specific application for dairy processing wastewater and the objective of using phosphorus rich products as fertilizers is not so thoroughly studied. Moreover, coupling with this phosphorus recovery technology, the biodrying process for sludge emerges as novel and promising alternative for nutrient recovery. Literature review has highlighted the favorable aspects of this technology regarding energy consumption and short residence times. Nevertheless, it is necessary to determine optimal biodrying operating conditions to allow bio generated products to be effectively and economically used, to remove as much water as possible in as little time as possible while maintaining high nutrient levels.

All in all, the proposed ESR1 research will provide significant arguments regarding the technical and environmental feasibility for scaling up the process for sustainable applications.

INTRODUCTION

This report constitutes the first deliverable of the project REFLOW (phosphorus recovery for fertilizers from dairy processing waste - DPW), a project that between January 2019 and December 2022 aims to (a) develop and demonstrate processes for the recovery and reuse of phosphorous (P) products from dairy processing waste (DPW) (b) establish their fertilizer value and optimum application rates through laboratory protocols and field trials, and (c) address the environmental, social, food safety and economical challenges of new proposed technologies. The project will ultimately find market driven solutions for the new processes and fertilizer products. This report is produced within Work Package 1 and focus on the literature review and state of the art of the proposed research topics. It precedes later work that will carry out empirical research on technology design and optimization. A systematic review was carried out to identify papers which describe the experience in applying the proposed technologies, and to discover the existing knowledge gaps. Search strings included varied terms for processing technologies, terms relevant to the dairy wastewater and those relevant to the biodrying technologies.

This report reviews scholarly literature, spanning several disciplines and consisting of several interrelated strands, on nutrient recovery / removal experience. Based on a quantitative and qualitative text analysis of existing publications, it provides a systematic review of how the research topic is handled in the academic literature.

As argued by Bryman (2008), the increasing popularity of the concept of systematic literature reviews is a response to internal criticism towards traditional literature reviews being characterized as either random or as mirroring the biases of the researcher and the requirements of much hyped evidence based policy making processes (Bryman, 2008; Tranfield et al., 2003). In systematic literature reviews, transparency is the key and serves as a guiding principle throughout the process. The aim of the review is explicitly stated, criteria for text selected clearly formulated and followed up upon, and results presented in a manner accessible to people beyond the core scholars of the field (Millar, 2004).

METHODOLOGY

Following PRIMSA methodology (Urrútia & Bonfill, 2010), different searches were performed in the Scopus database, one for each research tittle within the ESR1.

To begin with, for the DPW state of the art assessment, a review on latest reports on wastewater characteristics and novel treatment processes was performed. In this particular case neither a keyword frequency analysis nor an inclusion / exclusion criteria was included given the fact that the keywords “**dairy processing waste**”, its acronym “**DPW**” and “**wastewater treatment**” lead to all the relevant results needed

Then, for the “**EBPR”** and “**Biodrying”** assessment an overall review of the published papers following this inclusion / exclusion criteria was performed**:**

The initial search required that articles included in the review were studies that must: (a) be published in a peer-reviewed journal; (b) be in English language; and (c) use a relevant keyword for each of the topics addressed. To ensure novelty of the articles, a 2010-2020 temporal filter was applied, although afterwards some cross references beyond the specified time lapse were included. The keywords were determined by searching published articles to perceive what keywords were used by main authors. The keywords that appeared in most of the studies (frequency analysis; 3rd Quartile) were chosen to be the most potential ones. Once the keywords had been selected, a forward search was performed in Scopus. The number of articles containing the selected keywords retrieved was recorded.

Later, a second screening to assess eligibility against inclusion criteria was performed and then full text articles were retrieved for those that met the inclusion criteria. The inclusion criteria for the second screening required that the published peer-reviewed article meet all of the following specifications: (a) be an empirical study (i.e., not an essay, book review, letter, literature review, editorial, opinion or journalistic article); (b) discuss the addressed technology as the main topic; and (c) examine results quantitatively. Articles were excluded if any of these components was not addressed in the abstract, results, or discussion sections of the respective study. Also, additional articles meeting the inclusion criteria were found by examining the bibliographies of resources identified through the secondary screening.

Total citation count as an indication of the impact and/or popularity of a certain work was not used because it can bias the end selection in two main ways (a) it can skew the results towards older 'highly cited' publications which by definition have had more time to accumulate citations (Larivière et al., 2005) to the detriment of relatively more recent ones whose contribution may be more significant in the current research context; and (b) it may favor the selection of publications concerned with one specific topic, where the average citation count might be higher, obfuscating the importance of less 'citation-popular' ones in the same research field. The latter may occur particularly relevant if the topics are smaller and/or newer, as could be the case with emerging fields (Quang et al., 2019).

1 Enhanced Biological Phosphorous Removal (EBPR) And Simultaneous Nitrogen Removal (SNPR)

The initial significant keyword definition was carried out after the search of "EBPR" AND "nutrient removal" in the Tittle, Keywords and Abstract of the entire Scopus database (Every "Access type" and "Year")[1]. This search resulted in 574 document results representing 4748 author's keywords. Frequency analysis was performed. Relevant keywords were detected, and synonyms were included for the definitive search string. Also "confusing" keywords which appeared in a significant number of publications but leaded to studies addressing different research topics were identified and included in the search criterion as an AND NOT, thus indicating these keywords must be excluded from the definitive search. The final search string resulted as follows:

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[1] Search performed during March 2020

enhanced biological phosphorus removal	**AND**	phosphorus accumulating organisms	**AND NOT**	modelling
OR		**OR**		**OR**
biological nutrient removal		glycogen accumulating organisms		case study
OR		**OR**		**OR**
biological removal		denitrifying phosphorus accumulating organisms		wetland
OR				**OR**
nutrient recovery				seawater
OR				**OR**
phosphorus recovery				gold
				OR
				full scale

The search strategy was based on a broad search. Even though a broad search resulted in the inclusion of many papers which were later deemed irrelevant, it reduced potential biases that a narrower search would have produced, in other words, it increased the retrieval of relevant studies. Irrelevant studies were instead eliminated during the review of articles by inclusion/exclusion criteria.

This search returned 435 relevant articles.

Following, a selection of the total registries was made in attempt to narrow the review to those relevant articles by analyzing the tittles (stage 1) and the abstracts (stage 2). The workflow can be observed in **Figure 1.** The final selection consisted in 77 records relevant to the research topic for complete full text analysis for finding research trends and uncovering knowledge gaps.

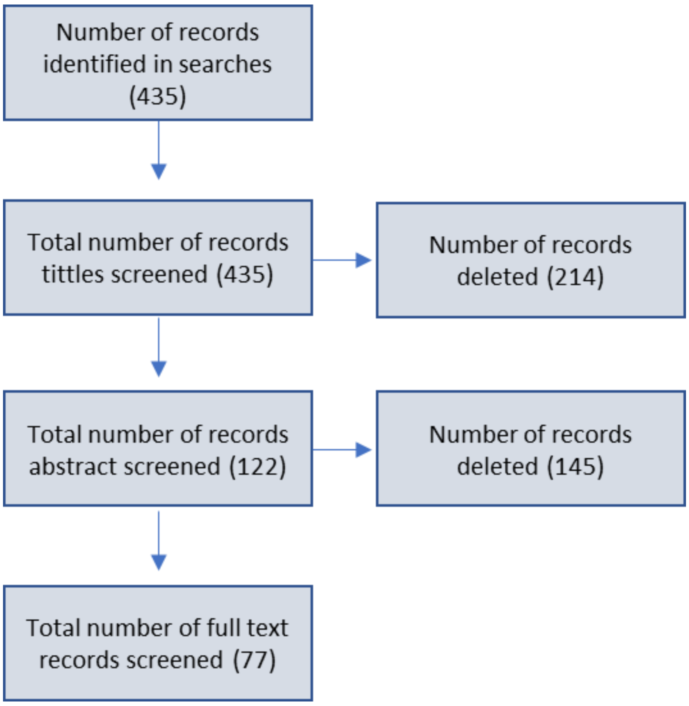

Figure 1: Screening workflow for records relevant to EBPR in SCOPUS

2 Biodrying

The initial significant keyword definition was carried out after the search of “biodrying” in the Title, Keywords and Abstract of the entire Scopus database (Every “Access type” and “Year”)[2]. This search resulted in 148 document results representing 1384 author’s keywords. Frequency analysis was performed. Relevant keywords were detected, and synonyms were included for the definitive search string. The review will mainly focus on sludge biodrying antecedents. Municipal solid waste and other solid waste matrixes are thoroughly reviewed elsewhere (Yang et al., 2017).

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[2] Search performed during March 2020

The final search string resulted as follows:

biodrying	**AND**	waste
		OR
		sludge
		OR
		sewage

The search strategy was based on a broad search, particularly with the inclusion of the term “waste” which returned many records related to municipal solid waste. Even though this broad search resulted in the inclusion of many papers which were later deemed irrelevant, it allowed to investigate on key operational parameters used in different solid matrixes.

This search returned 121 relevant articles.

In the same way as for EBPR review, a selection those relevant articles by tittles (stage 1) and abstracts (stage 2) was performed. The workflow can be observed in **Figure 2.** The final selection consisted in 29 records relevant to the research topic for complete full text analysis.

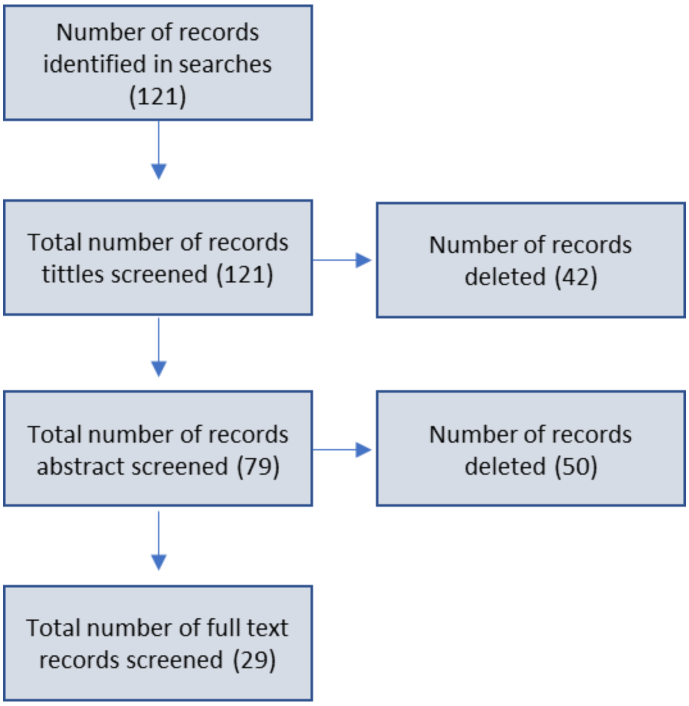

Figure 2: Screening workflow for records relevant to biodrying in SCOPUS

3 Dairy Processing Waste (DPW)

The industrialization of food production, to feed a rapidly growing population, is leading to a significant loss of the stock of P worldwide. At the same time, P discharges into surface waters cause environmental impacts that must be avoided. Particularly, dairy products manufacturing like milk, cheese and yogurt results in P rich waste (DPW). As a whole, the dairy industry is the largest contributor of P rich industrial wastewater and one of the main sources of P rich effluents (Carvalho et al., 2013; Vourch et al., 2008). The dairy industry includes the transformation of raw milk into pasteurized and sour milk, yogurt, hard, soft and cottage cheese, cream and butter products, ice cream, milk and whey powders, lactose, condensed milk, among other products. With the rapid industrialization observed in the last century (Nadais et al., 2010) and the growing rate of milk production (around 2.8% per annum), dairy processing is usually considered the largest industrial food wastewater source, especially in Europe (Britz et al., 2006; F. Carvalho et al., 2013; Cristian, 2010; Karadag et al., 2015) representing one of the main generators of pollution of rivers, lakes, groundwater and aquatic ecosystems. Hence, if management of DPW does not improve, the leakage of nutrients and other elements will continue to intensify, leading to environmental problems such as eutrophication, acidification and loss of aquatic life, environmental toxicity and risks to food safety derived from pesticide residues and others with the presence of heavy metals (Corominas et al., 2013).

Dairy wastewater treatment exhibits some particular challenges, for instance the effluents originated from various production technologies are not discharged simultaneously, thus forming a stream with wide qualitative and quantitative variations (Nadais et al., 2010). Furthermore, intensive effluent volumetric variations in time are commonly observed. Daily and hourly changes are the consequence of washing the equipment and floors as the final step in every process cycle, also, seasonal variations can be attributed to a higher dairy plant load in summer than in winter (Janczukowicz et al., 2008). Dairy effluents are distinguished by their relatively increased temperature, high organic content (Farizoglu et al., 2007; Sarkar et al., 2006; Tawfik et al., 2008) and a wide pH range, which requires special treatment in order to eliminate or reduce environmental damage (Britz et al., 2006).

The P in wastewater comes mainly from the handling activities of inputs as well as of finished products. Dairy processing effluents mostly include: milk or milk products lost in the technological cycles (spilled milk, spoiled milk, skimmed milk and curd pieces), starter cultures used in manufacturing, by-products of processing operations (whey, milk and whey permeates), contaminants from the washing operations, effluents from sanitary infrastructure; spills from equipment damage or operational problems and various additives introduced in manufacturing (Doble & Kumar, 2005; Schifrin et al., 1981; Tawfik et al., 2008; Watkins & Nash, 2014). Milk loss in wastewater is around 0.5–2.5% of process milk, but values of up to 3–4% have been reported (Cowi, 2000; W. Janczukowicz et al., 2008). Each effluent has different characteristics, according to the product obtained, climate, operating conditions and types of cleaning-in-place also influence the dairy effluents characterization (Pattnaik et al., 2008).

So far, finding a solution for P reuse from DPW, other than direct land spreading of dairy wastewater sludge, has been hampered by lack of available technology, suitably trained personnel and a suitable market for the products. To stimulate innovation in technologies for producing substitutes for mined phosphate rock from P rich wastes, the EU has proposed changes to the fertilizers regulations, which would permit CE labeling of waste based fertilizers in order to ease their access to the single market (EC, 2015). This opens opportunities for the dairy processing industry to innovate by adapting technologies and new waste management strategies to minimize P leakage while benefiting from emerging market opportunities. To ensure the long term economic and environmental sustainability of these non-mineral fertilizer products, they will need to provide plant crops with required nutrients and should not negatively impact the environment or adversely affect the safety of food or animal feedstuff.

Currently, dairy wastewaters treatments include the application of mechanical, physicochemical and biological methods. Mechanical treatment is necessary to equalize volumetric and mass flow changes and to reduce parts of the sedimentable solids (i.e. primary settling tanks and or clarifiers). Physicochemical processes are effective in the removal of emulsified compounds, but reagent addition and/or energy consumption increases water treatment costs (i.e. Dissolved Air Flotation, coagulation-flocculation methods). Another disadvantage is the very low elimination of soluble chemical oxygen demand (COD). Therefore, biological wastewater treatment systems are preferred due to the highly biodegradable contaminants contained in DPW (Cristian, 2010; Demirel et al., 2005; Schwarzenbeck et al., 2005; Umran & Oze, 2013). Contaminated water, including sanitary activities, reaches 50–80% of the total water consumed in a dairy factory.

All in all, dairy wastewater can be divided into the following categories: (a) processing water: formed in the cooling of milk in special coolers and condensers, as well as condensates from the evaporation of milk or whey; (b) cleaning wastewater: usually coming from washing equipment which is in direct contact with milk or dairy products, which also includes milk and product spillage; (c) sanitary wastewater: found in lavatories, shower rooms, etc. Dairy wastewater characteristics from different processes has been reviewed by Slavov (2017) and can be found in **Table 1**.

It is to be noted that cheese whey is the most contaminated waste generated in the production of cheese (Rajeshwari et al., 2000), thus the particular treatment alternatives are not included in this review but can be found in Prazeres et al. (2012).

Dairy manufacturing has a strong impact on the environment, producing large volumes of wastewater with high organic and nutrient loading and extreme pH variations. The changing nature of dairy effluents makes the treatment a difficult task. Without an appropriate treatment, these effluents pose serious environmental hazards (Rivas et al., 2011). This requires the application of effective and cheap wastewater treatment procedures which ensure freshwater preservation (Britz et al., 2006; Nadais et al., 2010). There are various dairy effluent treatment strategies available. This report will focus on the available biological treatment alternatives, particularly in EBPR technology for recovering P and removing N from wastewater complex streams.

Table 1: Composition of milk processing effluents (adapted from Slavov, 2017)

Effluent	g COD/L	g TS/L	g N/L	g P/L	Reference
Mixed dairy	0.5–10.4	0.71–7	0.01–0.66	0–0.6	Britz et al., 2006; Carvalho et al., 2013; Cristian, 2010; Demirel et al., 2005; Doble & Kumar, 2005; Janczukowicz et al., 2008; Karadag et al., 2015; Sarkar et al., 2006; Schifrin et al., 1981; Schwarzenbeck et al., 2005; Tawfik et al., 2008; Watkins & Nash, 2014
Milk reception	2.54	–	–	–	Janczukowicz et al., 2008
Dairy/sewage	2.04–4.73	–	–	0.02–0.03	Tawfik et al., 2008
Fluid milk	0.95–2.4	–	–	–	Demirel et al., 2005
Yoghurt	6.5	–	–	–	Umran & Oze, 2013
Butter	8.93	–	–	–	Tsachev, 1982
Ice cream	5.2	3,9	–	0.014	Janczukowicz et al., 2013; Tsachev, 1982
Cheese	1–63.3	1.92–53.2	0.018–0.83	0.005–0.28	Britz et al., 2006; Demirel et al., 2005; Janczukowicz et al., 2008; Schifrin et al., 1981; Tsachev, 1982; Watkins & Nash, 2014
Cottage cheese	17.65	–	–	–	Janczukowicz et al., 2008
Cheese whey	50–102.1	55–70.9	0.2–1.76	0.12–0.53	Demirel et al., 2005; Doble & Kumar, 2005; Prazeres et al., 2012; Watkins & Nash, 2014
Hard cheese whey	73.45	–	–	–	Janczukowicz et al., 2008
Soft cheese whey	58.55	–	–	–	Janczukowicz et al., 2008
Cottage cheese whey	79	68	2	–	Carvalho et al., 2013
Cheese whey wastewater	–	–	–	0.64	Britz et al., 2006
Milk permeate	52.94–57.46	11.61–15.39	0.3–0.4	0.35–0.45	Karadag et al., 2015; Nadais et al., 2010
Condensate	–	–	0.0006	0.0001	Watkins & Nash, 2014
Washing wastewater	14.64	–	–	–	Janczukowicz et al., 2008

4 Ebpr For P Recovery

EBPR was developed during the 1970s (Barnard, 1975; Yuan et al., 2012) and is currently used at some full scale wastewater treatment plants (WWTP). Having almost 50 years of research, this technology is already matured and stablished for treating different wastewaters streams. Hence, this review will not include a full description of the control parameters (i.e. COD content, volatile fatty acid (VFA) content, cation concentration, phosphorus load, pH, HRT, SRT, among others) which are thoroughly studied elsewhere (Dassanayake & Irvine, 2001; Mulkerrins et al., 2004; Serafim et al., 2002), nonetheless, **Table 3** reviews some of the key operational parameters of the process.

4.1 Process Description

EBPR relies on polyphosphate accumulating organisms (PAOs) and/or denitrifying PAOs (DPAOs) to accumulate P intracellularly as polyphosphate (poly-P) granules, without the need or requirement for chemical precipitants (Oehmen et al., 2007; Wong et al., 2013).

The process is enabled by alternating anaerobic and aerobic conditions; the first step is to carry out the anaerobic process, during which the organisms in the activated sludge hydrolyze poly-P and release P from cells in the form of orthophosphates (PO_4^{3-}), quickly and efficiently absorbing simple organic compounds, primarily short chain volatile fatty acids (VFAs) from the environment and storing them in the form of polyhydroxyalkanoates (PHAs). VFAs are used to replenish the cell's stored PHA for subsequent utilization in the aerobic zone but they can't be used for cell growth during the anaerobic phase (Jeyanayagam, 2005). The required energy for PHA accumulation and transport through the cell membrane is provided mostly from the hydrolysis of poly-P and partly from glycogen (Lopez-Vazquez et al., 2008).

PAOs exhibit advantages that allows them to outcompete other microorganisms There is a growing understanding of the biochemical mechanisms associated with PAOs favorable metabolism which are crucial for EBPR. Although not fully understood, operating conditions, including pre-requisites for metabolism, such as wastewater COD/P, diversity of VFAs, pH, temperature, glycogen and electron acceptor requirements are being adjusted to promote the growth and proliferation of PAOs (Bunce et al., 2018).

Subsequently, in the aerobic or anoxic zone the stored PHAs are used as a carbon and energy source to re sequester phosphate released during the anaerobic phase and any additional phosphate present in the wastewater to recover the intracellular poly-P levels (Jeyanayagam, 2005; McCullagh, 2013). This results in the net removal of orthophosphate from the influent. PAOs also use PHAs to grow, to cover the aerobic maintenance energy needs of PAOs and to replenish the intracellular glycogen pool (Oehmen et al., 2007). Net P removal is accomplished by wasting sludge at the end of the aerobic phase when the sludge contains high levels of poly-P (Karst et al., 2016; McCullagh, 2013) **Figure 3** shows a simplified scheme of PAOs metabolism.

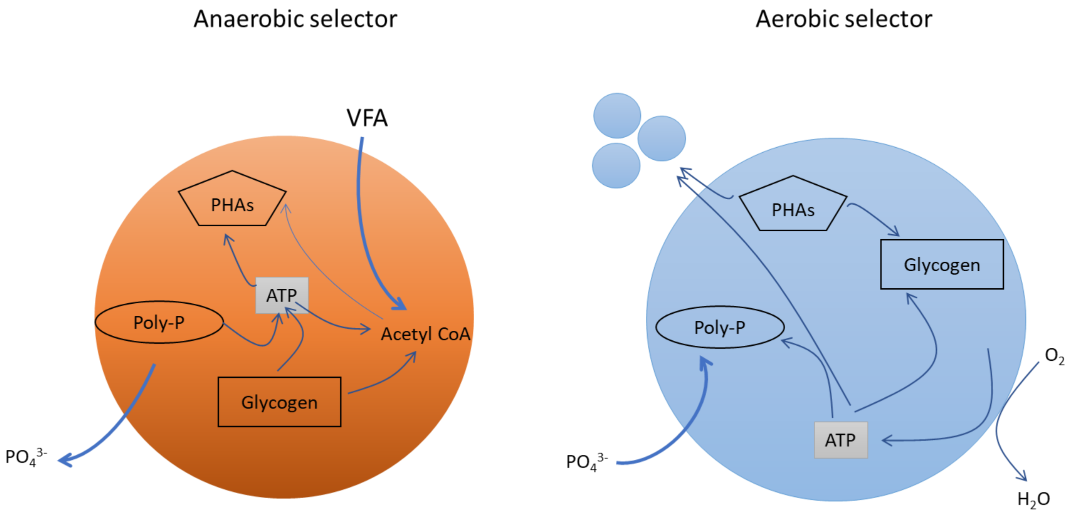

Figure 3: Schematic diagrams of the anaerobic (left) and aerobic (right) PAO metabolism in EBPR process. Adapted from Bunce et al. (2018).

After more than 40 years of study, attention has been put into two main aspects of the technology development and the search for effectiveness and efficiency: **(a)** correlation of operational conditions with process performance, theoretical frameworks for mechanisms and the identity and competition between the responsible organisms; and **(b)** EBPR process intensification, optimization and further justification for the technology application (Quang et al., 2019).

The literature review has shown that some topics are gaining attention in the last 10 years. The main research lines includes VFA production, simultaneous N and P removal, P recovery, effect of dissolved oxygen (DO), temperature and carbon sources on P recovery and N removal rates, competition between PAOs and glycogen accumulating organisms (GAOs), use of aerobic granular sludge for ameliorating the treatment`s efficiency and stability, genetical approaches towards identification of PAO/DPAO cultures responsible for the removal process and population studies of microbial ecology.

Latest advances in EBPR knowledge consist in addressing novel operational variables such as salinity (He et al., 2020; Wang et al., 2019), sludge arrangement and stability, and microbial community composition (de Graaff et al., 2020; Nielsen et al., 2019) as well as rethinking the traditional operational parameters (hydraulic retention time (HRT), solid retention time (SRT), and DO) for reaching effectiveness and efficiency maintaining low operational costs as well as stable effluent quality.

Up to date research lines are mainly focused on simultaneous N removal and P recovery including post-endogenous denitrification (Gong et al., 2019; Zhao et al., 2019) and for that purpose novel reactor designs and operational conditions are being studied.

Following, the main research trends spotted in the literature review are presented and developed to underpin the main findings and to highlight the still existing knowledge gaps.

4.2 Process Performance

4.2.1 PAOs vs GAOs

One of the traditional and most challenging aspects towards accomplishing P removal levels is represented by GAOs (Lopez-Vazquez et al., 2008) which compete with PAOs for carbon substrate (Oehmen et al., 2007; Yuan et al., 2012). GAOs can function under aerobic or anaerobic conditions (Zheng et al., 2013) and are found widely in EBPR processes (Burow et al., 2007).

Under anaerobic conditions, GAOs take up VFAs (particularly acetate) at the expense of energy (ATP) generated from the hydrolysis of their intracellular storage product glycogen. The acetate assimilated is further activated to acetyl-CoA with additional consumption of ATP. Later, under aerobic conditions, a fraction of the anaerobically synthesized PHA is oxidized, yielding energy for the conversion of PHA to glycogen and biomass (growth). **Figure 4** shows the simplified metabolic pathway for these microorganisms (Dai et al., 2008).

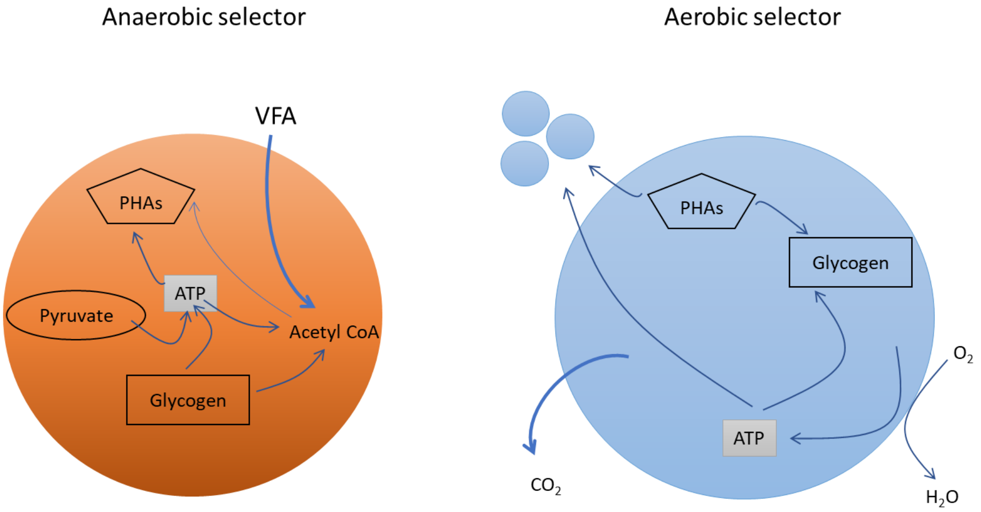

Figure 4: Schematic diagrams of the anaerobic (left) and aerobic (right) GAO metabolism. Adapted from Dai et al. (2008)

Studies have focused in optimizing the EBPR process to outcompete GAOs in favor of PAOs. Lab and pilot scale exhibit significant differences in microbial communities, thus showing the need of research over the most important selectors in each work scale. Operational parameters such as DO, pH, temperature, carbon sources (in particular, propionate has been suggested as an important selector for PAO over GAO (Lu et al., 2006; Wang et al., 2012) at lab and pilot scale), COD/P ratio, SRT, HRT and toxic substances are widely investigated (Carvalheira et al., 2014; Lopez-Vazquez et al., 2008; Nadais et al., 2010; Oehmen et al., 2005; Qiu et al., 2013; Shen & Zhou, 2016). While it is expected that high P/COD ratios select for PAOs, complete elimination of GAOs from the system has not been achieved with this ratio alone, and the precise effect of its manipulation on the population balance has not been quantified. Research in this aspect focus on PAOs selection in systems starved of carbon substrates and at low DO concentrations (Carvalheira et al., 2014; Tu & Schuler, 2013). Nevertheless, some recent studies (Nielsen et al., 2019) state that GAOs do not appear to be a real problem in full scale EBPR systems. Particularly, they claim that there are no reports to suggest that the GAOs should be a real problem in outcompeting PAOs. Instead they hypothesize that in real wastewater treatment systems, GAOs will only be abundant when VFAs or fermentable substrates are present in surplus (high C:P ratio), and that is largely determined by the amount of available P.

In a recently published paper, Meng et al. (2020) investigated the competition mechanism between PAOs and GAOs under the glycogen accumulating metabolism (GAM) pathway. They found that low acetic acid concentration made the GAM of PAOs outcompete GAOs in high C/P ratio (100:1). They showed that PAOs had higher specific surface area and lower nucleic acid content than GAOs, and high C/P promoted GAM rather than GAOs growth, possibly explaining PAOs dominant growth.

The relationship between EBPR-SBR operational stability and microbial diversity remains an evolving question which is addressed in various recent studies (Bassin et al., 2012; Huang et al., 2015; Kapagiannidis et al., 2011; Lee & Yun, 2014; Wang et al., 2015; Wong et al., 2018; Zhang et al., 2014). Studies using fluorescence in situ hybridization (FISH) to assign in situ storage patterns to specific PAOs clades and Raman micro spectroscopy has recently been applied to monitor glycogen, PHAs, and poly-P in microbial cells from EBPR systems (Majed et al., 2012; Majed et al., 2009; Majed & Gu, 2010). Deeper and specific studies on functional correlations between microbial cultures and EBPR performance needs to be performed.

4.2.2 Simultaneous N and P removal

Regarding simultaneous N and P removal processes, latest research interest consists in combining EBPR with simultaneous partial nitrification endogenous denitrification (SPND) and post-partial denitrification process, which involves the action of DPAOs in an anoxic stage (Gong et al., 2019; Li et al., 2019; Zhao et al., 2019). Traditional EBPR faces the problem of COD limitation due to the competition between PAOs and heterotrophic denitrifier bacteria. In addition to establishing the identity and metabolism of responsible microbial communities, the optimization of available COD use and alternative N removal processes have been the major lines of research (Obaja et al., 2003).

The initial findings established, by using molecular methods able to quantify this population directly, the existence of DPAOs along with the necessary operational parameters of anoxic P removal. It appears to be two groups of PAOs: those only capable of using oxygen, and those able to use both oxygen and nitrate as electron acceptors: DPAOs (Kerrn-Jespersen et al., 1994; Zaman et al., 2019).

DPAOs can take up carbon sources anaerobically, particularly VFAs, and store them as PHAs through the release of P and degradation of glycogen. Then at the anoxic stage, DPAOs utilize NO_3^- or NO_2^- (instead of oxygen) as electron acceptors to provide energy for P uptake (Carvalho et al., 2007; Zeng et al., 2003). High influent NH_4^+ wastewater could produce sufficient NO_3^- concentration to meet the need of electron acceptor for P removal at the anoxic phase in DPAOs process. Zhang et al. (2018) achieved an average of 95.7% COD, 98.2% TP and 97.8% N removals in 6 hours cycle using SBR systems.

Provided the correct microbiologic culture and operational parameters, DPAOs could achieve simultaneous N and P removal while reducing COD, oxygen consumption, as well as sludge significantly (Kapagiannidis et al., 2011). The importance of influent feed characterization and empirical knowledge for model calibration is also highlighted and deeper research is needed.

Concerning the role of nitrite (NO_2^-) on the efficiency of integrated N and P removal systems, although anoxic P uptake can occur regardless of whether the electron acceptor present is NO_3^- or NO_2^-, the ratio of P to N removed has been reported to increase along with the initial concentration of NO_3^-, whereas it decreased slightly with NO_2^- (Ahn et al., 2001). Moreover, it was suggested that the presence of nitrite inhibits both aerobic and anoxic (denitrifying) phosphate uptake, particularly the aerobic phosphate uptake was more affected than anoxic phosphate uptake, and that the presence of nitrite could be one of the factors enhancing the presence of GAO competitors to PAO for substrate in the anaerobic phase (Saito et al., 2004). However, further investigation (Zhou et al., 2008) found that the degree of inhibition was observed to correlate much more strongly with the free nitrous acid (FNA) concentration than with the nitrite concentration, suggesting that FNA, rather than nitrite, is likely the true inhibitor of the process.

On the other hand, and while the presence of NO_3^- in anaerobic conditions had been known to cause EBPR deterioration, it is unclear whether this is due to (1) the inhibitory effect of an intermediate molecule, or (2) COD limitations arising from competition for substrate with ordinary heterotrophic denitrifying bacteria. EBPR was found to be feasible even in the presence of NO_3^-, in the anaerobic zone (Guerrero et al., 2011). It has been suggested that NO_3^-, deteriorated EBPR not directly by inhibition of P release, but indirectly by inhibiting the fermentation of carbon substrates into simpler molecule (i.e., VFAs) (Fernandes et al., 2013).

Recently, Zhao et al. (2018) have presented a novel process, termed as PNEDPR (partial nitrification-endogenous denitrification and P removal) where denitrifying GAOs (DGAOs) play a central role. It is still not clear what conditions are favorable for a stable PNEDPR process, because PAOs, DPAOs, GAOs and DGAOs would compete for the limited carbon source. Compared with exogenous carbon sources, the endogenous ones are more advantageous in the post denitrification process, due to the obvious reduction in operation costs and efficient realization in deep level N removal. This method may accomplish, via combination of partial nitrification with post-endogenous denitrification in an EBPR system for advanced nutrient removal without external carbon addition.

Moreover, post-endogenous denitrification driven by DGAOs has been investigated in biofilm reactors (Vocks et al., 2005), granular sludge systems (Qin et al., 2005) and suspend sludge systems (Coats et al., 2011; Winkler et al., 2011) where stratification of the microbial community and the associated concentration gradients prevents inhibition of microbial activity, and achieved good N and P removal performance.

4.2.3 EBPR for DPW treatment

In an attempt to review the latest reactor's designs and operational parameters which are being used for DPW treatments, **Table 2** includes the review matrix of recent studies highlighting study focus, findings and possible gaps to be filled. Subsequently, **Table 3** provides the operational variables, design experimental design and % of P, N and COD removal.

Table 2: EBPR systems applied specifically to DPW. Research from 2010-2020.

Reference	Title	FOCUS	FINDINGS	GAPS
Rubio-Rincón et al., 2019	Effect of Lactate on the Microbial Community and Process Performance of an EBPR System	The effects of lactate on microbial selection and process performance of an EBPR lab scale study as lactate can be present in dairy wastewater treatment plants due to the fermentation of other organic compounds	The dominant metabolism shifted from PAM to GAM without EBPR activity. No P removal was accomplished using only lactate as C source	16s RNA amplicon analysis showed that the genera *Tetrasphaera* was the dominant organism, while a quantification based on FISH-biovolume indicated that *Ca. Accumulibacter* remained the dominant organism, indicating certain discrepancies between these microbial analytical methods
Gil-Pulido et al., 2018	Evaluation of dairy processing wastewater biotreatment in an IASBR system: Aeration rate impacts on performance and microbial ecology	Use of IASBRs , as a single tank biotreatment system for co removal of COD, nitrogen and P from synthetic dairy processing wastewater	Variation of the IASBR aeration rates, (0.8, 0.6 and 0.4 L/min), had significant impacts on the respective nutrient removal efficiencies and underlying microbial diversity profiles	Functional correlations are required between taxonomic abundance and possible contributors to nutrient removal efficiencies
Wu & Zhu, 2015	Simultaneous removal of nutrients from milking parlor wastewater using an AO2 SBR system.	Lab scale, anaerobic-aerobic-anoxic-aerobic SBR ((AO)2 SBR) to simultaneously remove biological organics, nitrogen and P from dairy milking parlor wastewater	HRT of 2.7 days with TM/TP mixing-to-process time ratios = 0.57 was the best to achieve simultaneous nutrients removal. Good correlations between pH / DO / ORP for developing real time controls	

Table 2 (Cont.): EBPR systems applied specifically to DPW. Research from 2010-2020.

Reference	Title	FOCUS	FINDINGS	GAPS
Liu et al., 2014	Polyphosphate and Glycogen Accumulating Organisms in one EBPR System for Liquid Dairy Manure.	Effect of aeration times over P removal and Microbial communities	Capability of EBPR of dairy manure and challenge conventional wisdom, since greater abundance of PAOs in EBPR system was not associated with improved P removal and greater abundance of GAOs did not indicate deterioration of the EBPR system.	Underlying mechanisms explaining different P removals related to microbiologic communities in Lab Scale possible unknown PAOs?
Janczukowicz et al., 2013	The effect of VFAs on nutrient removal in SBR with biomass adapted to dairy wastewater.	Determine the effect of VFAs on nitrates and orthophosphate removal in an SBR with activated sludge biomass adapted to process dairy wastewater	The reactor containing acetic acid was found to remove the highest amount of orthophosphate irrespective of the nitrate's concentration. Acids present in significant amount in dairy wastewaters (i.e. acetic, propionic and butyric) were more effective source of carbon in the denitrification process compared to low concentration acids	Is it the type of fatty acid applied that is responsible for the effectiveness of dephosphatation at varying nitrate:orthophosphate ratios, or whether these processes are additionally affected by the presence of microorganisms that have adapted to the specific carbon composition of the wastewater being treated.

Table 2 (Cont.): EBPR systems applied specifically to DPW. Research from 2010-2020.

Reference	Title	FOCUS	FINDINGS	GAPS
Balamane-Zizi, 2012	Biological P removal from dairy wastewater by alternating anaerobic and aerobic conditions	Determine an optimal HRT in aerobic conditions and to study the effect of VFAs (acetic and propionic acids) addition on the P release in anaerobic conditions.	Most favorable aerobic retention time was found to be 2 h with Acetic acid as a Carbon source	
Guerrero et al., 2012	Glycerol as a sole carbon source for enhanced biological P removal	Wastewaters with low organic matter content are one of the major causes of EBPR failures in full scale WWTP. This carbon source deficit can be solved by external carbon addition. glycerol is a perfect candidate since it is nowadays obtained in excess from biodiesel production	Using dairy wastewater with a low COD/P ratio confirms the feasibility of using glycerol as an external carbon source to increase P removal activity	Performance over N and COD removals must be investigated using Glycerol as a sole C source and using long anaerobic retentions times

Table 3: Operational variables, experimental design and % of P, N and COD removal

Reference	Vol (L)	Sequence	HRT (h)	SRT (days)	Carbon Source	Initial COD (mg/l)	Initial PO_4^{3-} (mg/l)	Initial NH_4^+ (mg/l)	O_2 (mg/l)	P Removal %	N Removal %	COD Removal %
Rubio-Rincón et al., 2019	2.5	AO	12	15	Lactate	400	25	28	0.91	-	-	87 - 95
Gil-Pulido et al., 2018	8	AO	96	20	-	3300	25.4	48.9	-	68 - 92 - 57	96 - 92 - 79	-
Wu & Zhu, 2015	8	AOA	60	-	-	2000	0.14	0.55	-	>95	>95	50
Liu et al., 2014	8	AO	24	4	-	2500	-	-	-	80	-	70
Janczukowicz et al., 2013	45	AO	-	17	Acetic, propionic, butyric caproic.	50	14	0.06	-	61	48	77
Balamane-Zizi, 2012	2	AO	24	-	Acetic, propionic.	4000	17.7	-	4	97	-	-
Guerrero et al., 2012	10	AO	12	20	Glycerol	355 - 455	35	20	3.5 to 4.5	>95	-	-

5 P Recovery Strategies

Circular economy framework stablishes the recovery of P for agricultural applications from wastewater. P recovery from wastewater can be achieved through concentrating P in the water stream or concentrating P in sludge for further use as biosolids.

Although a total agreement does not exist regarding the moment in which P will peak, it is certain that this resource is becoming more difficult to access and, therefore, more expensive. It is estimated that roughly 20% of the global demand for phosphate rock could be satisfied by P recovery from municipal waste streams alone. As such, there is growing interest in the technical and economic feasibility of large scale P recovery from municipal and agro industrial waste streams (Yuan et al., 2012).

5.1 Chemical Precipitation

One of the most studied recovery processes, is EBPR followed by P crystallization as struvite ($(NH_4)MgPO_4{\cdot}6H_2O$) or apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) and has been concluded be one of the most effective means of P recovery (Greaves et al., 1999). Struvite precipitates spontaneously in WWTP environments, where high concentrations of soluble P and ammonium are present. Unintentional struvite precipitation has long been recorded as a nuisance, disrupting operation of WWTP by blocking valves, pipes and pumps. This has been exacerbated by the increase of the required nutrients as a result of greater degrees of nutrient removal. As such, controlled struvite crystallization serves to alleviate routine operational problems, reduce sludge volumes by as much as 49% and recover a useful raw material (Doyle & Parsons, 2002).

Struvite and apatite represent the group of the best known P recovery technologies, since they have already been implemented in many plants, mainly in Japan (Yuan et al., 2012). Their most important advantage is the ability to obtain high quality phosphoric minerals, which can find a direct application in agriculture. Precipitated hydroxyapatite materials contain very low concentrations of heavy metals and are thus considered to be safe for the environment (Nakakubo et al., 2012). Furthermore, struvite is considered poorly soluble, which means that even in case of applying a vast amount of such fertilizer to the ground, the possibility of polluting the environment with a high load of P and enhancing the eutrophication process is low (Kataki et al., 2016; Shu et al., 2006).

However, a lot of parameters such as pH, COD, P, Mg and K content, temperature, time and intensity of aeration have a significant influence on the efficiency of the process (De-Bashan & Bashan, 2004; Havukainen et al., 2016). In many cases Mg contents are insufficient for achieving struvite precipitates and needs to be added to the wastewater stream, thus increasing operational complexity and costs. Moreover, conducting recovery from leachates does not guarantee a complete recovery of P (up to 40% recovery efficiency) or management of all process waste, including the remaining excess sludge (Biswas et al., 2009). What is more, the cost of producing 1 kg of P obtained in that way is around 1 euro which is three times higher compared to regular fertilizer prices (Weigand et al., 2012).

Recently, novel means of P recovery have been explored. For instance, instead of dosing magnesium salts at rapidly changing pH, electrolytic deposition using a sacrificial magnesium anode was shown to be an effective way to precipitate struvite at high purity, achieving a P removal efficiency of 98%, without any by-products (Kruk et al., 2014).

Within this framework, the European Commission has revised the EU Fertilizer Regulation ((EC) 2003/2003), expanding its scope to secondary raw material based fertilizing products, and resulting in the publication of the new EU Fertilizing Products Regulation ((EU) 2019/1009). There is the need of exploring the technical and market conditions for a possible legal framework for the manufacturing and placing on the market of specific safe and effective fertilizing products derived from biogenic wastes and other secondary raw materials. The STRUBIAS (STRUvite, BIochar, or incineration AShes) project has delivered a list of materials that show a substantial potential to provide safe sources of P that can constitute an alternative for the primary raw material phosphate rock for “closing the loop”, as stated by EU action plan for the circular economy. DPW is included as an input which shows a significant potential for P recovery in the form of precipitated phosphate salts (Huygens et al., 2019) even taking into account the typical cleaning agents used in the food processing industry sector (European Commission, 2006) such as: alkalis, acids, pre prepared cleaning agents containing chelating agents such as EDTA and oxidizing and non-oxidizing biocides. All in all, P rich materials must undergo a strict quality assessment in order to be acceptable for use as a fertilizer accomplishing the following three principles (Huygens et al., 2019):

(i) The use of the materials will not lead to overall adverse environmental or human health impacts.

(ii) The material shall provide plants with nutrients or improve their nutrition efficiency, either on its own or mixed with another material.

(iii) Trade on the internal market can be expected for such a fertilizing material, based on the current market and the future market and trade forecasts.

5.2 Biosolids Accumulation

Besides P precipitates, biological uptake and P concentration on biomass can be used for obtaining a P rich sludge at the same time as a water stream which achieves discharge limits. Although originally considered a residue, sludge can be used as a source of energy or resources, thus replacing an equivalent amount of materials/energy that would otherwise need to be produced from non-renewable resources with considerable environmental impacts (Fijalkowski et al., 2017).

Due to the legislation that limits landfilling and land application as sludge disposal methods, many researchers have attempted reuse and recycling sludge as possible sustainable environmental options (Smol et al., 2015). In relation to this, European Commission (2011) considers that “if waste is to become a resource to be fed back into the economy as a raw material, then, much higher priority needs to be given to reuse and recycling". Sludge reuse as raw material in different industries represents a good possibility of waste management considering the circular economy concept (Eliche-Quesada et al., 2011).

Specifically regarding the reviewed research lines, P rich EBPR sludge contains 5–7% dry weight P in contrast with normal activated sludges, which contain P in the order of 1–2% dry weight (Tchobanoglous et al., 2014). The obtained dewatered biosolids can be directly applied to the soil at a rate determined either by contaminant or nutrient content (normally N is limiting for biosolids). Plants are able to directly utilize the P as it is released by degradation of the biosolids (Yuan et al., 2012). There is research already that shows P supplied in the form of EBPR biosolids is as effective as mineral P (Erdincler & Seyhan, 2006). Biosolids can be applied in a broad range of soil pH and buffer concentrations, and with a better plant response than comparable mineral fertilizers in unproductive soils (McLaughlin & Champion, 1987).

There are various sludge forms for agriculture utilization such as dewatered sludge, dried sludge, biodried sludge, compost, digested sludge, and incineration ash and biochar (Grundmann & Maaß, 2017). Currently, in respect of fertilizer effectiveness, convenience in handling, and sanitary affairs, compost is one of the preferred forms.

Composting is defined as the biological decomposition and stabilization of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds and that can be beneficially applied to land (Haug, 1993). It is the main biological process applied to sewage sludge in Europe and is a generally accepted and highly beneficial method of stabilizing its organic matter (Oleszczuk, 2008).

According to Eurostat data form 2017, "compost and other applications" were used to treat 22% of sludge produced in Europe. Composting reduces the volume of sludge and its transporting costs, eliminates the risk of disseminating pathogens and removes mal odorous compounds. Moreover, the addition of compost to agricultural soils has the following positive effects (Gantzer et al., 2001; Taherzadeh & Richards, 2015):

(i) lead to a slow release of nutrients (95% of N is in organic form)

(ii) has a high binding capacity for organic and inorganic elements (contaminants or nutrients)

(iii) improves water storage and soil water content due to its increased water holding capacity

(iv) aids in the creation of soil agglomerates that can facilitate aeration of plant roots and improve water infiltration into the soil

(v) prevents soil erosion and runoff

Haug (1993) stated that composting processes achieving thermophilic temperatures (>45°C) can fulfil the sanitation requirements of pathogen microorganism (Salmonella and viable pathogen nematode eggs among others). When composted materials are used as organic amendments in soils, it is of great importance that the material is sufficiently stabilized in order to avoid negative growth effects due to N mineralization, oxygen depletion or the presence of phytotoxic compounds. In addition to that, sewage sludge may present some difficulties to produce a high quality compost that could be allowed in agriculture, including its metal content and presence of emergent organic pollutants. Ramirez et al. (2008) showed that composting is an effective way to reduce phytotoxicity of sewage sludge before being applied to agricultural soils. In addition, no ecotoxicity correlations were found with heavy metals or organic pollutant content.

There exist, though, some scenarios in which neither dewatered sludge nor composted sludge would be allowed to be used in agriculture. For instance, some characteristics inherent of sludge such as heavy metal content, may make impossible their valorization as fertilizer due to increasingly stringent standards. Therefore, in some cases, thermal processing of sludge might be an alternative trend which allows energy recovery and minimizes the environmental impacts of sludge disposal. By-products generated during thermal processes such as ashes or biochar can be also applied in agriculture if they comply with the regulations. Incineration ash is known to be rich in phosphorus (4-9%) which could be comparable to commercial superphosphate (Franz, 2007).

Before thermal treatment drying is often necessary from a technological and economical point of view. Drying by conduction and convection are the most widespread sludge drying technologies (Bennamoun et al., 2013) but they usually rely on non-renewable energy sources that make those processes less sustainable. As alternatives, traditional solar drying and biodrying have been proposed, which are not dependent on external energy sources and are able to dry sludges up to a level suitable for self-sustained combustion (Oladejo et al., 2019).

Biodrying is indeed a recent topic studied for sludge, with a relevant number of papers on the subject published as early as 2010 and gaining research attention in the last years (Dos Reis et al., 2019) due to its high efficiency (i.e. Sugni et al. (2005) achieved biomass drying in 8–9 days), and the fact that the solid derived fuel from biodrying process is a good quality renewable fuel (Adani et al., 2002; Staber et al., 2008; Sugni et al., 2005) besides its possible use as an organic fertilizer in attempt to supply a replacement for inorganic fertilizers. As stated by Navaee-Ardeh et al. (2006) biodrying shows the potential to raise the dry solids content of sludge to dry solids levels allowing for adequate transport, land disposal as fertilizers and/or to be destinated for power generation through combustion of biodried product.

DPW EBPR sludge, being a P rich biosolid and showing excellent characteristics for valorization and reutilization as an agricultural input has not been thoroughly researched. Ashekuzzaman et al. (2019) reviewed the DPW sludge using Ireland as a case study, they estimated volumes and characteristics of four sludge types (biochemically treated activated sludge; lime treated dissolved air flotation processing sludge; a combined treatment sludge and anaerobically digested sludge) and found that the median values (g/kg dry weight) for N:P:K for the four sludge types were N: 57.2, 19.5, 46 and 70.4, P: 36.8, 65.9, 20 and 14.6, and K: 7.2, 3.9, 2.9 and 6.1, respectively. Moreover, heavy metal concentrations across all samples were significantly lower than those regulated by the European Union for controlling metals accumulation in agricultural land due to sludge recycling. Their results indicate that DPW sludge is a valuable resource, but still more scientific research is to be completed on the different aspects of biosolids concentration, purification and management in order to make it a feasible resource for the sustainable development. However, due to the high water content present in sludge, which hinders the efficiency of energy recovery (Hamidian et al., 2017; Tom et al., 2016; Yuan et al., 2017) a pre drying step is usually required for subsequent valorization methods such as thermal processes or biodrying, the latter emerging as novel and promising alternative for nutrient recovery.

Biodrying technology, based on composting process, consists of an aerobic biological evaporation process which reduces the moisture content (MC) of the waste, with minimum aerobic degradation. Process of biodrying utilizes the auto thermal heat generation due to microbial action on waste material instead of heat produced from non-renewable energy sources as in conventional drying process as above mentioned. Hence, this is an energy saving process when compared to drying since it effectively utilizes the biological heat energy (Rada et al., 2007, 2010). Nevertheless, biodrying exhibit some key operational parameters which need to be optimized to successfully treat sludge, such as: temperature, air flow rate (AFR), turning regime, initial MC and the use of bulking agents (BA) as well as some key process variables to be quantified such as: energy consumption, gaseous emissions and reaction times.

Biodrying is distinct from composting in attempting to dry and preserve most of biomass content of the waste matrix, rather than fully stabilize it, requiring less space to treat the same flux of material than composting, and with lower gaseous emissions generation (Velis et al., 2009).

Biodrying of DPW EBPR sludge has not been assessed and it would present some innovative P rich sludge valorization opportunities: (i) partially stabilized nutrient rich fertilizer and (ii) renewable solid fuel for its energy recovery and possible recovery of P from ashes for its use in agriculture.

6 Biodrying For Obtaining Valued Biosolids

6.1 Process Description

As an aerobic compost-like process, biodrying also requires a first conditioning of the waste. Sludge presents some inherent difficulties for any aerobic process related to its high moisture content and low porosity. Therefore, in the case of sludge, needs to be conditioned before its valorization through biodrying (Winkler et al., 2013). Conditioning includes proper dewatering of sludge and adjustment of porosity by using a BA which permits the adjustment of the mixture structure together with its porosity and moisture content (Velis et al., 2009).

Once the sludge is conditioned, when air is pumped into the sludge matrix in the biodrying process, the microbial community naturally existing in the sludge consumes oxygen and the organic matter in the sludge itself to produce carbon dioxide and heat. The biodrying reactor is self-heating, relying on microbial heat production to obtain the required process temperatures. This is an advantage over conventional drying systems that depend on external heat sources (Mason & Milke, 2005a, 2005b). Bacteria responsible for biological activity can be classified into four groups based on temperature preferences: psychrophiles (active at 0–20°C), mesophiles (active at 8–48°C), thermophiles (active at 42–68°C) and hyperthermophiles (medium and extreme) (active at 70–110°C) (Madigan & Martinko, 2001). However, mainly mesophilic and thermophilic bacteria are important in the biodrying process because they are active within the typical temperature range of the reactor. Indeed, as reported by (Frei et al., 2004), the typical temperature range in the biodrying process is 15–55°C, although temperatures of up to 72.5°C have been observed (Cai et al., 2013; Pecorini et al., 2020). These bacteria are sensitive to the temperature of the matrix in which they grow. Too high temperatures kill mesophilic bacteria while favoring the growth of thermophiles. A portion of the biologically generated heat in the solid matrix is utilized by the microorganisms to support their preservation, growth, and multiplication, whereas the rest serves to enhance the evaporation of bound water in the porous matrix (Bailey & Ollis, 1986; Prescott et al., 1993).

Thermal phases of the process vary between treated materials, environmental temperature, AFR, initial MC, among other parameters. The usual sludge biodrying process show 4 clearly differentiated stages whose length would vary depending on the raw material used and operational conditions set: (i) temperature increasing phase in which aerobic bacterial community is growing after getting used to new aerobic conditions, (ii) thermophilic phase in which biological activity is maximum, as well as heat production and where temperature peak is achieved, (iii) second mesophilic phase in which biological activity is reduced due to a limitation on available biodegradable organic matter and a (iv) cooling phase in which heat production is limited and bulk temperature falls below 35ºC (see reference lines in **Figure 5**). As an example, Cai et al. (2013) reported a study treating SS pile. The pile had an initial temperature of 22.5ºC, then increased above 55ºC on day 3 and reached its peak value of 72.3ºC on day 9. After the first turning on day 9, the pile temperature decreased to 47.2ºC, then entered the second temperature increasing phase, during which the temperature increased to

57.8ºC. After day 15, the pile temperature decreased gradually, finally reaching 21.7ºC on day 20. The pile temperatures for the run with turning events on days 9, 12, 15 and 18 are shown on **Figure 5**. The pile entered the thermophilic phase on day 3 and the cooling phase on day 15 (Cai et al., 2013).

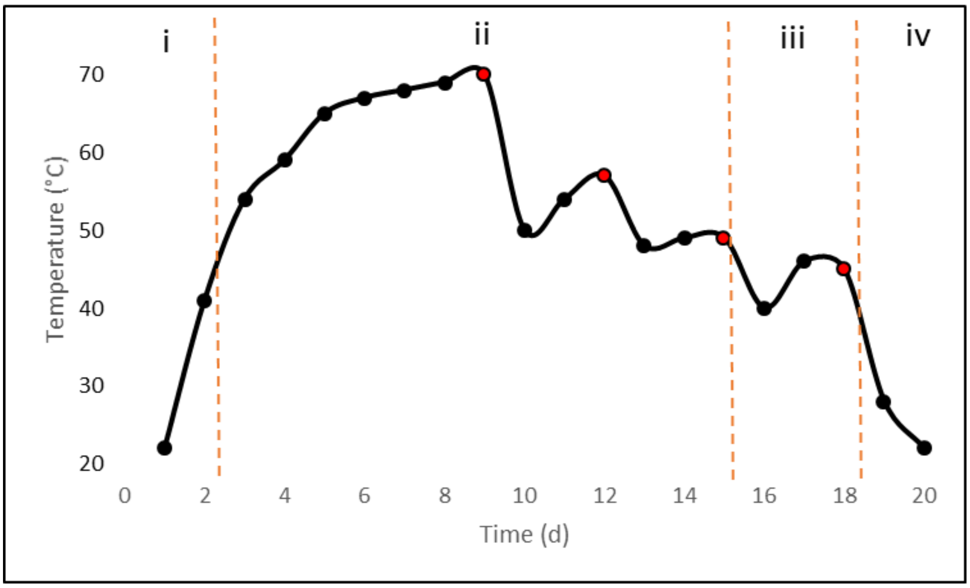

Figure 5: Temperature profiles of sewage sludge biodrying piles for run with turning events (red markers) on days 9, 12, 15, 18 (Adapted from Cai et al. (2013).

From the perspective of the biological process, during the initial temperature increasing phase (mesophilic stage (i) in **Figure 5** Temp. ≈ 20 to 42ºC), dewatered SS primarily contains bound water such as vicinal water and water of hydration; therefore, there is little free water that can be evaporated by airflow (Vesilind, 1994). As the process goes into the thermophilic phase (stages (ii and iii) in **Figure 5** Temp. ≈ 42 to >70), the high temperature destroys the vicinal boundary water layers thus, increasing the effective drying of the inner sludge (Vesilind, 1994). During the thermophilic phase, the volatile solids (VS) degradation, water generation, and water evaporation all reaches their peak values. The water evaporation peak could be due to the large amount of bioheat produced by the microorganisms and the convection promoted by the mechanical aeration. The elevated temperature also contributes to the effective elimination of pathogens, such as *Arcobacter* and *Prevotella*, which exist in the SS, (Cai et al., 2016). Thermophilic phase is the most efficient for moisture reduction. In their work, Ma et al. (2016) reported that about 72–79% of the total water removal was obtained in coincidence with the high temperature profile. Moreover, their results showed that the temperature was positively and significantly correlated with the water removal suggesting that high temperature promotes the water to shift to vapor, thus improving the water holding capacity of the air passing through the matrix. Therefore, the high temperature profile is a pursued target for biodrying process. Similar results were

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reported by Cai et al. (2013) who found that the water removal rate increased from day 1 to day 6 of their trials and had its peak rates on days 5 and 6 (thermophilic phase); later, the daily water removal rate decreased gradually as the process entered the cooling phase (**Figure 6** shows temperature profile and water removal rates). In this final cooling phase (stage (iv) in **Figure 5** Temp. ≈ 42 to 20ºC), large air volume has little effect on water loss as the air reaches the hygroscopic limit (Velis et al., 2009). Consequently, during SS biodrying, the demand for aeration varies based on each phase of the process, this is particularly important for developing biodrying systems designed for efficient biodrying with reduced excessive aeration (Chen et al., 2011; Zhao et al., 2010).

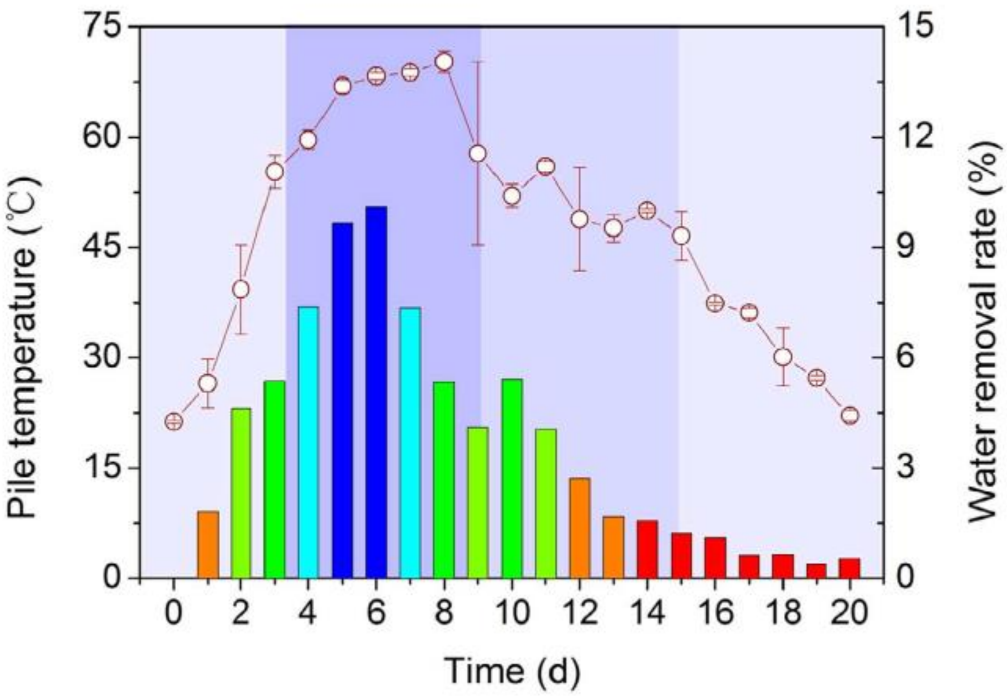

Figure 6: Pile temperature profile and water removal rate during the sewage sludge biodrying process. The areas from left to right are I-mesophilic phase, II-initial thermophilic phase, III second thermophilic phase, and IV-cooling phase. Line series indicate the pile temperature (ºC) and bar series the water removal rate (%). Extracted from Cai et al. (2013)

A relevant disadvantage of a biodrying system is represented by the potential odorous compounds emissions. Various VCs including NH_3, malodorous sulfur compounds, aromatics, ketones, terpenes, and chlorinated compounds are released from aerobic processes of MSW biodrying (He et al., 2020). NH_3, VOCs and H_2S are responsible for malodor and health problems, and therefore decrease the environmental benefits of biodrying.

Volatile sulfur compounds (VSCs) have been found to be the predominant odorous chemicals in emissions, and this is because they have very low odor thresholds and extremely negative hedonic values (Wu et al., 2010; Zang et al., 2016). H_2S is the most abundant of the VSCs produced making up 39–43% of the total amounts of VSCs that are released, because of the partially anaerobic conditions that may occur in piles of biological treatment waste (Drennan & DiStefano, 2010; Yuan, Zhang, et al., 2018; Zhang et al., 2013). González et al. (2019) found significant variability between the results of different studies treating the same type of organic waste and emphasized that the substrates nature and process conditions (AFR and initial MC) and mainly the high temperatures reached promotes the emission of the odorant pollutants. However, reaching thermophilic conditions during the process is inevitable and needed to obtain a proper drying of the material.

6.2 Process Performance

6.2.1 Moisture reduction

In order to assess the biodrying performance, some key variables have been established in the literature to confirm de effectiveness of the process. Biodrying aims to primarily reduce the MC of the end product to make it a costly effective to transport and to make it feasible for land application as a nutrient rich bio fertilizer for grass / crop production. Evaporation as water loss (%) is therefore used as an indicator of the effectiveness of biodrying; that is, the more water evaporated, the more effective the biodrying process (Cai et al., 2012, 2015; Ragazzi et al., 2007; Viganò et al., 2016).

Literature review acknowledges different research findings: Zhao et al. (2012) researched the impact of BA and temperature in biodrying of dewatered SS in laboratory scale reactors, with up-flow air distribution, achieving water removal rates up to 31 % w/w; Navaee-Ardeh et al. (2010) worked with pulp and paper mill sludge in pilot scale biodrying reactors (800 L volume) achieving dry solids contents greater than 45 % w/w within 4–8 days departing from a mixture of primary sludge (45% dry mass basis) and secondary sludge (55% dry mass basis). According to Velis et al. (2009) MC in MSW biodrying, is usually reduced from almost 35–55 % to 20–10 % w/w. Bilgin & Tulun (2015) and Colomer-Mendoza et al. (2012) reported reduction values from 80 to 89 % w/w in lab scale experiments. Finally, Tambone et al. (2011) who monitored a full scale plant with a retention time of 14 days for 5 months, calculated a 66 % water loss during the process.

If energy recovery is intended, a minimum level of MC is needed to successfully achieve efficient combustion (≈ 50% w/w dry solid level). Navaee-Ardeh et al. (2010) set the economic dry solids levels threshold of 45% w/w or more for combustion purposes.

6.2.2 VS reduction

Since biological processes are dominant in the biodrying process, biological activity measurements are essential to evaluate biomass degradation activity and the quality of the final product (Adani et al., 2004). On one hand, VS reduction is a key performance parameter to monitor: Zhao et al. (2010) reported, based on the ash conservation principles, an average VS reduction of 20% achieved within a biodrying facility after a 15 days retention time. The abovementioned organic matter range is in accordance with the work of Tambone et al. (2011) who also found VS to be between 77 and 70% for raw and biodried materials, respectively (inlet VS ≈ 771 ± 60 (g kg^{-1} TS)). Other input-output organic matter values (d/w) during biodrying that have been also reported in the literature are, respectively: 82 and 70% for MSW (Shao et al., 2010) 81 and 74 % for various organic substrates (He et al., 2013) 80 and 72% for dewatered sludge (Zhao et al., 2012). The above values indicate that despite the fact that the main goal of biodrying is not the extensive degradation of the organic matter, partial stabilization can occur depending on the operational conditions (aeration, retention time, cell volume) and the feedstock used (Evangelou et al., 2016).

Another way of addressing the activity/stability of a final biodrying product found in the literature are aerobic respiration indexes, which are used to monitor the organic degradation of substrates of different origins and biodegradabilities (Adani et al., 2006; Barrena et al., 2009; Komilis et al., 2011; Pognani et al., 2012). Respiration techniques based on the measurement of the loss of O_2 are the most accepted because of the precise information about the real biological activity of the samples (Barrena et al., 2006). The parameter O_2/96 h obtained during respiration technics presents the microbiological oxygen consumption over 4 days and determines the ability of the waste for further biological decomposition (Dębicka & Zygadło, 2017). Also, the dynamic respiration index in the 24 h of maximum biological activity (DRI24h) and the cumulative oxygen consumption in 4 days (AT4) are broadly used (González, et al., 2019a; González, et al., 2019b; Ponsá et al., 2010). Finally, Evangelou et al. (2016) monitoring data from a 1.5 year sampling period using microbial respiration indexes to address the decomposition process and the stability status of the wastes, reported a significant respiration activity reduction in biodrying samples (from 133 to 60 g O_2 kg TS^{-1} for AT4 and from 1.7 to 0.8 g O_2 kg TS^{-1} h^{-1} for DRI24h).

6.2.3 Biodrying index

In order to quantitatively present the relationship between water removal and VS consumption the biodrying index, which was defined as the ratio of water removal to VS consumption, was introduced to evaluate the biodrying performance (Ma et al., 2016; Zhang et al., 2008). The biodrying index (I) as performance indicator for biodrying process is expressed as below:

$$\boldsymbol{It = \frac{WLt}{OLt}} \qquad \textbf{Equation 1}$$

where It is I at time t; WLt (kg) the water loss at time t and OLt (kg) the VS loss at time t.

The higher biodrying index, the more water is removed with less organics consumed thus, more energy is retained in the drying product, which is beneficial for some product utilization, such as solid recovered fuel. Evangelou et al. (2016) studying a biodrying facility reported an average biodrying index of 4.1. This value agrees with findings of Zhang et al. (2008) who reported a typical range for that index that ranged from 3.4 to 4.2 with MSW as a substrate.

6.3 Control Parameters

Biodrying is affected by the physicochemical properties of the waste, the initial MC, forced ventilation (Cai et al., 2013) the sludge temperature (Cai et al., 2017), the ventilation conditions (Huiliñir & Villegas, 2014), and the added biological agents (Yuan et al., 2018). Careful management of the process and suitable climatic conditions are critical for successful biodrying (Velis et al., 2009).

6.3.1 Bulking agents

Due to its compactness and high water content, sludge cannot be subjected to a biodrying process alone thus, BAs must be added to provide the structural support to create inter-particle voids or free air space (FAS) (Eftoda & Mccartney, 2004). The FAS is an important factor in determining the quantity and movement of air through the solid matrix. Adequate FAS is needed to provide oxygen to aerobic microorganisms. The metabolic reaction can theoretically take place at high moisture levels, but moisture levels typically found in sludge decrease the availability of oxygen needed to sustain aerobic decomposition, due mainly to the slow diffusion of oxygen into the liquid film surrounding the microorganisms. Therefore, the FAS between dewatered sludge particles is easily clogged by compaction and the excessive moisture in the sludge. Also, sludge also tends to compact under its own weight, which further reduces the FAS preventing proper air movement throughout the matrix (Cai et al., 2016; Ma et al., 2016). BA provides structural support and high FAS within the voids between particles, increases the size of pore spaces, and allows easier air movement (Cai et al., 2017). As so, air dried sludge, previously biodried sludge, wheat straw, sawdust, wood chips, pruning remains and shredded rubber are frequently recommended as BAs for biodrying of dewatered sludge (Cai et al., 2017; Kim et al., 2018; Shao et al., 2010).

BAs can also supply carbon sources contributing to the biodegradation materials (wood chips, leaves and yard trimmings, corn cobs, stalks and straw (Yang et al., 2014; Yuan et al., 2016) and are preferred by some authors over chopped rubber or sawdust because chopped rubber is extremely resistant to microbial decomposition, and therefore is not expected to contribute to the production of metabolic heat.

Adding a BA, however, increases the cost of processing, e.g. purchase of BA and increased material volume to process. Operators, therefore, strive to determine the critical BA requirement (CBAR) for their operation. The CBAR is defined as the minimum amount of BA required to maintain adequate FAS levels and MC of the solid matrix (Eftoda & Mccartney, 2004).

6.3.2 AFR and Initial MC

According to the literature, AFR is the main operational variable used for process control in biodrying, both in laboratory (Adani et al., 2002; Navaee-Ardeh et al., 2006; Sugni et al., 2005) and commercial applications (Tambone et al., 2011).

Zhao et al. (2010) studied the effect of AFR and turning frequency on biodrying of dewatered sludge, showing that with the higher AFR (0.0909 m^3 h^{-1} kg^{-1}), heat consumed by sensible heat of inlet air and heat utilization efficiency for evaporation was higher than with the lower one (0.0455 m^3 h^{-1} kg^{-1}). Cai et al. (2013) showed that forced aeration controlled the pile temperature and improved evaporation, making it the key factor influencing water loss during the process of SS biodrying. Colomer-Mendoza et al. (2013) studied the effect of AFR on the biodrying of gardening wastes, showing that high AFR (> 10 L/(min·kg d/w) affects the biodrying process because the waste mass is cooled (the heat is taken away) thus, the biomass is dried mainly by physical effects but not by metabolic heat from aerobic degradation, because the thermophilic phase is not reached. Sharara et al. (2012) showed that high aeration level (1.5 L min^{-1} kg VS^{-1}) was superior in terms of both drying energy and time requirements than the other considered rates (0.05 and 0.8 L min^{-1} kg VS^{-1}). Finally, it was found that low AFR favor bioactivity, but results in hampering the biodrying process.

MC is another critical parameter involved in biodrying technology that influences the complex biochemical reactions associated with microbial growth and the biodegradation of organic matter that occurs during the process (Cai et al., 2012; Ryckeboer et al., 2003).

Huiliñir & Villegas (2015), designed an experiment focusing on the interactive influence of AFR and MC on outlet air temperature and water removal of dewatered sludge as a biomass resource. They established a 3 x 3 factorial design with 3 levels of MC (59 – 68 – 78%) and 3 levels of AFR (1 – 2 – 3 L min^{-1} kg^{-1} TS) and found that that the initial MC has a remarkable effect on the matrix and outlet air temperature, with higher matrix temperatures obtained around 68% and the lowest matrix temperature obtained at initial MC = 78%. Regarding water loss, initial MC also influences the water removal, initial MC of 68% showed the highest moisture removal conditions. Also, the highest VS consumption obtained was at initial MC = 68%. This situation, together with the temperature rise, shows that the initial MC close to 70% increases the overall effectiveness exploiting physical and biochemical processes as well as microbial activity. All these observations are in accordance with Yang et al. (2014) who showed that the optimal initial MC of sludge for biodrying seemed to be in the range of 50-70 %.

6.3.3 Pile turning

Mechanical turning is an effective way to promote aerobic fermentation of organic waste (Pujol et al., 2011). Turning is a mechanism of aeration and temperature control and turning frequency affects the rate and quality of the biodrying process (Ogunwande et al., 2008). Turning increases the porosity of the material, exposes fresh material for microbial colonization, promotes degradation of organic material (Kalamdhad & Kazmi, 2009; Stanford et al., 2009), mass transfer conditions are improved, water evaporation is enhanced and is particularly profitable for homogenization of pasty sludge with poor mechanical strength (Léonard et al., 2008). Nevertheless, turning events also implies a negative effect on biodrying processes as it causes a temperature drop in the biodrying pile (Zhao et al., 2010).

Extensive research and information on aeration is available for composting operations (Guardia et al., 2008; Ekinci et al., 2006; Lu et al., 2009) but limited to biodrying, especially referring to sludge biodrying. Compared to aeration, mechanical turning consumes more time and energy (Hong et al., 2014; Zhao et al., 2010). Cukjati et al. (2012) reported that there is a significant negative impact on the process temperature every time a pile was turned, so it is important that turning was completed as quickly as possible. Furthermore, Awasthi et al. (2014) considered that low pile temperatures and slow increases in pile temperatures were the result of increased heat and water losses caused by higher turning frequency (daily) during a municipal solid waste drying process. Turning frequency influences the rate of moisture removal (Shao et al., 2015) because pile temperature is related to moisture removal and heat is lost in the SS biodrying process when the pile is turned, which affects both the process of self-heating and the preservation of heat in the pile.

Cai et al. (2013) studied the drying effects of mechanical turning and found that turning once in the later stage of the first thermophilic phase and turning twice after the first thermophilic phase achieved a satisfactory biodrying result. Zhao et al. (2010) found that more water was removed using a higher turning frequency (once every 2 days) than using a lower turning frequency (once every 4 days). They state that high AFR and turning frequency improves the biodrying efficiency, but due to the adverse characteristics of sludge, the increment is not always notable. They conclude that turning results in an effective approach to sludge biodrying success, while it was also time and energy consuming when compared to aeration, so an energy balance must be performed (Zhao et al., 2010).

6.3.4 C/N Ratio

Roy et al. (2006) reported the C/N ratio as one of the most influential experimental parameters in the batch biodrying process. The biodrying process is influenced by the C/N ratio, which has an important role in the continuity of this process (Wiharyanto et al., 2018). The C/N ratio describes microorganisms in oxidizing carbon as an energy source and consuming nitrogen (N) for protein synthesis (Ryckeboer et al., 2003). Larsen & Mccartney (2013) found that bioheat has a negative correlation with C/N ratio. An out of range C/N ratio (<15 or >30) can therefore jeopardize the success of the biodrying process (Navaee-Ardeh et al., 2010), because it is considered that the microorganisms require 15 to 30 parts of C per unit of N (Bernal et al., 1996). The C/N ratio of sludge is part of the biodrying feed characteristics. As a critical variable, the C/N ratio needs to be measured to ensure good operation of the biodrying reactor.

Following, **Table 4, Table 5** and **Table 6** offers a systematic review of the recent papers addressing different control parameters and states the performance indicators obtained for several biodrying process. Each table focuses on one controlled parameter and shows the diversity of the other control parameters and provides the performance indicators of each study.

Table 4: AFR as the principal controlled parameter

Table 5: BA influence over the biodrying process

Table 6: Turning regime, stage supplementation, ventilation methods and trial duration influence over the biodrying process.

Table 4: Reviewed papers controlling mainly AFR in different biodrying processes.

Reference	Tittle	Substrate	Initial MC (%)	Initial VS (%)	Bulking agent (BA)	Controlled parameters		PERFORMANCE YIELDS					MAIN FINDINGS
								MC Removal ratio (%)	VS degradation ratio (%)	I (Biodrying Index)	Final Dry Solids (%)	LCV (MJ/Kg)	
Navaee-Ardeh et al., 2010	Key variables analysis of a novel continuous biodrying process for drying mixed sludge	Pulp and paper dewatered sludge	50.7	-	Biodried sludge	AFR (28 to 75 m^3/h)	Residence times 4 - 8 Days	-	-	1.5 - 3.3	51	-	Different operating conditions were applied and, in all cases, economic dry solids levels (45% w/w or more) were achieved. Through a variable analysis, it was found that the air outlet relative humidity profile is the key variable for this process, and the best biodrying efficiency index was achieved at an outlet relative humidity profile 85/85/96/96%.
Colomer-Mendoza et al., 2013	Effect of airflow on biodrying of gardening wastes in reactors	Garden waste	67.35 - 77.73	-	Pruning waste and wood shavings	AFR (0.88 to 6.42 L/ (min ·kg d/w))	BA: 0 and 15% of BA (pruning waste and wood shavings	51 - 87	-	-	-	4.5 - 13.7	A weight loss between 40% and 57% and a volume reduction between 40% and 60% was reached. Furthermore, adding even a small amount of BA (15%) resulted in a greater weight loss. Thus, BA promotes a positive influence on biodrying. Reactors injected with a low airflow, i.e., the reactor with 4 L/min airflow had the best results
Zhao et al., 2010	Effect of air-flow rate and turning frequency on biodrying of dewatered sludge	WWTP dewatered sludge	67.9	81.1	Straw and saw dust	AFR 0.045 - 0.0909 $m^3\ h^{-1}\ kg^{-1}$. w/w	Turning regime Per 2 - 4 days	57 - 68	31 - 36.7	-	21	14.7	The higher AFR rate enhanced VS degradation thus improving heat generation between 1.95% and 8.96% with turning per two days and four days.
Tambone et al., 2011	Effects of biodrying process on municipal solid waste properties	Municipal solid waste	32.72	77	-	AFR (10 - 20 Mg TS-1 h^{-1})		65.5	28	-	62	16.77	After 14 d, biodrying reduced the water content of waste in 66% (From 32,72 Mg to 11,28 Mg) showing a high LCV for use as a biofuel
Evangelou et al., 2016	Monitoring the performances of a real scale municipal solid waste composting and a biodrying facility using respiration activity indices	Municipal solid waste	50	63-77	-	AFR (5.7 to 28.3 m^3 air/m^3 MSW/h)		20	6.5	4.1	>45	10	The initial and final MCs were 50 % and less than 20 % w/w, respectively, and the biodrying index was equal to 4.1 indicating effective biodrying.
Huiliñir & Villegas, 2015	Simultaneous effect of initial MC and AFR on biodrying of SS	Dewatered secondary sludge	59. 68. 78	-	Wood shavings	AFR 1. 2 and 3 L/min kg VS	Initial MC 59, 68 and 78%	7.6 – 26.36	4.0 - 10.0	0.54 - 1.66	52 - 77	-	It was found that the main mechanism for water removal was the aeration, with higher water removal at intermediate initial Mc (68%) and high AFR (3 L/min kg TS).
Cai et al., 2013	Influence of forced air volume on water evaporation during SS biodrying	WWTP dewatered sludge	66	-	Biodried sludge + saw dust	AFR (19 - 41 $m^3\ ton^{-1}$ matrix d^{-1})		17.24	-	-	-	-	The peak air velocity and water evaporation occurred in the thermophilic phase and second temperature-increasing phase, with the highest values of 0.063 m s^{-1} and 28.9 kg ton^{-1} matrix d^{-1}, respectively,
Huiliñir & Villegas, 2014	Biodrying of pulp and paper secondary sludge: Kinetics of volatile solids biodegradation	Pulp and paper dewatered sludge	64 – 66	25 - 29	Rice husks	AFR (0.51. 1.61. 3.25 and 5.26 L/min kg VS)		15 - 55	0 - 17.0	-	35 - 55	3.7 - 6.4	Higher AFR rates cause greater MC reduction, lower temperature in the matrix, and lower VS reduction. At an AFR as high as 5.26 L/min kg VS there is no biodrying but only convective drying.

Table 5: Reviewed papers controlling BAs in different biodrying processes.

Reference	Tittle	Substrate	Initial MC (%)	Initial VS (%)	Turning regime	Controlled parameters	PERFORMANCE YIELDS				MAIN FINDINGS
							MC Removal ratio (%)	VS degradation ratio (%)	I (Biodrying Index)	LCV (MJ/Kg)	
Zhao et al., 2012	Sludge Biodrying Process at Low Ambient Temperature: Effect of Bulking Agent Particle Size and Controlled Temperature.	Dewatered SS	54.3 - 72.0	72.0 - 80.1	Per 7 days	BA (Rice straw (2 -5 and 20 - 30 mm diameter))	25 - 31	9.7 - 17.0	-	15.3	As a common BA, straw, which has a small particle size of 2–5 mm, was beneficial for organic matter degradation, while it had a negative effect on water removal. The use of different types of straw (with larger particle size of 20–30 mm) as the BA gave poor performance, in which the organic matter degradation rate was 9.75% and the water removal rate was 25.9%.
Yang et al., 2014	Importance of Initial MC and Bulking Agent for Biodrying SS	Dewatered SS	Controlled	71.6	Day 6	BA: rubber, sawdust, air-dried sludge and biodried sludge MC 23 - 81%	8.1 – 45.7	0.84 – 7.96	>3	-	50–70 w/w % was found to be the optimal initial MC range for effective sludge biodrying. Among the BA tested, air-dried and biodried sludge showed higher temperature increase, greater weight reduction, and greater water removal than shredded rubber and sawdust.

Table 6: Reviewed papers controlling turning regime, stage supplementation, ventilation methods and trial duration influence over the biodrying process.

Reference	Tittle	Substrate	Initial MC (%)	Initial VS (%)	AFR	Bulking agent (BA)	Controlled parameters	PERFORMANCE YIELDS				MAIN FINDINGS
								MC Removal ratio (%)	VS degradation ratio (%)	I (Biodrying Index)	LCV (MJ/Kg)	
Cai et al., 2015	The Effects of Different Mechanical Turning Regimes on Heat Changes and Evaporation During SS Biodrying	WWTP dewatered sludge	83.5	68.3	-	Biodried sludge and Sawdust	(R1) turned on days 3, 12, 15, and 18; (R2) turned on days 6, 12, 15, and 18; and (R3) turned on days 9, 12, 15, and 18	7.99- 23.32	5.39 – 9.50	-	-	Turning once in the later stage of the first thermophilic phase (day 9) and turning twice after the first thermophilic phase were recommended for a satisfactory biodrying result.
Zhang et al., 2008	Biodrying of municipal solid waste with high water content by aeration procedures regulation and inoculation	Municipal solid waste	72	-	0.45 $(m^3/(kg\cdot m^2\cdot h)$	-	Supplementing a hydrolytic stage prior to aerobic degradation and inoculating the biodrying products	50.5	10 -- 30	4.20 – 3.67	-	Compared with the aerobic processes, the combined processes had a higher biodrying index (4.20 for non-inoculated and 3.67 for the inoculated trials). The biodrying index (I) in the aerobic stage was affected by temperature and the accumulation of the products of AFR and saturated vapor pressure.
Shao et al., 2012	Biodrying of municipal solid waste under different ventilation modes: drying efficiency and aqueous pollution	Municipal solid waste	74	71	0.014 m^3/kg initial waste/h	-	Intermittent negative ventilation (IN), continuous negative ventilation (CN) and intermittent positive ventilation (IP)	68.4 - 68.7 - 67.2%	48	5.35 - 5.93 - 4.82	-	From the aspect of biodrying efficiency, continuous negative ventilation was the most preferable ventilation mode for biodrying of MSW due to the lower instantaneous AFR and longer air residence time
Rada et al., 2007	Lower heating value dynamics during municipal solid waste biodrying	Municipal solid waste	-	-	14.5 nm^3 kg^{-1} MSW	-	Trial duration	30	33	6.8 – 7.0	23 - 26	Biodrying indexes equal to 6.8 and 7.0, after 2 and 4 weeks of biodrying respectively, concluding that time did not significantly affect the process.

7 Ebpr-Biodried Product Quality

7.1 Bio Combustible End Product Quality

The constituents of sludge are made of blends of organic matters such as carbohydrates, proteins, fats and oils, a range of microorganisms (both living and dead), and inorganic elements which are characterized by high energy content (Velis et al., 2009). Simple processing such as drying can easily improve its organic contents and calorific value significantly. Also, recovery of energy from waste materials contributes to the preservation of natural resources, to decrease gas emissions such as methane and carbon dioxide and other environmental advantages (Bilgin & Tulun, 2015). In the case of biodrying, the end product can be used as a source of energy. Biodried sludge has a high energy content that can be used to produce steam and/or electricity if combusted. Therefore, a major benefit of biodrying is the opportunity to incorporate the biogenic content of the input waste, a CO_2 neutral energy source, into a fuel product (Velis et al., 2009). Compared with biodrying of MSW, which is already widely applied in Europe, there are some limitations associated to biodrying of dewatered sludge. Mainly, dewatered sludge (**i**) contains fewer biodegradable organic substances, (**ii**) has higher moisture and (**iii**) has lower biomass matrix porosity, all of which are disadvantageous for effective aeration and energy recovery (Zhao et al., 2010). Nevertheless, maintenance of a sufficiently high lower calorific value (LCV) and even increasing the LCV of the end-product compared to the raw waste are reported (Adani et al., 2002; Villegas & Huiliñir, 2014; Zhao et al., 2010). On average, Evangelou et al. (2016) achieved an LCV increase from 6.4 ± 1.6 MJ/wet kg (inlet, N= 11) to 11.6 ± 1.5 MJ/wet kg (outlet, N= 11), accomplishing a net increase of almost 81%. Other researchers have reported either increases from 41% (Tambone et al., 2011) to 157% (Shao et al., 2010) or final product LCVs from 10.9 MJ/kg (Zawadzka et al., 2010) up to 19.6 MJ/kg (Bilgin & Tulun, 2015). Other studies reported that MSW and SS biodried products exhibit LCV of 7.7–10.4 MJ/kg (Winkler et al., 2013); 7.1 MJ/kg (González et al., 2019); 20.61 MJ/kg (Elnaas et al., 2015); 8–11 MJ/Kg (Gajewska et al., 2019) (ANNEX I provides details of various LCV reported by different researchers). According to the guidelines of the World Bank (Georgieva & Varma, 1999), in order for incineration to be applicable, the average LCV of the waste must be at least 6 MJ/kg throughout all seasons and the annual average LCV must be higher than 7 MJ/kg. Thus, biodried MSW exhibits the calorific quality needed the combustion. Combustion of biodried solids can be performed alone or mixed with other materials for optimizing the reaction. In the first case, P can be recovered from the obtained ashes.

Ponsá et al. (2017) provide a summary of the main advantages and limitations/bottlenecks of biodrying technology; main findings are included in **Table 7**

Table 7: Summary of the main advantages and limitations/bottlenecks of biodrying technology (Adapted from Ponsá et al. (2017))

Parameters	**Findings**
Energy product obtained	Biomass fuel
LHV of energy products	6 to 14 MJ kg biodried sludge^{-1} (depending on the final moisture content)
Energy consumption (Electricity and/or fuels)	200 to 400 kwh t^{-1} DS (reactor aeration, other energy consumption not included)
Electricity generation	650 to 1250 kwh t^{-1} DS
Heat generation	Heat self-consumed in the process (sludge biodrying)
Sludge retention time	7–21 days
photReactants/material consumption	– Woodchips/ bulking agent
by-products and or waste streams	Ashes
Main advantages	– Reduced energy consumption compared to thermal drying
Bottlenecks	– Necessity of co-substrates to carry out the process – Treatment of off-gases usually required
Compatibility with other technologies	Biodried sludge can be used in subsequent, pyrolysis or gasification processes

DS: Dry solids

No detailed analysis for DPW EBPR biodried sludge is currently available regarding its calorific value and thus, the opportunity of using it as a solid recovered fuel. As reference biodried SS exhibit values above 7 MJ/Kg (González et al., 2019; Zhao et al., 2010, 2012), enough for self-combustion.

7.2 Bio Fertilizer End Product Quality

Although traditional goal of dried sludge is its energy valorization it is possible, and increasingly studied in the last years, to use it as soil amendment. There is evidence that P supplied as EBPR biosolids is as effective for crops as mineral P (Kahiluoto et al., 2015) but biosolids are bulky to transport, require specialist spreading equipment, thus needing an efficient drying step before land application. Sludge drying reduces volume of the product, making its storage, transportation, packaging and retail easier. Sludge drying also inactivates pathogens and volatile chemicals and leads to a sanitized final product in pellets in relatively short time, with low odors and good handling characteristics (Fernández et al., 2007). The reuse of biosolids in agriculture provides the necessary nutrients and micronutrients necessary for plant and crop growth. They may be used as a soil conditioner, improving its physical and chemical properties and reducing the possibility of soil erosion (Colón et al., 2017). Their use also addresses EU policy on sustainability and reuse of resources. Numerous studies have documented their effectiveness in increasing crop yields (Latare et al., 2014) and soil phosphorus (Shu et al., 2016) while having negligible adverse ecological impacts (Adair et al., 2014). The use of dried sludge in agriculture also enhances the organic content of soils, increases the water holding capacity, the soil aggregation, reduces the soil bulk density, increases the cation exchange capacity, and enhances the plant root environment. Therefore, plants are better able to withstand drought conditions, extract water, and utilize nutrients (Colón et al., 2017). Hence, the biodrying process as a cost-effective technology for recovering nutrients from sludge is a promising alternative for manufacturing organic P rich fertilizers.

As stated, sludge biodried solids are nutrient rich materials which can be directly applied to the soil. Nevertheless, the fertilizer replacement value in terms of crop nutrient availability of biodried sludge is presently unknown. Also, the physicochemical characteristics must be addressed in order to comply with land application regulations. Winkler et al. (2013) treated SS in a biodrying process and found that their final product complied with the microbial European and Dutch quality standards ((ABP) EU1069/2009 and EC 142/2011) meaning that the initial sanitation step (50–70°C) produced a product which can safely be applied as fertilizer on land. These regulations demand a complete removal of *S. Senftenberg* (no detection in 25 g sample) a detection of *E. coli* to values lower than 1000 (CFU/g) and a minimal 5 log reduction of general pathogens such as *E. faecalis*. Within these regulations it is stated that all animal by-products and/or SS need to be treated at 65°C for at least 5 days, 60°C for at least 7 days or 55°C for at least 14 days.

Likewise, heavy metal concentrations of their final product (dried sludge) remained within the allowed threshold concentrations of the European Union (EU 86/278) needed for an application as fertilizer on agricultural land. Each country in the EU has its own threshold values and some are more stringent than others. In that regard, a good review on different quality standards within the EU is given by Kelessidis & Stasinakis (2012).

DPW EBPR biodried sludge can help closing the phosphorous loop for the dairy industry by providing with a cost-effective P recycling process which minimize nutrient leakage, while producing a safe, effective high value fertilizer product. Nonetheless, further study is necessary for scaling up the process and guarantee the necessary characteristics of the final product for land application, but as above stated, promising insights exist in the literature.

8 Greenhouse Gas (GHG) Emissions

Sludge is an important source of GHG emissions, both in the form of direct process emissions and as a result of indirect carbon-derived energy consumption during processing.

A detailed GHG budget for DPW EBPR treatment coupled with a biodrying technology aiming at recovering P rich biosolids for land application as fertilizers has not yet been performed. Both stages of the proposed technology (EBPR and biodrying) account for GHC emissions which shall be addressed. Following, a review on the present knowledge of GHG emission for each of these processes is presented.

8.1 EBPR GHG Emissions

Due to a very high global warming potential, nitrous oxide (N_2O) has received a lot of attention in the municipal wastewater treatment sector in recent years. Furthermore, N_2O has also been identified as an important intermediate or end product of several pathways of the N removal processes, including autotrophic nitrification and denitrification, and heterotrophic denitrification (Wisniewski et al., 2018).

In the latter case, N_2O is an obligatory intermediate, but under normal operating conditions in anoxic compartments, nitrate (NO_3^-) and nitrite (NO_2^-) are instantaneously reduced to nitrogen gas (N_2) without any observed N_2O emissions. This behavior results from the fact that the reduction rate of nitrous oxide reductase (N_2Or) is approximately four times faster compared to nitrate reductase (NAR) and nitrite reductase (NIR) (Law et al., 2012). Nevertheless, if any dissolved N_2O remains in the system, as it goes through the subsequent aerobic phase, it can be air stripped thus generating N_2O emissions (Wang et al., 2020).

The N_2O generation pathways have been explained in detail by Massara et al. (2017). N_2O production by autotrophic ammonia oxidizing bacteria (AOB) has its first step is the oxidation of NH_3 to NH_2OH with the reduction of molecular oxygen; this process is catalyzed by ammonia monooxygenase (AMO). Afterwards, NH_2OH is oxidized to NO_2 by the aid of the hydroxylamine oxidoreductase (HAO) with oxygen functioning as the primary electron acceptor. At this point, N_2O can be produced if NH_2OH is not completely oxidized to NO_2^- (**Figure 7:** NH_2OH oxidation pathway). The AOB related enzymes also include an amount of nitrite reductase (NirK) and nitric oxide reductase (Nor). NirK catalyzes the NO_2^- reduction to NO, and Nor the NO to N_2O (**Figure 7:** nitrifier denitrification pathway). Although nitrifier denitrification is not an important bioprocess in terms of total N removal, it can be critical in terms of N_2O emissions (Ahn et al., 2010; Law et al., 2012; Li et al., 2019; Ni & Yuan, 2015). As shown in **Figure 7:** N_2O is also an intermediate product of heterotrophic denitrification (Law et al., 2012; Ni & Yuan, 2015; Peng et al., 2015). It is a 4 step chain of reactions with three intermediate products: NO_2^-, NO and N_2O (**Figure 7:** heterotrophic denitrification pathway). The steps are catalyzed by the following enzymes: the nitrate reductase (NaR), the nitrite reductase (NiR), the nitric oxide reductase (NOR) and the nitrous oxide reductase (N_2OR) (Ni & Yuan, 2015).

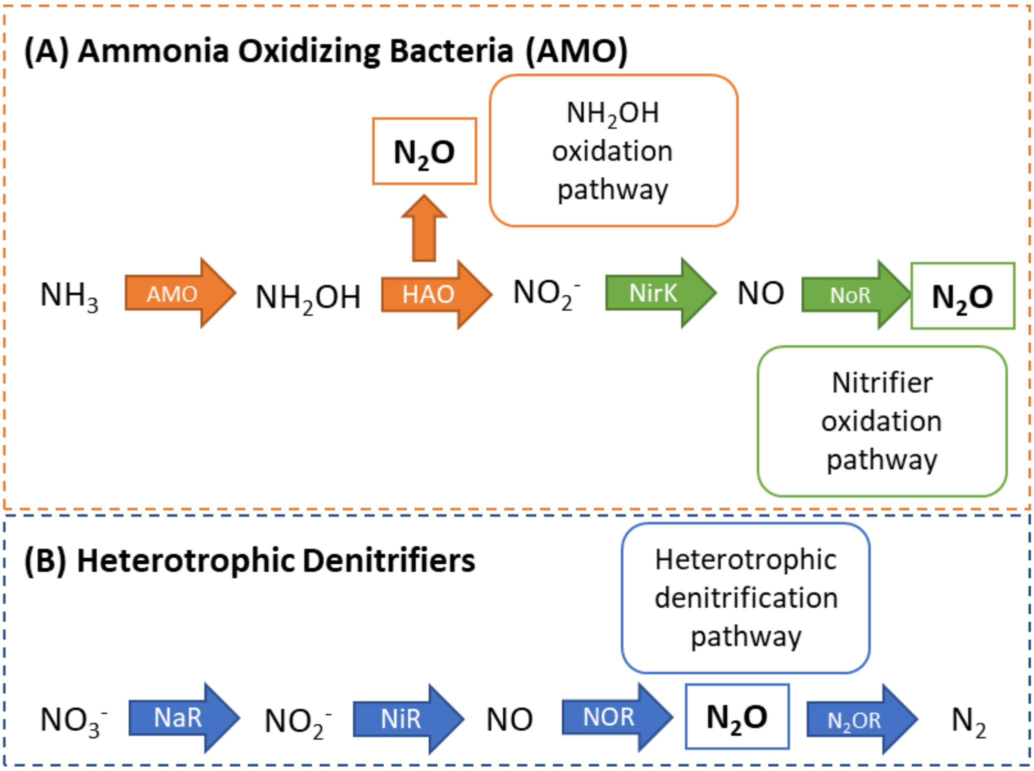

Figure 7: A simplified presentation of the biological N_2O generation by: (A) AOB (NH_2OH oxidation and nitrifier denitrification pathways), and (B) heterotrophic denitrifiers (heterotrophic denitrification pathway) (Adapted from Massara et al., 2017; Ni & Yuan, 2015)

Liu et al. (2015) developed a new denitrifying EBPR model to describe N_2O production in this process, particularly during the anoxic PHA utilization phase. The model was successfully evaluated against four data sets originating from laboratory scale anaerobic/anoxic SBRs. The authors linked N_2O production entirely with the PAO metabolism. However, the primary deficiency of that study was the lack of experiments with NO_2^--N as an anoxic electron acceptor and consequently the lack of model validation under such conditions. In contrast, Hu et al. (2016) carried out experiments with NO_2^--N and found that the anoxic uptake of PO_4^{3-}-P was completely inhibited by NO_2^--N, whereas the denitrification rate with NO_2^--N as an electron acceptor was only slightly affected in comparison with the rates observed in the experiments with NO_3^--N. This finding could suggest that ordinary heterotrophic organisms (OHOs) may play a more important role than PAOs in N_2O production in the combined N-P removal systems. In order to verify this hypothesis, Wisniewski et al. (2018) focused on the model-based investigation of the mechanisms of N_2O production in EBPR by PAOs and external carbon-based denitrification by OHOs. The simulation results revealed that only OHOs were responsible for N_2O production, whereas the present DPAOs reduced only nitrate to nitrite.

Moreover, Real et al. (2017) did an assessment of environmental costs (i.e. the global warming potential (GWP) and eutrophication potential (EP) in an EBPR-SBR system for a population equivalent of 45 people and compared it to a conventional activated sludge system. They found that the GWP and EP were reduced by 43% and 14%, respectively, in the SBR in comparison to the activated sludge.

In another study, Gao et al. (2017) presented a coupled aerobic-anoxic nitrous decomposition operation (CANDO) as a promising emerging bioprocess for wastewater treatment that enables direct energy recovery from N in three steps: (1) ammonium oxidation to nitrite; (2) denitrification of nitrite to N_2O; and (3) N_2O conversion to N_2 with energy generation. However, CANDO does not currently target P removal. In their work, they showed that DPAOs enrichment cultures are capable of catalyzing simultaneous biological N and P removal coupled to N_2O generation in a second-generation CANDO process, CANDO+P. Over 7 months (>300 cycles) of operation of a prototype lab scale CANDO+P sequencing batch reactor treating synthetic municipal wastewater, they observed stable and near complete N removal accompanied by sustained high rate, high yield N_2O production with partial P removal.

All in all, gaseous emissions in a variety of designs working with different operational key variables remains to be fully investigated and results of GWP, EP and energy consumption must be reported along with every technology presented.

8.2 Biodrying GHG Emissions

In the case of biodrying, water removal occurs along with both biological degradation of VS and heating of the sludge matrix (40–75 ºC) (Yang et al., 2014; Zhao et al., 2010). According to previous results (Liu et al., 2017), during sludge biodrying CO_2 is generated from decomposing organic matter. Also, CH_4 (GWP 28 times higher than that of CO_2 (IPCC, 2014)) emissions might be generated if oxygen content in the sludge pile is lower than 10%, (anaerobic spots can be created by the oxygen demand at the temperature range reached due to the rapid degradation of organic matter during thermophilic phase (Yuan et al., 2016)), heterogeneity of the solid matrix, insufficient FAS or mishandling of the process. Moreover, and according to (Liu et al., 2017) the main GHG in this process is N_2O (GWP 265 times higher than that of CO_2, (IPCC, 2014)).

Panagiotis & Komilis, (2019), following the IPCC guidelines according to which CO_2 comprises biogenic derived CO_2 (CO_2b) and fossil fuel derived CO_2 (CO_2f), with the former not contributing to global warming, calculated for MSW biodrying treatment, the net GHG emissions (CO_2eq – including CH_4 and N_2O emissions). All in all, they concluded that (using some theoretical figures typical for composting (IPCC, 2006) as no specific figures were available for biodrying) the total equivalent CO_2 (CO_2eq) emissions during biodrying are: 41.5 kg CO_2eq/t MSW.

In one of the first attempts to measure real GHG emissions and establish profitable information in terms of environmental impact of the technology, González et al. (2019), described the emission patterns for CH_4 and N_2O. Both gasses showed emission peaks at the beginning of the trials, mainly due to the stripping effect of the remaining gasses present in the SS, which rapidly decrease to lower values. Methane gas will probably not be formed because of the aerobic nature of the process, as long as enough FAS and aeration is provided. However, an increase of the N_2O emission was observed when the temperature of the material was below 40°C, suggesting that an increase in the SS biodrying process time would have a negative effect in terms of GHG emissions. Under mesophilic conditions some denitrifying bacteria can promote the N_2O formation by NO_3^- denitrification at the end of the process (Ahn et al., 2010; Fukumoto et al., 2003). González et al. (2019) stated that this fact should be confirmed by characterizing the activity and the diversity of the bacterial communities in future works. They finally concluded that ensuring aerobic conditions in a SS biodrying reactor is a key factor to minimize GHG emissions, as reported by different authors studying SS composting processes: low aeration and inadequate initial MC have a great impact on increasing GHG emission (Villegas & Huiliñir, 2014; Yuan et al., 2016).

9 General Conclusions

Increasingly stringent requirements on P removal demand innovative solutions for removing P from domestic and agro industrial wastewaters. Promising work has been performed to better understand metabolic pathways associated with luxury P uptake by bacteria in wastewater treatments such as EBPR, which provide viable, sustainable and low-cost solution for P recovery as well as simultaneous P recovery and N removal. However, achieving high levels of P recovery via such systems is often at the expense of system simplicity, particularly in the case of heterogeneous effluents. Thus, more study efforts are needed to accomplish stable operation and sufficient levels of nutrient removals in EBPR systems must be achieved. Also, gaseous emissions must be addressed in order to elucidate the key operational parameters for meeting a successful wastewater treatment, resulting in a utilizable end product while minimizing GHG emissions as well as energy and resource consumption. Microbial communities and operational variables play a key role in finding optimal functioning of EBPR processes in order to satisfy (a) wastewater discharge limits and (b) agricultural needs so as to maintain or improve actual crop yields without harming the environment.

The performed literature review indicated that there is a vast amount of information on the mechanisms of EBPR process and its application to domestic wastewaters and other effluents, but little successful research on its application on DPW. As is has been stated, within the circular economy framework there is a great opportunity for treating DPW through EBPR technology aiming to accomplishing water discharge legislation, avoiding eutrophication phenomena in surface waters, as well as obtaining a P rich biosolids for valorization and reutilization as an agricultural input. Specifically, there are promising results regarding N, P and K concentrations in DPW sludge furthermore, several micronutrients required by plants including Cu, Fe, Mn and Zn were identified. Concentration of these elements from DPW into manageable biosolids is the first step towards obtaining a high value product for agricultural reuse as bio based alternative fertilizer.

Coupled with this P recovery technology, the biodrying process for DPW sludge emerge as novel and promising alternative for nutrient recovery. Literature review has highlighted the favorable aspects of this technology. Nevertheless, it is necessary to determine optimal biodrying operating conditions to allow bio generated products to be effectively and economically used, to remove as much water as possible in as little time as possible while maintaining high nutrient levels.

In summary, the main advantages that can be highlighted are that SS biodrying is a fast-biological treatment, generating nutrient rich products, requiring less space to treat the same flux of material than composting, and with lower gaseous emissions generation. In order to enhance its performance aiming towards nutrient recovery, robust study on operational parameters and reactor optimization must be performed. Biodrying is in a developing phase with just a few full-scale facilities operating but almost uniquely with MSW. Consequently, sludge biodrying must be fully developed to scale it up. Success in development of full-scale facilities will provide a solution for an environmental challenge related to the increasing volumes of agro industrial sludge production and will, at the same time, relieve pressure over the P shortage for fertilizer production.

Hence, the expected research included in WP1, specifically for ESR1 within the REFLOW project, will provide with the very much needed investigation which will fill the existing knowledge gaps regarding P recovery form DPW and P-rich biosolid obtention for use as fertilizers.

Anaerobic membrane process optimization for the production of a P-rich concentrate from organic effluent (ESR2)

Dairy Processing Waste (DPW) is one of the largest industrial wastewaters and contributes to the elevate concentration of phosphorus (P)-rich industrial effluent. Thus, appropriate and effective treatments draw more attention among the scholars, considering that P is one of the critical elements for securing food productions for the growing world population. Combining the needs of P recovery from DPW and securing finite sources of the nutrient provide an opportunity for its recovery. The main objective of this project is to evaluate P recovery from DPW with novel technology of Anaerobic membrane bioreactor (AnMBR) coupled with Freeze concentration (FC).

Therefore, this literature review aims at analysing the state-of-the art of AnMBR and FC technologies applied for the treatment of DPW, paying special attention on the fundamentals of both technologies. In that sense, the document pretends to collect relevant information about advantages and configurations, applications and development in various streams treatment, and the influence of the main operational parameters on the process performance.

Finally, a first proposal of the methodology that will be used during the development of this project is also presented. Firstly, the work will be focused on the laboratory scale for testing and optimization of both, AnMBR and FC. Once the AnMBR + FC process has been optimized, the system will be scaled up at pilot scale and further tests will be done to better evaluate the process performance. Finally, the life cycle assessment (LCA) and life cycle cost (LCC) will be also performed.

Introduction

The dairy industry produces complex matrices of wastewater characterized by elevated biological oxygen demand (BOD) and chemical oxygen demand (COD) concentration which viewed as culprit environmental pollution (Demirel et al., 2004; and Song et al., 2018). According to some studies (Kasapgil et al., 1994; Najafpour et al., 2008; Pesta et al., 2007), dairy processing waste (DPW) contains high carbohydrates, proteins, fats and generates high organic matters which simultaneously dispose without prior treatment and thus can generate serious problems in sewage systems. Moreover, the effluent of dairy industry addressed as the staple sources of industrial effluent in Europe which requires immediate and comprehensive management approach including the treatment of mechanical, physicochemical and biological method (Rajagopal et al., 2013; Slavov, 2016).

In recent years, wastewater especially DPW has no longer seen as environmental problem but rather valuable sources which need to be recovered (Song et al., 2018). One of the important nutrients within DPW effluent is phosphorus (P) (Carvalho et al., 2013 and Vourch et al., 2008). P is a non-replaceable element for all forms of life. Specifically, P fertilizers are critical for securing the food production for the exponential growth of global population. Nonetheless, along with the application of P, the environmental concern has become the foremost issue for a global challenge, i.e. eutrophication in aquatic environment (Amann et al., 2017; Hakkou et al., 2016). Furthermore, the economic and geopolitics sectors have led to the concern of P shortage within European Union (EU) considering that less than 1% of mining site is located in EU (USGS, 2015). Therefore, the European Commission declared that phosphorus rock as one of the twenty critical raw materials in 2014 and it is also an increasingly scarce and expensive finite resource (EC, 2014).

1 Dairy processing waste

The development of dairy industry such as cheese, milk and yoghurt has created significant volume of DPW across Europe. In 2015, the significant increase of DPW seen approximately up to 2.8 percent annually with 500 m^3 waste effluent produced in one production day (Slavov, 2017). The diverse compositions of DPW effluent are eventually depending on the type of dairy products which needs different technological line for manufacturing process, therefore, DPW is characterized by an elevated temperature, large variation of pH, BOD, COD, total nitrogen (TN), total phosphorus (TP), fats and grease (Britz et al., 2006; Christian, 2010; Karadag et al., 2014; Slavov 2017). This section will be used as a reference and comparison for the later obtained results.

Characteristically, the colour of DPW effluent and whey is white and yellowish-green, respectively; with obnoxious odour (obtained by butyric acid concentration) and relatively high turbidity (Carvalho et al., 2013; Quasim et al., 2013). In general, the temperature of DWP effluent is seemingly warmer than municipal wastewater and greatly depends on the season. The DWP effluent temperature is approximately between 17-18 ^oC in winter and 22-25 ^oC in summer (Tsachev., 1982). Furthermore, the vital requirement of physicochemical treatment of DWP is the pH close to neutral (pH = 6.8 -7.4), while after discharging to the water body, the pH of the effluent dropped to below 6.2. This phenomenon is due to the acidification process by lactic acid fermentation caused by the anaerobic condition (Gannoun et al., 2008; Schifrin et al., 1981).

Due to the high organic matter content within DWP effluent, the variation of COD and BOD ranged from 0.1 to 100 g/L (Demirel et al., 2005; Karadag et al., 2015). For example, as reported by Slavov (2017), the highest whey BOD and COD have been reported is between 30-50 g/L and 60-80 g/L, respectively. Some authors mentioned that almost 90% of COD and BOD concentration caused by lactose activities while around 12% caused by protein removal (Farizoglu et al., 2007; Wang et al., 2009). Generally, nitrogen found in the form of amino groups, urea, uric acid and mainly in ionic form (NH_4^+, NO_2^- and NO_3^-) with TN content in wastewater from DWP is ranged from 0.0006 to 2 g/L (Britz et al., 2006; Janczukowicz et al., 2008; Watkins and Nash, 2010). On the other hand, phosphorus mainly characterized by inorganic and organic P, phosphate (PO_4^{3-}) and diphosphate ($P_2O_7^{4-}$) form (Demirel et al., 2004; Venetsaneas et al., 2009) with TP is in the range from 0.0001 to 0.7 g/L (Britz et al., 2006; Janczukowicz et al., 2008; Watkins and Nash, 2010). In cheese effluent, for example, the ratio of C/N/P of approximately 200:3.5:1 which is suitable to treat anaerobically (Henze, 1983).

To the best of our knowledge, the salinity of DWP effluent is seemingly high causes non-volatile suspended solid (SS) concentration (approximately 0.71 – 7 g/L) and contains inorganic impurities. The inorganic impurities are mostly presented in the form of Na^+, K^+, Ca^{2+} and Cl^- ions (Carvalho et al., 2013; Prazeres et al., 2012). Furthermore, the DWP effluents are known to have very low alkalinity which is approximately 2.5 g/L expressed as $CaCO_3$ in milk permeate. The lower alkalinity characterized in DWP, the reagent cost and pH maintenance potentially increased the post-treatment costs (Farizoglu et al., 2007; Wang et al., 2009).

2 Principle of Anaerobic Membrane Bioreactor

Over the past century, the study of wastewater treatment technologies on the most economic, efficient and low energy used has been published. The traditional aerobic methods have been mostly used to treat domestic wastewater, however, the main drawbacks with this technology were its high energy demands for the aeration, abundant sludge productions, considerably high operational and maintenances costs and uncontrolled greenhouse gas emissions (methane (CH_4), carbon dioxide (CO_2), and nitrogen dioxide (NO_2) (Musa et al., 2018; Tock et al., 2010). Hence, due to those obstacles, the interest has moved to another efficient technology: anaerobic digestion (AD) treatment. Generally, AD has been used for the treatment of a high strength industrial wastewater and high organic content such as whey and ice cream effluent industry (Dereli et al., 2009; Rajeshwari et al., 2000). The application of AD has been performed previously with different reactor configuration. For example, Gannoun et al. (2008) and Patel et al. (1994) configured up-flow anaerobic fixed film bioreactor to treat concentrated cheese whey, while Brown et al. (2016) configured the anaerobic co-digester process to treat cheese whey and dairy manure. The technology has been proofed to effectively produce good quality of effluent including the low operational maintenance (Kim et al., 2016).

Although this technology shows the improvement in terms of energy and operational costs, some constraints were identified: the long hydraulic retention time (HRT) and a slow growing of the bacteria. Therefore, the research has moved the focus to combine AD process with membrane technology; later denominated anaerobic membrane bioreactor (AnMBR) (Harb et al., 2017; Kim et al., 2016). The application of AnMBR is widely spread to treat various type of wastewater especially worked frequently at high biomass concentration and complex matrices of wastewater as well as with long SRT and HRT (Skouteris et al., 2012). According to literature review, the wastewater can be treated with AnMBR is including municipal wastewater (An et al., 2009), pulp and paper mills (Hu and Stuckey, 2006; Saddoud et al., 2006), petrochemical effluent (Van zyl et al., 2008) and dairy waste effluent (Saddoud et al., 2007; Wong et al., 2009). However, only few scientific studies reported the application of AnMBR of DPW at the pilot scale and almost all researches are working in bench scale application (Saddoud et al., 2007; Skouteris et al., 2012; Wong et al., 2009).

Table 8 shows the comparison of conventional anaerobic treatment and AnMBR according to Lin et al. (2013).

Table 8. The comparison of conventional anaerobic treatment and AnMBR

Feature	Conventional anerobic treatment	AnMBR
Effluent quality	Moderate-poor	High
Sludge volume	Low	Low
Substrate loading concentration	High	High
Organic removal efficiency	High	High
Biomass retention	Low	Complete
Footprint	High-moderate	Low
Alkalinity requirement	Depends on microbial activity	Depend on microbial activity
Nutrient requirement	Low	Low
Startup period	2-4 months	Less than 2 weeks
Temperature requirement	Low-moderate	Low-moderate
Energy input	Low	Low
Pre-treatment requirement	Not necessary	Mostly for high solid substrate
Biogas recovery	Yes	Yes

The coupled system of anaerobic treatment and membrane technology is reported to reduce the overall energy requirement and the membrane used to facilitate the total blockade for microorganisms to pass (Dvorak et al., 2015; Padmasiri et al., 2007). The membrane used in AnMBR system could be placed in three different configurations: side-stream configuration, submerged configuration and combination of submerged configuration with membrane in a separate chamber and vacuum-driven operation.

2.1 Side-stream configuration

In the side stream configuration, the membrane eventually integrated outside the system

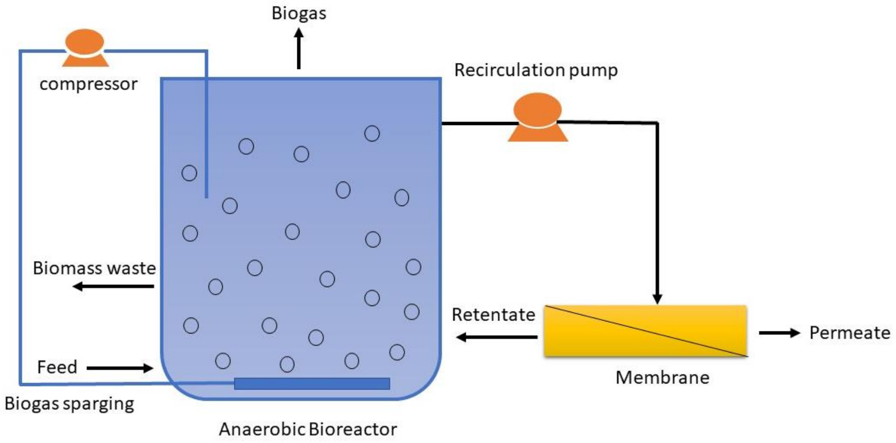

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Figure 8). The recirculation pumps guarantee required trans-membrane pressure in the membrane chamber. Hence, crossflow velocity constantly interrupts the formation of a filtration cake on the surface of membrane (Dvorak et al., 2015). Although this process requires high energy demands, any remaining energy can be used to mix the suspension in the anaerobic reactor. In order to remove and control the filtration cake on the membrane's surface, gas sparging and additional shear force are needed, however, elevated shear in the system might disturb the microbial activities (Chu et al., 2005).

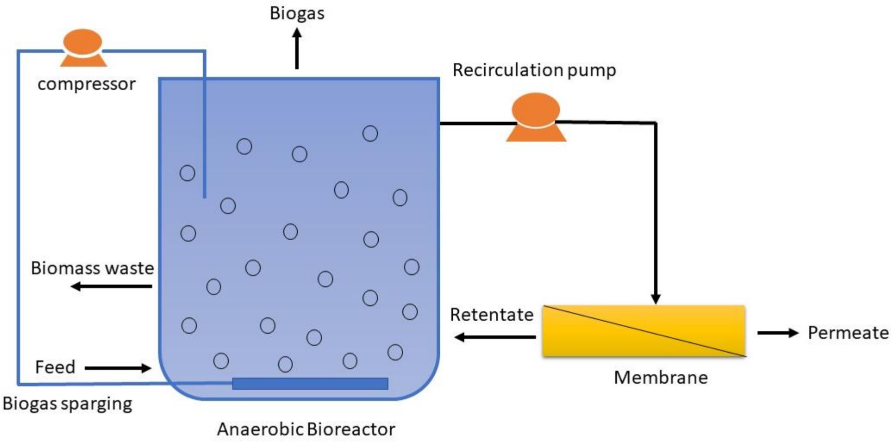


Figure 8. Side-stream configuration of AnMBR (adapted from Liao et al., 2006)

The advantage of installing this side-stream configuration is easy access to the membrane when the membrane is fully fouled with the cake filtrations and without disturbing the whole system (Andrade et al., 2014; Cote et al., 2000). Furthermore, membrane maintenance and replacement are more accessible to accomplish (Dvorak et al., 2015)

2.2 Submerged configuration

As seen in **Figure 9**, the membrane is installed inside the anaerobic bioreactor and working without the recirculation pump in the membrane compartment, therefore, the energy demand is lower compared to side-stream module. Moreover, it also benefits in lowering shear force and so no cross-flow effect within the system. As a result, the microorganism activity is less stress (Andrade et al., 2014). The aim of employing biogas sparging in the system is to simultaneously reducing the cake filtration and clogging, however, with the direct mixing with biogas, the system could be inhibited. This phenomenon is due to the disruption from toxic compounds which might contain within biogas. According to Aslan et al. (2014), mentioned that installing the magnetic stirrer inside the system and lowering the biogas production to the lowest level are the effective way to avoid the membrane cake formation and system's disruption. Some research mentioned that this system is way more effective in low strength organic load, especially domestic wastewater (Gao et al., 2011; Gimenez et al., 2011; Zhang et al., 2011).

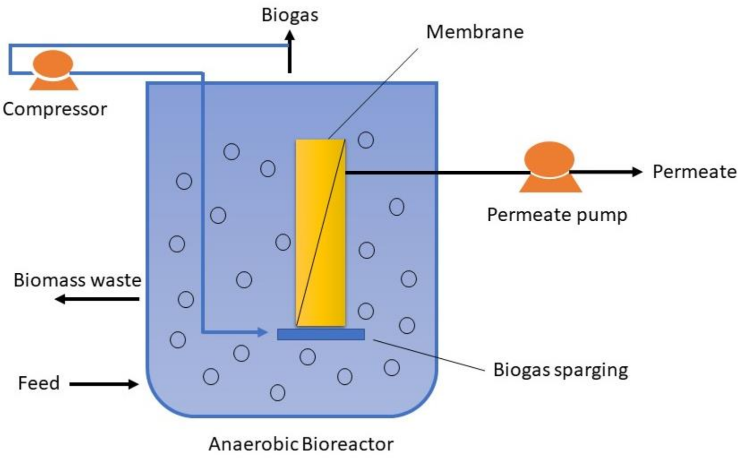


Figure 9. Submerged configuration of AnMBR (adapted from Liao et al., 2006)

The drawbacks of the submerged module are the inconvenient way of cleaning the membrane cake formation and has to disrupt the operation and the membrane has to be removed before cleaning. Furthermore, this configuration requires a large membrane surface to accomplish the same HRT as side-stream installation (Cote and Thomson, 2000; Pandey, 2014).

2.3 Submerged configuration with membrane in a separate chamber

This configuration can be installed as two-stage configuration by submersing the membrane in a separate chamber from the working anaerobic bioreactor (see **Figure 10**). As depicted in **Figure 10**, the retentate from the external chamber can be recirculated to the working bioreactor for another mixing process. The full-scale of this system has successfully installed and mentioned by some authors. Shin and Bae (2018), for example, mentioned that ten out of eleven recent pilot-scale configurations have implemented the two-stage module.

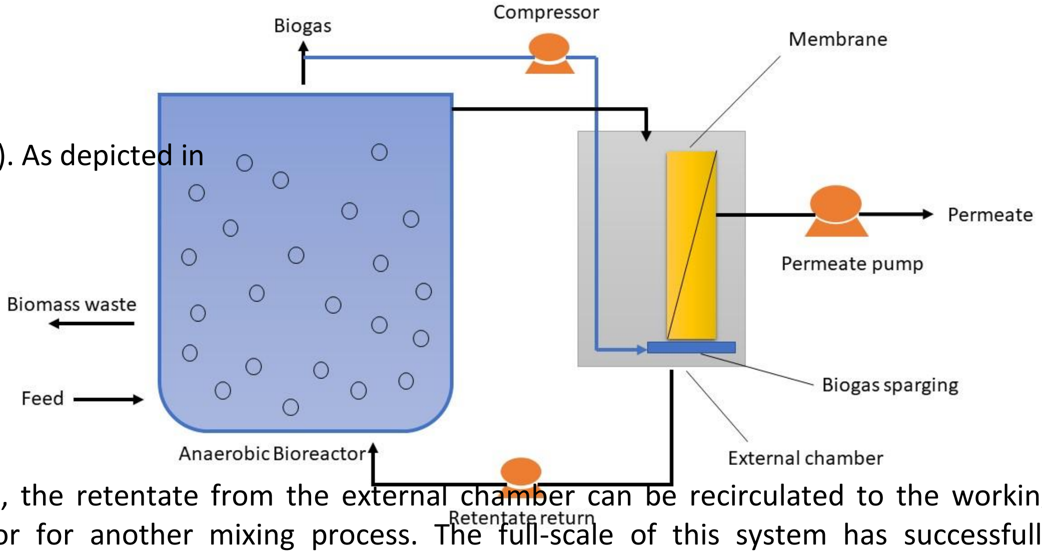


Figure 10. Submerged configuration with membrane placed in separate chamber (adapted from Liao et al., 2006)

Compared with those two mentioned membrane configurations, this type of membrane setting facilitates membrane maintenances, monitoring and cleaning by intensive shear force and chemicals. Furthermore, retentate from membrane tank can also be recirculated to the working anaerobic reactor for further contaminant biodegradation (Shin and Bae, 2018). Hence, according to Song et al. (2018), this two-stage setting can be potentially used for full scale applications.

2.4 The limitations of anaerobic membrane bioreactor

As mentioned previously, the numerous advantages of AnMBR has been described, including the low sludge productions, produced high quality of effluent and low operational costs, but the limitations of such system are still remained. The major obstacles of AnMBR, as reported by some authors, are the membrane fouling (Lin et al., 2013; Meng et al., 2009). Fouling becomes the multifaceted problem in membrane technology because it can decrease the hydraulic performance of the working system. In general, membrane fouling is primary caused by the accumulation of microorganisms, cell debris, colloids, precipitation of organic carbon (struvite, $MgNH_4PO_4$), accumulation of inorganic salts (potassium struvite, $K_2NH_4PO_4$ and calcium carbonate, $CaCO_3$) (Choo et al., 2000; Judd, 2011; Kim et al., 2007; Meabe et al., 2013).

Several techniques have been used to monitor and clean membrane fouling. In the side-stream configuration, high cross-flow velocity can minimize the foulant accumulation in the membrane surface. Whereas in the submerged configuration, typically, the fouling can be controlled by using the biogas sparging (Song et al., 2018). As reported by Stuckey (2012), the application of granular activated carbon could successfully minimize the fouling. Furthermore, the other techniques have been investigated to solve the fouling issue including the physical, chemical and biological methods. Physical treatment of membrane fouling cleaning could be accomplished by backwashing, surface flushing and ultrasonic (Lin et al., 2013). While chemical cleaning is reported using sodium hypochlorite, hydrochloric acid, nitric acid and EDTA. However, the application of chemicals might disrupt the microbial activities and lowering the performance of AnMBR (Song et al., 2018).

Besides the membrane fouling, the foreseen problem has been addressed by some researchers, inhibitory substances for example. As mentioned by Chen at al. (2008), free ammonia and sulphate could greatly become the inhibitory substance. The free ammonia is seemingly toxic and can directly penetrate through the membrane cell, therefore, it results in the inhibition of cellular haemostasis. Elevated concentration of sulphate can be an inhibitor for AnMBR. This is due to the competition between sulphate reducing bacteria and methanogenic microbes (Chen et al., 2006). Furthermore, the availability of sulphate can promote the precipitation with non-alkaline metals, so that reducing the concentration of micro-nutrients for methane producing bacteria (Siles et al., 2010).

Temperature is the important aspect that should be considered when installing the AnMBR, and in the same time, it also could be in inhibitory factors. Generally, AnMBR works efficiently under thermophilic (50 - 60 °C) or mesophilic conditions (30 - 40 °C) (Martinez-Sosa et al., 2011; Gouveia et al., 2015). However, the operation in the cold condition could address some negative issues, includes slow biodegradation of the contaminants and leading the accumulation of suspended solid inside the reactor (Martinez-Sosa et al., 2011).

3 Underlying operational parameters of AnMBR

Many studies have been reported on the underlying operational parameters when installing AnMBR. Modifying the operational parameters is clearly related to the membrane fouling, COD removal, reactor's efficiency and biogas production. Thus, monitoring and investigating the operational parameters would greatly reducing the operational cost (Meng et al., 2009). For instance, to lower the concentration of extracellular polymer substances, SRT and HRT should be elevated to some extent. In this section, some underlying operational parameters of AnMBR will be discussed.

3.1 Temperature

Temperature is an important parameter to intensely influences the anaerobic process. Generally, AnMBR could be operate under three different temperature conditions: psychrophilic (< 20 °C), mesophilic (25-40 °C) and thermophilic (> 45 °C) (Gouveia et al., 2015; Martinez-Sosa et al., 2011). According to Song et al. (2018), psychrophilic condition works unsuccessfully in municipal wastewater. Hence, the energy requirements needed is considerably high because the system should be heated until the temperature of mesophilic reached. AnMBR shows a favourable performance when working either psychrophilic or mesophilic conditions. Regarding the biogas production, however, both conditions achieved comparable methane production rates (Trzcinski and Stuckey, 2010).

Thermophilic condition offers more benefits compared to mesophilic conditions in terms of specific growth of microorganism and metabolic rates and so less ammonia inhibitions. Furthermore, working in thermophilic conditions offers another advantage; pre-cooling and post heating used in mesophilic condition could be avoided, therefore, the operational cost is lower (Lin et al., 2013). In addition, thermophilic AnMBRs are identified to have a rate-advantage due to a faster reaction time and higher volumetric loading rate, and so producing higher biogas productivity (Chen et al., 2016).

The drawbacks if working in thermophilic condition, however, are microbial death rate is higher, modest supernatant quality and low stability (Musa et al., 2018). According to literature search, to date, AnMBR operates under mesophilic condition with great advantages; this advantage associated with COD removal efficiency (Tchobanaglous et al., 2002).

3.2 Hydraulic Retention Time and Solid Retention Time

Operational parameters such as HRT and SRT are two factors that draw a vital role in AnMBR performances. Typically, the HRT applied for AnMBR system varied from 2.6 h to 14 d, whereas the normal HRT for high strength wastewater treatment is 1-10 d (Lin et al., 2013). The research of Hu and Stuckey (2006) reported that an exponential decrease in COD removal (5% removal in average) when the HRT lowered from 48 h to 24, 12, 6 and 3 h. However, Liao et al. (2006) strongly suggested that, lower HRTs will provide a room for shorter contact time between microorganisms and substrate and therefore might pave way for a part of influent COD leaving the reactor without proper treatment. Regarding the biogas production, the longer HRT was reported more favourable to increase the methane production and recovery (Ho and Sung, 2009). However, Yuzir et al. (2011) detected the decreased of methane recovery from AnMBR with longer HRT. This phenomenon is due to the availability of COD as a substrate of methane production is seemingly low.

SRT becomes one of the pivotal parameters to determine the treatment performance and fouling on the membrane surface. Trzcinski and Stuckey (2010) investigated the performances of AnMBR at psychrophilic condition with SRT decrease from 300 to 30 d, the results showed that longer SRT was greatly related to higher COD removal. On the other hand, Baek at al. (2010) observed that the decreased of SRT from 213 to 40 h did not have significant treatment performance as well as membrane fouling. All in all, the relationship between SRT and treatment performance is hardly to understand and seemingly complex to some extent, but it highly depends on HRT and the effluent characteristics.

One very essential aspect of AnMBR is the enabling environment that allows SRT to be completely independent from HRT irrespective of the sludge properties. Furthermore, AnMBR operation with relatively long HRTs and SRTs was favourable, to enhance methane recovery, treatment performance and reduce sludge production (Ho and Sung, 2009). One aspect that should be considered, according on the literature review on the effects of HRT and SRT conducted so far, is that prolonging HRT may result in inadequate utilization of AnMBR’s volume and its reduction may lead to rapid volatile fatty acid (VFA) accumulation which may hinder methanogenic activities. Prolonged SRT might also result to membrane fouling (Musa et al., 2018). Finally, it can be concluded that optimized HRT and SRT are greatly depending on the compositions of wastewater, reactor configuration etc. (Chen et al., 2016).

3.3 pH

pH is one of the influential factors determining the effluent quality. Neutral pH is likely more favourable to some extent. This due to the operational cost would be pressed into the minimum value; the post-treatments are not needed to treat the effluent from the working system (Lin et al., 2013). Different range of pHs have been tested for AnMBR system, comprehensively between 4.0 to 8.5. Considering that AnMBR systems operate in anaerobic condition, the bacterial growth should be taken into account. Typically, most of the methanogenic bacteria is suitably working in the neutral pH (6.8 -7.2) (Wang et al., 2012; Zhou et al., 2016) and so yielding the maximum biogas productions (Weiland, 2010). These range of pH usually achieved through the neutralization process which can be done by dosing additional chemicals (either acid or base), because some waste streams have an extremely acidic or basic condition. Therefore, the pH adjustment into neutral pH is greatly needed to avoid the microbial granules disintegration if the effluent is in alkaline conditions (Weiland, 2010).

3.4 Organic loading rate (OLR) and organic compound concentration

Generally, OLR represents the quantity of volatile solid fed into biogas digester per day under continuous operation. When OLR increases, the biogas yield is seemingly also rose to some extent. It should be noted that the increase of OLR may risk the biogas productions due to VFA accumulation and inhibition of microbial activity (Wijekoon et al., 2011).

Regarding to the characteristics of organic compounds within the waste effluent totally determines the biogas quality. For instance, the organic compound is full of carbohydrates (biowaste and corn silage) is increasing the biogas productions, especially the percentage of methane (CH_4) (Zhou and Wang, 2012)

3.5 Membrane properties

Generally, membrane materials can be categorized by three main classifications: polymer, ceramic and metallic. Polymeric membranes are reported made of: Polyvinylidene difluoride (PVDF), Polyether sulfone (PES) (Santos and Judd, 2010), Polyethylene (PE) (Vyrides and Stuckey, 2009), polypropylene (PP) (Jeong et al., 2010) and or polysulfone (PSF) (Stuckey, 2012). Based on the literature review, PVDF is the most frequently polymeric membrane used in AnMBR for wastewater treatment. Furthermore, polymer membranes have some downsides, including lower permeability and decreasing the stability of chemical cleaning (Judd, 2010).

On the other hand, according to Dvorak et al. (2015), ceramic membrane is working way more efficient than polymer membrane. This phenomenon is due to ceramic membrane have an excellent stability for both chemical and thermal, and maximize the resistance of corrosion and abrasion (Lin et al, 2013). Furthermore, this type of membrane materials is more effective for the cleaning process compared to polymer membranes because it does not affect the life span in a negative way (Ersu, 2008). Conversely, metallic membrane is commonly limited used for AnMBR system. This is due to the price of this materials is higher compared to polymer and ceramic membrane; thus, the application of this membrane is only for specialized purposes. The benefit of employing this type of membrane is having a high hydraulic performance, easier permeability after the membrane clogging, better in stability performance and excellent tolerance to oxidation and high temperature (Deowan et al, 2015; Lin et al., 2013).

Most of membrane modules used in AnMBR are implemented either using microfiltration (MF) (Kocadagistan and Topcu, 2007) and ultrafiltration (UF) (Van zyl et al., 2008), with membrane pores ranging from 0.03 μm to 1 μm in the MF region and 20,000 Da to 140,000 Da in the UF region (Hu and Stuckey, 2006; Huang et al., 2007; Padmasiri et al., 2007). The configurations of membrane modules are reported scientifically are flat sheet (FS) (Casu et al., 2010; Spagni et al., 2010), hollow fibre (HF) (Hu and Stuckey, 2006) or tubular (Padmasiri et al., 2007; Zhang et al., 2007). The details of membrane materials and modules are summarised by Lin et al. (2013) and can be seen from **Table 9** as follows:

Table 9. Membrane materials and modules used in AnMBR studies

Membrane Material	Module configuration	Pore size (μm)	Type of waste treated	Reference
PVDF	Hollow fiber	0.04	Municipal wastewater	Rezania et al., 2006
PVDF	Hollow fiber	100 kDa	Low strength municipal wastewater	Zeigler, 2007
PVDF	Flat sheet	70-140 kDa	Municipal wastewater	Lin et al., 2009
PVDF	Tubular	0.03	Agricultural wastewater	Wong et al., 2009
PVDF	Tubular	0.1	Municipal wastewater	Baek and Pagilla, 2006
PES	Flat sheet	20-70 kDa	Food wastewater	He at al., 2005
PES	Tubular	20 kDa	Swine manure	Padmasiri et al., 2007
PE	Flat sheet	0.4	Municipal solid waste	Trzcinski and Stuckey, 2009
PE	Hollow fiber	0.4	Waste activated sludge	Xu et al., 2010
PP	Hollow fiber	0.45	Acidified wastewater	Jeong et al., 2010
PSF	Tubular	0.2	Municipal wastewater	Jeison et al., 2008
Ceramic	Tubular	40 kDa	Municipal wastewater	Herrera-Roblledo et al., 2010
Ceramic	Tubular	0.2	Municipal wastewater	Jeison et al., 2009
Metal	Tubular	0.1	Municipal sewage sludge	Kim and Jung, 2007

Recently, the application of HF membrane draws significant interest for the treatment of industrial wastewater. This is due to their outstanding performance on high packing density and low operational price. The excellent advantages using this membrane are showing great stability, easy cleaning process, low propensity of membrane clogging, and high cross-flow velocities (Lin et al., 2013). While, flat-sheet membrane modules also catch more attention amongst research community. This is due to the advantages of good stability, easy for cleaning and replacement of membrane's defective (Kanai et al., 2010). The tubular membranes are also having the benefit over the other membrane module in low fouling, relatively easy for membrane cleaning, and easy handling of suspended solid. However, the drawbacks of this membrane are high operational cost, low packing density and high pumping costs (Lin et al., 2013).

3.6 Cross-flow velocity

Cross-flow velocity (CFV) aims at decreasing the particle deposition on the surface of membranes. Applying high CFV in the system would not be recommended, due to the high shear force over the membranes that could actively be a detrimental agent for anaerobic activity. Furthermore, according to Ifelubuegu et al. (2011), high shear force over the membrane is responsible for the physical disruptions of syntrophic association and actively being a foremost factor in organic matter degradation. A research conducted some researchers mentioned that the typical value of CFV is 2-3 m/s. This value is seemingly adequate to avoid the fouling effect over the membrane surface and so not inhibiting the microbial activity (Choo and Lee, 1996; Ifelubuegu et al., 2011).

4 Freeze concentration

Industrial wastewater composed with complex matrices starting from chemicals to suspended solid contaminants would greatly become a wicked environmental pollutant. The treatment of various pollutants present in the wastewater requires also different methods. Regardless of the treatment methods applied to wastewaters, it is an advantage if the volume of wastewater could be reduced extensively. The reduction of wastewater volume is directly related to the reduction of operational costs in terms of utility (Jusoh et al., 2008). The reasons why the solution needs to be concentrated are requiring small energy consumptions, relatively produces minor footprints and relatively safe (Jusoh et al., 2008). In this research, the main objective of the concentrated solution is to reduce the volume of excessive water and obtain a P-rich concentrate from DWP.

To concentrate the solutions, there are three techniques that are mainly used: evaporation, membrane processes (mainly reverse osmosis) and freeze concentration (Sanchez et al., 2011). Evaporation is the simplest and oldest method and works based on gas-liquid separation. It uses very large amount of energy to supply for the heat and yet highest maximum concentration (>50 ^{o}Brix) (Jusoh et al., 2009). Moreover, when the solution contains hazardous volatile organic compounds (VOCs), it might produce highly toxic gas (Rogers, 1999). Reverse osmosis (RO) is a pressure-driven membrane process that works according to molecular-sieve mechanism of semipermeable membrane. Compared to the evaporation technique, RO obtains lower concentration rates (~30 ^{o}Brix). Despite the energy consumption is lower, the membrane cost is rather high and the membrane clogging is easily obtained (Jusoh et al., 2008; Miyawaki et al., 2005).

Compared with the most commonly used concentration methods, FC is strongly more favourable in terms of the quality of the end products obtained and also presents the lower investment, operational and maintenance costs (including energy consumption, capital and cleaning process) (Jusoh et al., 2008). FC works based on solid-liquid phase separation at considerably low temperature, hence the thermally sensitive component is expected to be well preserved. The maximum concentration accomplished for FC is approximately 50 ^{o}Brix (Heldman, 2003). To the best of our knowledge, FC defines as a process for concentrating the solutions by freezing the water content and subsequently removing the so-formed ice crystals and eliminating solutes or impurities simultaneously (Hamid et al., 2015; Jusoh et al., 2008; Miyawaki et al., 2005).

Recently, FC is gaining more attention in dairy processing industry. However, from the literature review, there are no studies evaluating the nutrient recovery from DPW, since the study mostly focused on cheese whey treatment and treatment of dairy processing industry. For example, the works of Abd El-Gawad and Ahmed (2011) researched in milk processing industry and applying FC process. The objective of the research was to see the effectiveness of FC related to the energy consumption and the capital costs. The results showed a promising result in terms of energy consumptions. Theoretically, the heat of evaporation is about 2260 KJ/kg and the enthalpy of freezing is approximately 335 KJ/Kg. The data depicts that the FC seems to be cheaper in terms of energy consumption. The results are also supported by the works of Miyawaki (2005) and Ruemekorf (1994), reported that another benefit of applying the FC is smaller operational capitals required compared to biological treatment.

Furthermore, as said, FC is favourably attractive for dairy processing industry for the treatment of the effluent produced (Abd El-Gawad and Ahmed, 2011). For instance, Munoz et al. (2019), reported the application of FC in skimmed milk industry. The objective of the study was to investigate the FC of skimmed milk in three different temperatures and stirring rate. The results showed that FC is a promising way for the dairy processing industry from economic, technological and nutritional perspectives. The application of FC in bio-food industry waste was also reported by Aider et al. (2008). A freezing method was successfully conducted in -10, -20 and -40 ^oC while defrosting process took place at 18 ^oC. The results showed that the bio-food waste can be concentrated approximately 35% of dry matters and total protein concentrated was up to 20% of dry matter.

An example of FC applied to the treatment of dairy wastewater is the study conducted by Belen et al. (2018). The aim of this study was to evaluate the behaviour of FC in cheese whey treatment by considering the physicochemical and statistical analysis. The results revealed that FC of cheese whey was increasing the solids concentration from 7.7 to 25 % wt, which correspond to an 83% reduction of the initial volume processed and can optimize the management and use. Additionally, the fat content in the ice fraction reduces the efficiency of the last stage of the freeze concentration process. The mean energy consumption for concentration from 7.7 to 25.0 % wt was 0.25 kWh·kg-1 of ice.

The dairy process waste stream can be obviously treated by separating the ice crystals formed in the system, because the ice crystals only contains the pure water and no components (impurities) from wastewater (Halde, 1979). However, the final quality of the ice is greatly affected by several issues during the freezing concentration process. For instance, as reported by Vrbka and Jungwirth (2005), the ions can be ejected into a very small volume of unfrozen ice, but sometimes the ions can be trapped into the ice crystal. Due to the mentioned issue, currently, researcher develop more comprehensive technology to obtain the higher quality of ice. Wakisaka et al. (2001) developed the square pillar-shape plant and studied the effect of ice seeding, including the ice crystallization flow rate. Shirai et al (1998) also investigated the purity of ice layer on aluminium plat heat exchanger. Furthermore, Amran et al (2018) constructed Vertical Finned Crystallizer to investigate the efficiency of crystal ice formed.

4.1 Freeze Concentration techniques

According to a comprehensive literature review, to date, there are four techniques of freeze separation process including: direct contact freezing, vacuum freezing, indirect contact freezing and eutectic separation.

4.1.1 Direct contact freezing

The application of direct contact freezing has been reported by some authors in desalination industries (Rahman et al., 2006; Randall and Nathoo, 2015; Williams et al., 2014). In direct freezing, the volatile liquid hydrocarbon (such as butane and propane) refrigerant is used to cool the solutions and directly brought into contact with the brine, but not with water. Initially, the volatile liquid hydrocarbon adapted with high pressure and dispersed into the brine using the jet sprays. Due to the lower pressure in the freezer, the liquid hydrocarbon is evaporated and so cooled the brine under its freezing point and resulting in ice brine slurry formation. The schematic process of direct contact freezing, can be seen in **Figure 11** below:

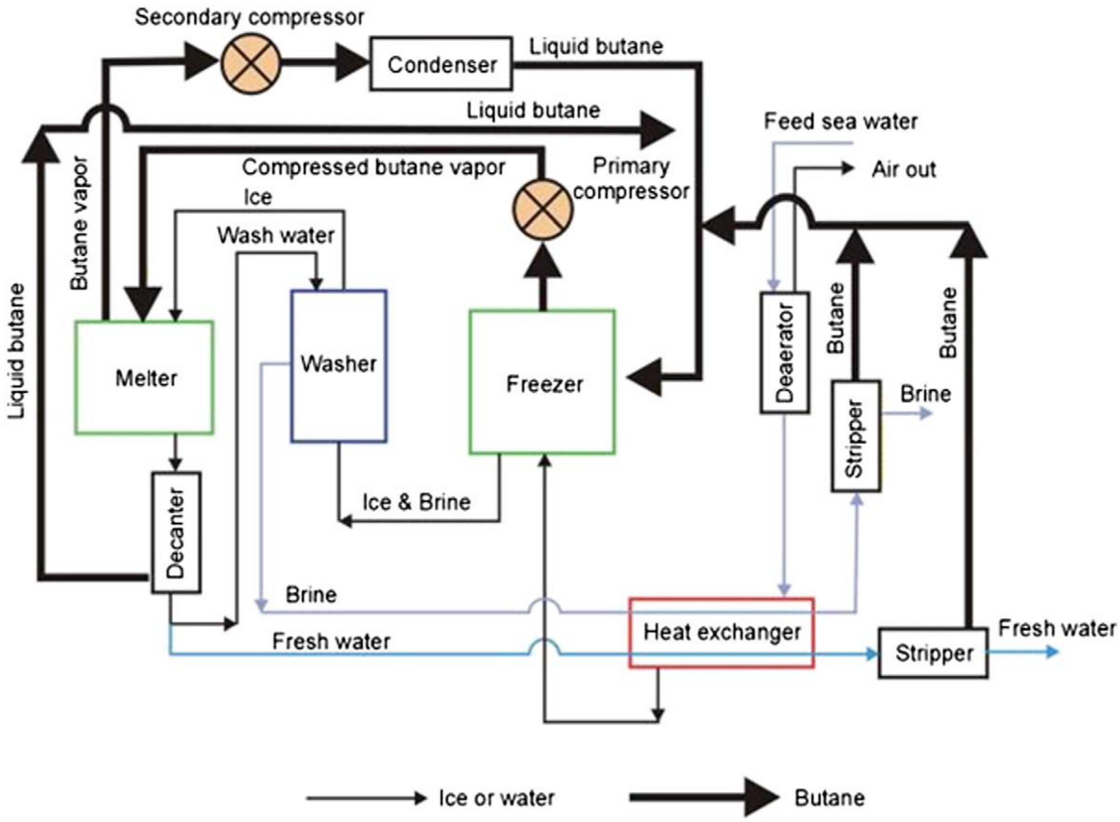


Figure 11. Schematic process of direct contact freezing (adopted from Lu and Xu, 2014)

As can be seen in **Figure 11**, after the ice brine slurry is formed, it then pumped to wash chamber where the separation of ice occurs and simultaneously cleaned by the wash water and transferred to the melter. Previously, the heat initiated in the freezing chamber is them used to melt the ice in the melter. The remaining hydrocarbon liquid vapor is compressed, condensed and recycled to the freezer (Williams et al., 2014).

The foremost advantages using this technique are having high production rate, relatively low energy consumption because the absence of heat transfer system and no moving parts (Gibson et al., 1974). On the other hand, the disadvantages foreseen of this method are the ice product obtained easily contaminated because the refrigerant is in direct contact with the solution (van der Ham, 1998). The water produced within this system is non-potable (Williams et al., 2014). The application of volatile and explosive hydrocarbon refrigerant may cause the safety related problem (Wang and Chung, 2012), but this limitation can be solved by using the hydraulic refrigerant compressor which initiated by Rice and Chen (1997).

4.1.2 Vacuum freezing

In this method, both evaporation and freezing process take place in the freezer while ice slurry and water vapor are removed. To do so, a high vacuum is used to vaporized the water, so the temperature of brine simultaneously drop resulting in crystallisation process. The compressing water process spends a major cost for the energy consumption (see **Figure 12**). Accordingly, the deaerator is an important part to install which aims at withdrawing dissolved gases and so affecting the overall operation of the system (Williams et al., 2014). The advantage of employing this system is that the ice production efficiency is relatively high. This is due to the evaporation of 1 kg of water will produce 7 kg of ice and theoretically, the ratio of the latent heat of vaporization of water to the latent heat of freezing is approximately 7:1 (Rane and Padiya, 2011).

On the other hand, the limitation of the process is that the design of the compressor is challenging to the large volume of water vapor (Rane and Padiya, 2011). The drawback, therefore, can be solved by installing alternative process; vacuum freezing vapor adsorption (VFVA) and the vacuum freezing high pressure ice melting (VFHPIM). VFVA process adsorbs the water vapor and reclaim the vapor from the absorbent. The main energy supply is provided as a latent heat by stem in absorbent generator. On the other hand, VFHPIM process does not need a compressor nor an absorbing solution, yet highly energy efficient and low cost compared to other desalination process (Lu and Xu, 2014).

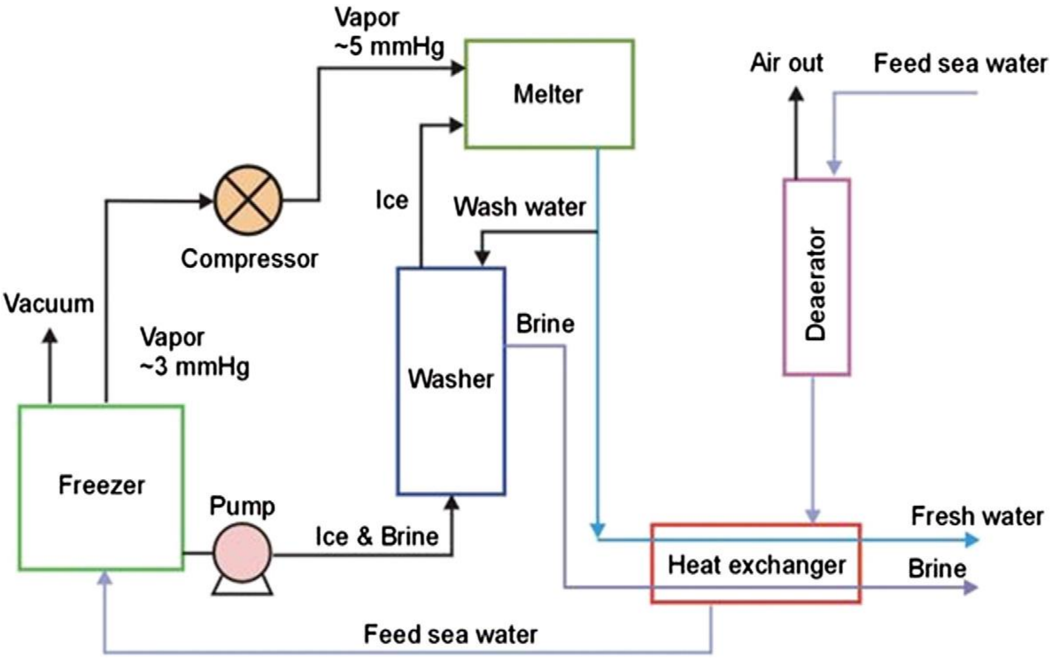


Figure 12. Schematic process of vacuum freezing (adopted from Lu and Xu, 2014)

4.1.3 Indirect contact freezing

According to **Figure 13**, initially, the brine pumped through the heat exchanger to the freezing chamber and so the brine is precooled in the heat exchanger before entering the freezer. The temperature of brine will be reduced until its critical temperature obtained. Hence, the ice crystals are formed in the freezing chamber. The ice slurry, including ice crystals and reject brine, is pumped to the separation unit where the ice crystals and reject brine are split into two streams. The reject brine is removed from the system, while the ice stream is transferred to the melting unit where the ice absorbs heat from the refrigerant through a heat transfer surface, leading to melting of the ice resulting in fresh water, as the refrigerant is condensed (Williams et al., 2014). Prior to discharging the melted ice from the system, a small amount of product water is taken to the separation unit as washing liquor. The disadvantages of this system are the energy demand is relatively high and the capital cost to install metallic heat transfer surface (Johnson, 1976).

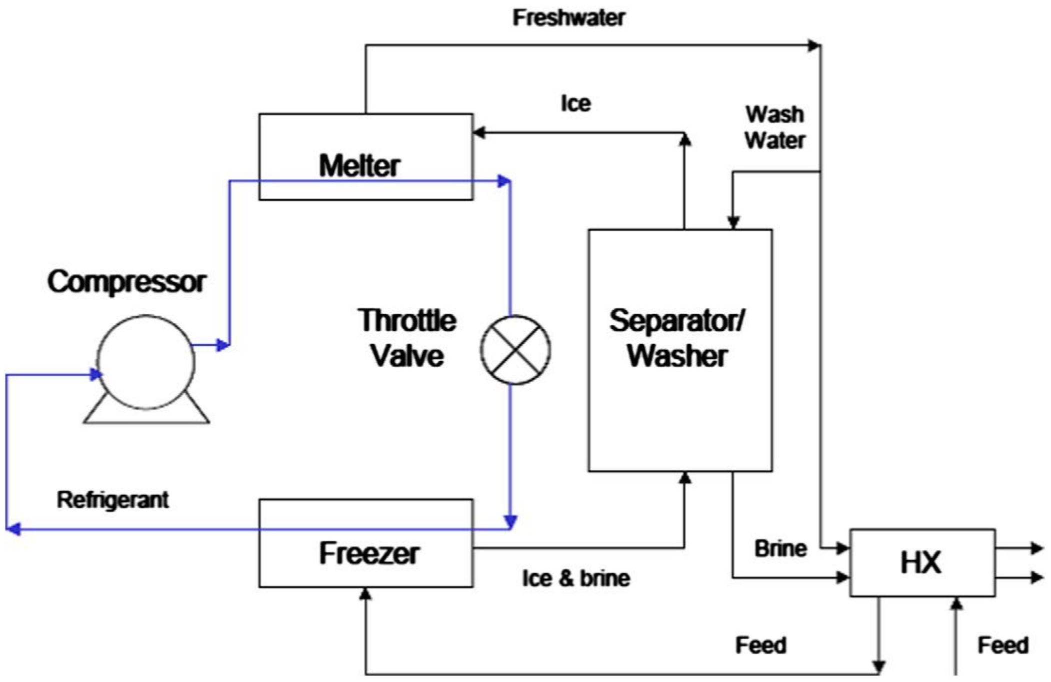


Figure 13. Schematic process of indirect contact freezing (adopted from Lu and Xu, 2014)

Among indirect contact freezing technique, there are two possible strategies of operation: conventional suspension freeze concentration (SFC) and progressive freeze concentration (PFC) (Hartel and Morison, 2006; Miyawaki et al., 2005). SFC is a technique of concentrating the solutions where the ice crystal blocks are formed in the suspension of the main liquor and produced the ice crystal layer by layer on a cooled surface isothermally (Jusoh et al., 2009; Miyawaki et al., 2005; Gu et al., 2005). In this conventional technique, however, the limited size of ice crystal is formed and the whole systems need a very long step: ice nucleation, crystal growth and ice crystal separation. This method gives a high capital cost for the operation (Jusoh et al., 2008).

To fill the gaps of unfavourable SFC, the researchers find a new development technique which much cheaper and not required numerous steps for the whole system, then PFC has introduced. Unlike SFC produced small layered ice crystal, PFC proudly produces a large size of ice crystal. Due to the bigger size of ice crystal produced, the separation from mother liquor requires less steps and so less expensive. On the other hand, according to Jusoh et al. (2008), the quality of the ice crystal and the productivity are lower compared to SFC.

The pivotal factors affect the quality of ice crystal are fully relaying on the design of the apparatus which combines the concept of heat balance and the optimal parameters. If the heat balance can be maintained in a whole system, the large ice crystal and easily separated ice will be obtained, including the high productivity of the system. A phenomenon could affect the heat balance is the ice clogging which formed massively ice layer in the system (Sanchez et al., 2011). The parameters that suggested to maintain during the ice crystallizations are: the refrigerant temperature, crystal growth rate, and agitation rate.

Ojeda et al. (2007), designed the FC apparatus including the parameters to maintain the ice crystallizations and heat balance (**Figure 14**).

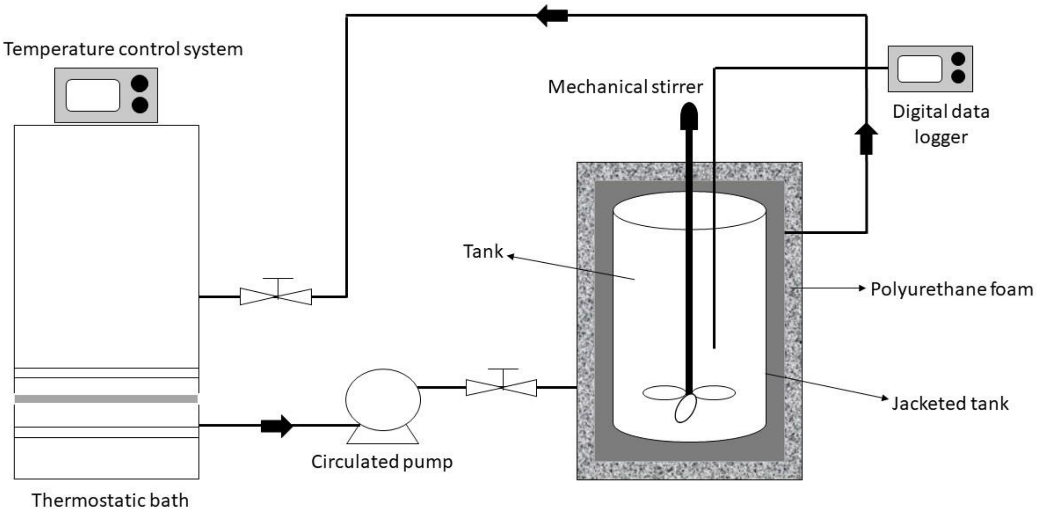


Figure 14. The design of PFC to control the heat balance (adopted from Ojeda et al. 2017)

From the experiment using the FC apparatus, it can conclude that the best operation condition to produce best quality of ice crystal and maintain productivity of system is by maintaining the stirring rate and applying coolant temperature of -5 ^oC and continuously checking the temperature of refrigerant. This technique is strongly recommended by Ojeda et al (2007) because this technology is claimed as environmentally friendly technology and can be applied in dairy industry.

Another report from Amran et al. (2008), mentioned that to improve the efficiency of the PFC methods is by improving the efficiency of crystallizer where the crystallizations process occurred. Furthermore, this technology guarantees to provide better heat transfer to a whole system. Hence, the quality of ice crystal can be obtained. The design of the crystallizer depicted in **Figure 15** called as vertical finned crystallizer (VFC).

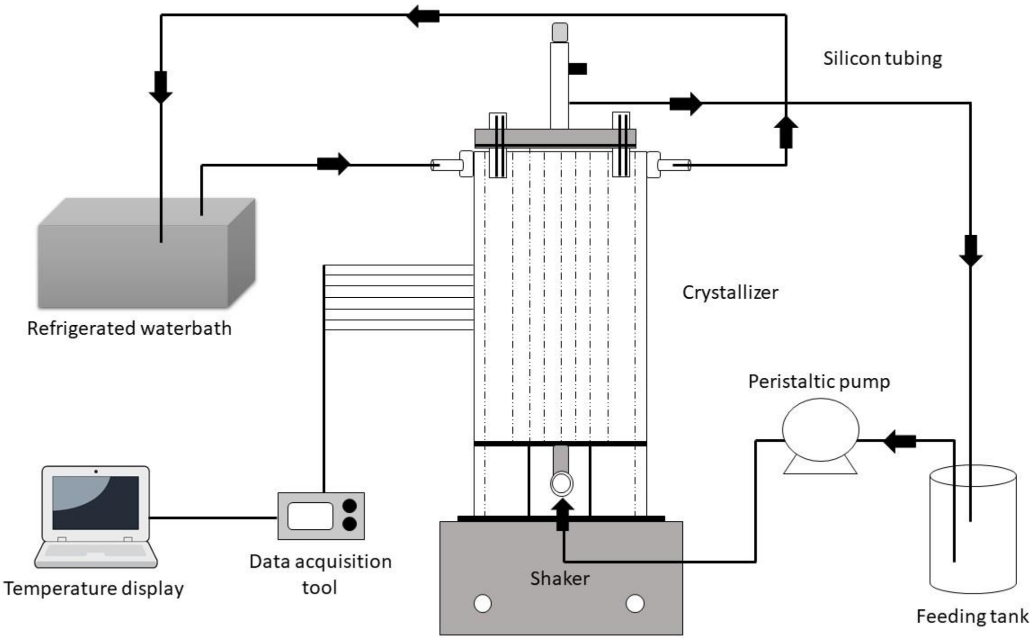


Figure 15. Experimental setup for VFC system through PFC (adopted from Amran et al., 2008)

According to the research of Amran et al. (2008), reported that VFC through PFC is capable to obtain high productivity of the system and produce highly concentrated concentrate solution as well as more pure ice. In addition, the performance of the system has evaluated through the identification of effective partition constant (K) and solute recovery (Y) which obtained 0.383 and 0.96, respectively.

4.1.4 Eutectic freezing

Eutectic freezing utilizes the density differences between ice and salt produced to ensure good separation process. An aqueous solution is cooled down to a eutectic temperature where both salt and ice simultaneously form. The salt, being denser than the solution and ice, sinks to the bottom of the crystallizer. While the ice, being less dense, floats to the top (Himawan et al., 2006; Randall et al., 2011; Vaessen et al., 2003). The advantage of this system is 100% yield can be achieved. This is due to the mother liquor only contain a pure salt which crystallize at eutectic temperature (Williams et al., 2004).

4.2 Theoretical bases of freeze concentration technique

To determine the performance of FC technique, K is used. Noted that K value which approaching 0 indicates the separation process is completely achieved. While, if the K value is reach to 1, it reveals that there is no separation process (Miyawaki et al., 2005). Hence, the lower K value is more favourable to determine if the system reaches high efficiency. The K value can be estimated by using **Equation 1** which derives from Bae et al. (1994):

$$(1-K) \log (V_L/V_0) = \log (C_0/C_L) \quad \textbf{Eq 1}$$

Where V_0 and C_0 represent the initial volume and concentration of the sample, respectively. V_L and C_L represent the volume and concentration of solute in concentrated mother solution, respectively.

Furthermore, to define the efficiency of FC technique, Y have to be evaluated. The Y value can be calculated by using **Equation 2** (Samsuri et al., 2015).

$$\mathbf{Y} = \frac{\mathbf{M_{S,L}}}{\mathbf{M_{S,0}}} \qquad \textbf{Eq 2}$$

Where $Ms_{,L}$ is the mass of solute in concentrated solution, while $Ms_{,0}$ is the mass of solute in the original solution. Y has a unit of g solute/g of initial solute, and a higher value of Y is preferable, as it reflects a better efficiency of the PFC process.

5 Underlying operational parameters of FC

5.1 Freezing temperature

The freezing temperature is considerably the pivotal parameter which determines the time to reach several wanted thicknesses of the ice and directly defines the freezing rate (Ab Hamid and Jami, 2019). According to Luo et al. (2010), under various temperatures applied, it needed different time for sample to reach the same thickness of the ice. It clearly stated that the lower the freezing temperature, the shorter freezing time needed to have the wanted thickness. Hence, defining the freeze temperature conditions is obviously needed in order to determine the best temperature for the system which directly correlated to the capital cost (Ab Hamid and Jami, 2019).

The effects of freezing temperature on the FC performance were analysed by the evaluation of K and Y values (Ab Hamid and Jami, 2019). Figure16 shows the relationship between freezing temperature against K and Y values. It can be observed that K value falls as the freezing temperature drops from – 4 ^{o}C to -10 ^{o}C, while Y on the other hand increases. This obtained result is also supported by Amran et al. (2008) and Samsuri et al. (2015) which indicates that the lower temperature will result in lower K value and higher Y value. As the coolant temperature declined, the temperature difference between coolant and glucose solutions became larger, hence increased the heat transfer rate which indicates to a higher efficiency of the PFC process performance. However, as the coolant temperature was further decreased from -10 ^{o}C to -12 ^{o}C, the trend shifted where the value of Y dropped while the K value increased slightly.

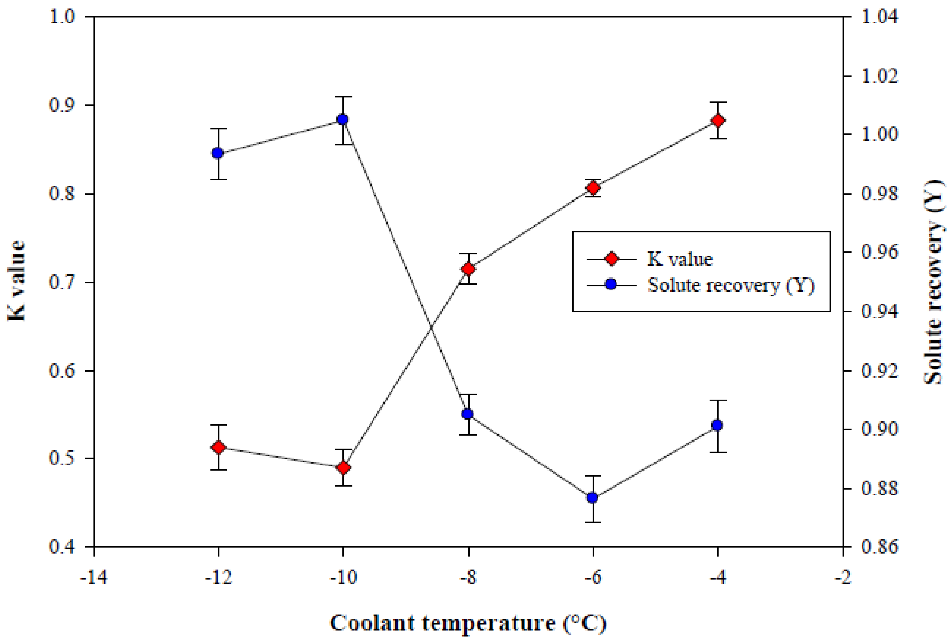


Figure 16. Freezing temperature against Y and K value (adopted from Ab Hamid and Jami, 2019)

According to Figure16, the temperature of -10°C was considered as the best temperature for this system due to its lowest value of K and higher value of Y were 0.490 and 1.005, respectively. The highest amount of glucose was also recovered at this temperature, leading to higher purity of ice crystal (Ab Hamid and Jami, 2019). From the experiment, it can conclude that the best operation condition to produce best quality of ice crystal and maintain productivity of system is by applying coolant temperature of -10 ^{o}C and continuously checking the temperature of refrigerant (Ojeda et al., 2007).

5.2 Freezing time

Freezing time is another influencing parameter which directly affect the performance of the FC system. By understanding the duration for a cycle of FC process, the maximum yield of purity ice could be accomplished.

The effects of freezing time against concentration of glucose was reported by Jusoh et al (2009) using glucose solutions as a shifting of real wastewater. To the best of our knowledge, the operating conditions applied by authors were circulation flowrate 100 mL/min, coolant temperature of -8 ^{o}C, and the initial concentration of 7 mg/L. As seen in **Figure 17**, the time required for the new crystallizer to be filled with ice lining was 23 minutes. Therefore, the authors had decided the range studied for freezing time was in between 5 to 20 minutes, while the other parameters were kept constant. The highest yield of solute concentration was for 5 min circulation (Jusoh et al., 2009). From the recorded investigations, the ice formed during this period of time was not in a solid form but more likely to a dendritic-structure. This phenomenon indicated that the freezing process was possibly incomplete.

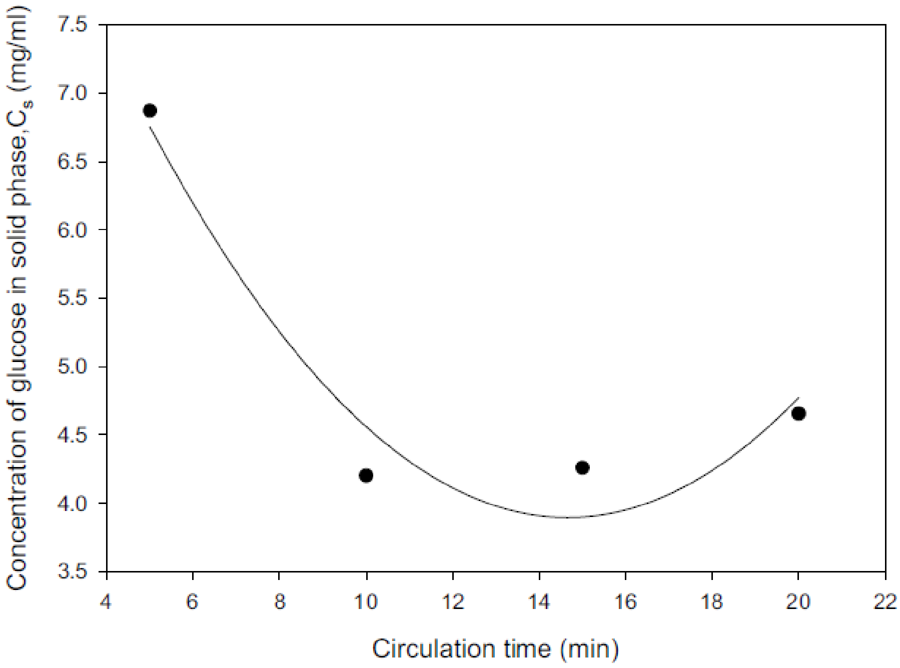


Figure 17. Concentration of glucose in solid phase VS Circulation time (adopted from Jusoh et al., 2009)

Accordingly, from **Figure 17**, it reported that as the freezing time rose, the solute concentration in the ice phase was decreased and described to be satisfactorily low at 10 to 15 minutes with 40 percent of solute reduction. However, the trend has changed after 15 minutes freezing time where the ice contamination started to increase. Therefore, it can be concluded that the for the efficiency, the range of circulation time is between 8 to 16 min not taken between 5 to 20 min.

5.2.1 Stirring speed

Stirring speed also represents how the efficiency of the system and directly indicates the flow rate of the solutions (Ab Hamid and Jami, 2019). The stirring speed contributed to the advance rate of mass transfer between the ice and liquid interface, and finally contributed to the efficiency of a FC system. Moreover, the solution flowrate for the FC process controlled in order to prevent solutes from being trapped into the ice crystal formation, hence high solute concentration in the concentrated solution can be recovered (Amran et al. 2016).

The effects of stirring speed on the FC performance were analysed by the evaluation of K and Y values (Ab Hamid and Jami, 2019) and can be seen in **Figure 18**. It was illustrated that when the stirring speed increased from 100 rpm to 500 rpm, the K value was decreased while the Y value increased. Accordingly, the optimum efficiency was found at the stirring speed of 500 rpm with the lowest K value and highest Y value of 0.625 and 0.904, respectively. The research of Okawa et al. (2009) reported that the higher flowrate stimulates slower solidification rate, hence less concentration captured in ice. As a result, more solutes will remain in liquid phase and high purity ice crystal will be attained.

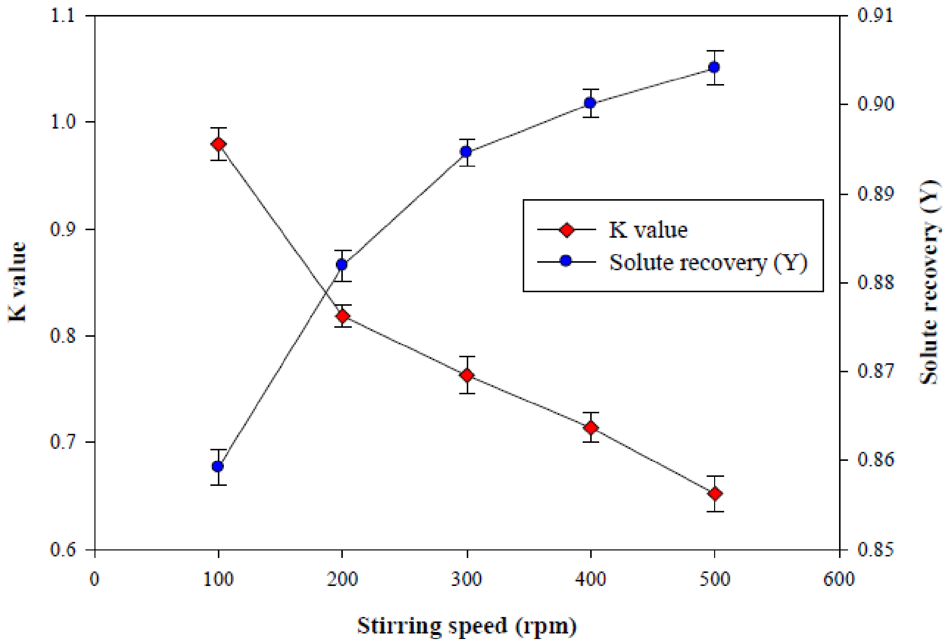


Figure 18. Effect of stirring speed against K and Y value (adopted from Ab Majid and Jami, 2019)

5.2.2 Circulation flowrate of solution

The circulation flowrate is one of the important parameters to determine the purity of ice obtained from the system. Higher or adequate circulation flowrate is needed in order to eliminate the trapped solutes from the crystal so that the high purity of the concentrated can be obtained (Shirai et al., 1998). The effect of circulation flowrate on the efficiency of PFC system has also been studied by Jusoh et al. (2009) (see **Figure 19**) using sucrose solution as a sample where the flowrate was ranged from 400 – 1000 mL/min while the other parameters like initial concentration (7 mg/mL), freezing time (15 min) and coolant temperature (-8 °C) were kept constant. From the result, the value of K was decreased while the circulation flowrate increased, which means better efficiency. The same finding was also reported by Miyawaki et al. (2005), stated that a better efficiency of the system could be achieved at a higher circulation flowrate.

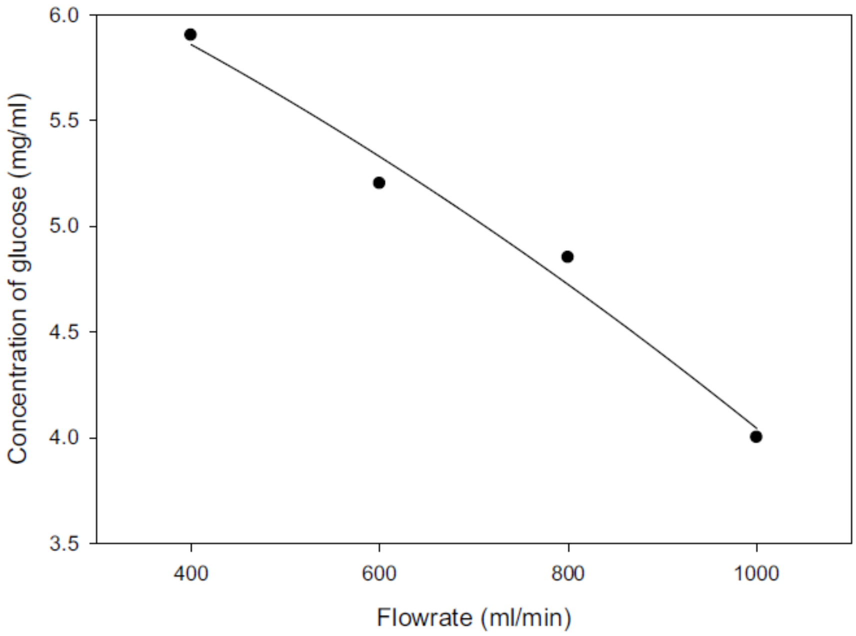


Figure 19. The effect of circulation flowrate on the purity of water produced (adopted from Jusoh et al., 2009)

Furthermore, Wakisaka et al. (2001) made a significant conclusion of the effect of circulation flowrate on the ice purity. Higher flowrate will provide higher shear stress at the ice-liquid interface which decreases the amount of solute trapped into the ice (Wakisaka et al., 2001). The trend may change again if the circulation flowrate is further increased until it reaches its maximum limit (saturation point). This phenomenon is due to the increment of heat transfer between then coolant and the solution (Rodríguez et al., 2000).

Hydrothermal carbonisation of P-rich organic waste (ESR3)

The following paper discusses the potential application of hydrothermal carbonization on biomass for phosphorous recovery. Despite its abundance as a resource, the economic utilization of phosphorous faces several challenges, the major of which include the imbalance in distribution and the large losses associated with the processing and consumption of this natural resource. For this reason, exploring the options for recovering phosphorous has become a necessity, particularly in regions where the natural abundance of phosphorous is scarce, such as in the case of the EU. Wastes, including sewage sludge, agri-processing and animal wastes, possess potentially extractable phosphorous content, which nominates it as a secondary resource of phosphorous requiring treatment.

Hydrothermal carbonization enjoys several advantages among more conventional thermochemical treatment techniques, particularly its ability to efficiently treat a wide range of low solids biowastes. The availability of phosphorous in biowaste, in addition to the product yield, is subject to feedstock type, temperature, residence time and biosolids/water ratio. The characterization of HTC products shows that phosphorous is concentrated and immobilized in the hydrochar, whereas the soluble phosphorous migrates towards the liquor. The fate and form of the phosphorous present in each product is dictated by the HTC reaction mechanism, and both are affected by several parameters, primarily temperature, pH and residence time.

This review concludes that HTC is a suitable treatment technique that enhances phosphorous recovery from biowastes. Further studies are required to understand the mechanisms of phosphorous transformation in the HTC products, in addition to further insight into the challenges facing the application of phosphorous recovery from HTC on an industrial scale.

Phosphorous as a Resource

Phosphorous is an essential element, whether on the level of human anatomy, food security or agricultural products. Ranked as the 11th most common element on Earth, phosphorous plays a critical role in the formation of DNA, cell membranes and bone repair, and its distribution in the human body reaches around 1.5% of total mass, making it the second most abundant mineral after calcium(Marcus, 2013). However, the major contribution of phosphorous lies in the field of agriculture, mainly in the production of fertilizers and management of food supply (Cho, 2013).

As a natural resource, phosphorous is derived from primary and secondary sources, which differ in terms of distribution and renewability. The primary source of phosphorous are phosphate rocks, which are sedimentary or igneous rocks having high phosphorous content. The production of phosphate rocks occurs mostly from surface mines, while some underground mines exist(Zowada, Gulacar, Siol, & Eilks, 2019). Phosphate rocks represent the main source of phosphorous, and studies have shown that around 85% of P (phosphorous) used in agriculture is derived from phosphate rock mines(Nedelciu, Ragnarsdottir, Stjernquist, & Schellens, 2020). However, phosphate rocks are considered a non-renewable source of phosphorous since the process of formation of these rocks requires millions of years. The secondary source of phosphorous comes from the Phosphorous Cycle, which refers to the accumulation of phosphorous in water streams and solid wastes(Smol, 2018). This source of phosphorous is considered renewable because it circulates between living and dead organisms. The terms “primary” and “secondary” do not refer to the availability of phosphorous in each resource, but rather they reflect the level of reliance on the source in extracting and producing phosphorous. In general, the main source of phosphorous used in agriculture and food processing comes from phosphate rocks, dominating more than 90% of the total phosphorous present in the market. However, due to losses in extraction and processing, only one fifth of the phosphorous present in phosphate rocks is available for consumption(Neset & Cordell, 2012).

Challenges

Due to its essential role in basic life functions and agricultural cycles, phosphorous represents a non-substitutable resource facing several challenges in terms of distribution, consumption and management. The first and main challenge related to phosphorous is the dispersed distribution of phosphate rock mines. As mentioned earlier, phosphorous production is highly dependent on phosphate rock mines. However, the natural resource experiences a significant uneven distribution on a geographic scale, where less than five countries possess more than 85% of the total reserves of phosphate rocks, including Morocco (72%), China (5%) and Algeria (3%) according to the United States Geological Survey(Nedelciu et al., 2020).

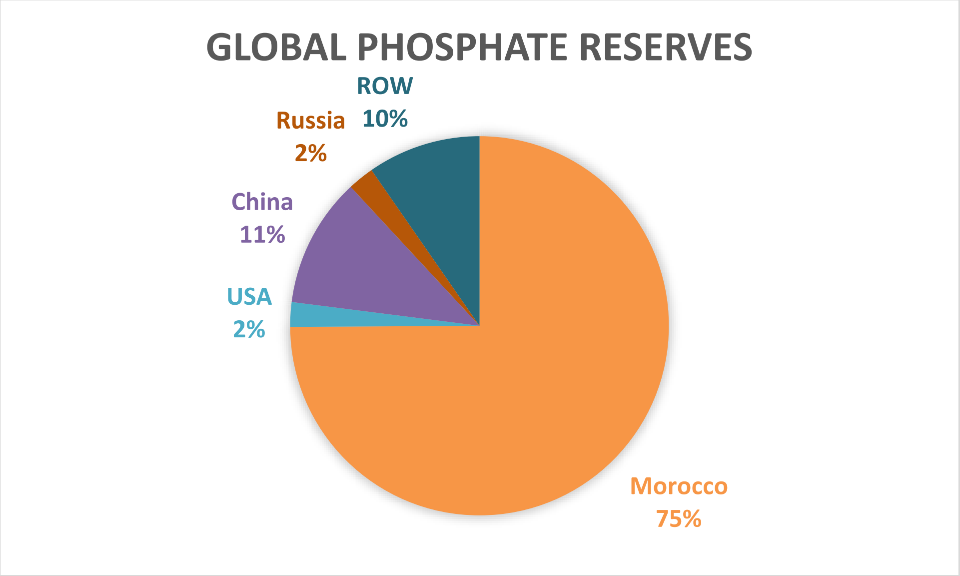


Figure 20: Phosphate Rock Reserve Distribution (Walan, Davidsson, Johansson, & Höök, 2014)

On the other hand, phosphorous production experiences a similar imbalance, with 6 countries dominating the production of phosphate products, Figure 21 shows the percentage distribution of phosphorous production among the major countries for the year 2019.

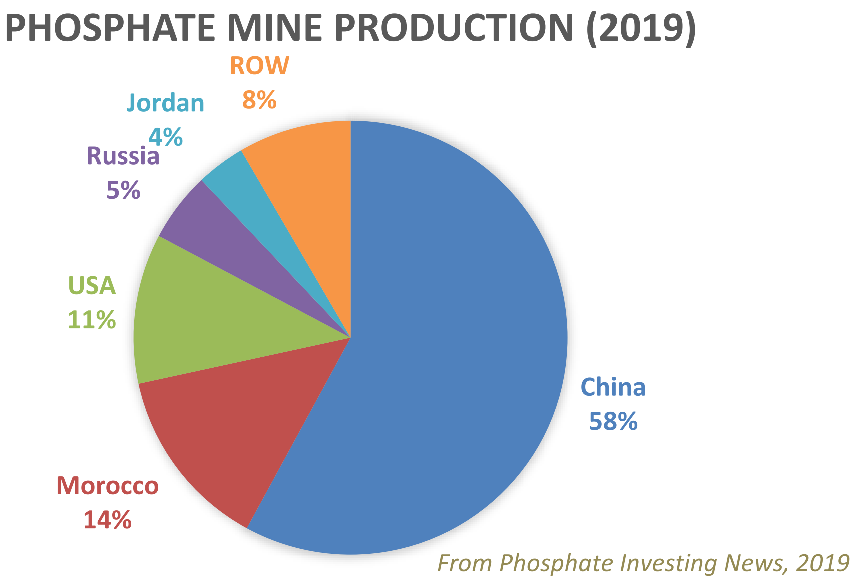


Figure 21:Phosphate Mining Production Distribution (Williams, 2019)

Therefore, the main obstacle facing the phosphorous industry lies in the uneven distribution of resources, which results in an imbalance in control over production. Combined, these two obstacles have raised questions over the sustainability of phosphorous as a mineral resource with concerns over a “phosphorous peak”.

EU Need for Phosphorous

In Europe, phosphorous plays a significant role in both the fertilizer industry and food processing, where the consumption of P is expected to reach 2.9 million tonnes by the year 2027(Europe, 2019). However, Europe lacks resources of phosphate rock, which increases its dependence on phosphate imports. This dependence has been highlighted by the European Commission as an economic and geopolitical threat after reaching a level of 88%(Rahimpour Golroudbary, El Wali, & Kraslawski, 2020). In fact, the balance of phosphorous imports and exports has been experiencing a significant gap in favor of imports, accompanied by a slight decrease in consumption(Schoumans, Bouraoui, Kabbe, Oenema, & van Dijk, 2015). Therefore, the EU declared phosphorous to be a critical raw material in 2014, and efforts have been directed towards prioritizing strategies for a circular economy to enhance its recovery and reuse particularly as fertilizer products.

Therefore, the need for phosphorous along with the challenges associated with its management increase the necessity to look for sustainable and renewable sources of phosphorous. Biowaste has been identified as a potential source of phosphorous, due to its availability, variety and potential efficient recovery via thermal treatment.

1 Techniques for Thermochemical Treatment of Biomass

The first step towards phosphorous recovery from biowaste is thermochemical treatment, which is applied to transform the biowaste into products and intermediates. The significance of thermochemical treatment lies in overcoming the structural inferiority of biomass, which enhances the chances of energy and resource recovery from biowaste (Kambo & Dutta, 2015). Understanding the mechanisms and conditions of each technique provides the necessary background for the choice to treat the initial biowaste feedstock, where the final product influences the choice of treatment method. Some of the widely used processes include, but are not limited to, combustion, gasification, pyrolysis, and hydrothermal carbonization.

1.1 Combustion

Combustion is the oldest form of biowaste treatment for energy production(Basu, 2010). During combustion, biowaste undergoes structural and chemical transformations in the presence of excess air in order to produce two major products, carbon dioxide and steam as well as an inorganic ash containing the majority of the phosphate. The growth in the application of incineration has reduced significantly due to the potential hazards embodied with the process, in addition to some serious concerns regarding air and water pollution. Furthermore, since some potentially more useful products can be obtained using more energy-efficient and environmentally friendly techniques, the application of combustion has been limited in the biowaste-to-energy field.

1.2 Gasification

Gasification is the transformation of a solid biomass into gaseous products through partial combustion (Minaret, 2015). The first application of gasification dates back to an experiment performed by Thomas Shirley in 1659, and the first gasification patent dates back to 1788 (Basu, 2010). Feedstock biomass is heated at a range of 600℃-1200℃ within short residence times (10-20 s) in a gasification reactor, which could be a fixed bed, fluidized bed or entrained flow reactor (Minaret, 2015). The main product of gasification is syngas, which is a combination of gases such as CO, H2 and CO2, which is significant for its role in producing valuable fuel products through Fischer-Tropsch synthesis (Kambo & Dutta, 2015). In general, gasification occurs at a lower temperature than combustion and produces a small amount of solid product, biochar, which retains the majority of the inorganic material but can contain the a high amount of heavy metals, thus, reducing the potential of using this product for fuel production or soil amendment.

Despite its importance in producing syngas, gasification falls short among candidates for thermal processing of biowastes, mainly due to the yield and high mineral content of biochar, environmental concerns related to the production of gases, and the difficulties related to promoting the technique in terms of public opinion. In fact, the major application of gasification aims at increasing the heating value of fuels, as well as enhancing the properties of the fuel by increasing C/H ratio and reducing the sulfur and nitrogen content(Basu, 2010; Toptas Tag, Duman, & Yanik, 2018).

1.3 Pyrolysis

The third technique for thermal treatment of biowaste taken into consideration in this study is pyrolysis, which is one of the widely used processes in the field of biomass-to-energy production. Pyrolysis was originally proposed by Canadian physician Abraham Gesner in the mid-1840s in an attempt to produce an alternative gas to the whale oil used in lamps (Jeguirim & Limousy, 2019). Pyrolysis is defined as the thermochemical treatment of biomass to produce a solid-phase biochar, liquid phase bio-oil and a stream of gases such as CO, CO2, H2 and CH4. (Kambo & Dutta, 2015) Pyrolysis occurs in the complete absence of oxygen, and it is usually carried out at temperatures ranging from 300℃-650℃. The final desired product dictates the type and operating conditions of pyrolysis, but in general, the four common categories of pyrolysis are: slow, fast, flash and intermediate(Atallah et al., 2020). Slow pyrolysis aims at increasing the yield of solid biochar, whereas fast pyrolysis enhances the production of liquid bio-oil, while under intermediate conditions, the three phase products of pyrolysis are produced in almost equal ratios(Leinweber, Hagemann, Kebelmann, Kebelmann, & Morshedizad, 2019). Despite its significance in industry, the application of pyrolysis encounters several setbacks related to high operational costs versus a moderate return of valuable products. Also, maximizing the yield of solid biochar through pyrolysis requires increasing the residence time and reducing the heating rates, which contributes to higher energy costs (Atallah et al., 2020). Pyrolysis also requires a dry (<20% H2O) feedstock which render it unsuitable for most abundant biowastes such as sludge.

Despite the differences in operation and products, all of the above processes for thermal treatment of biomass require the drying of feedstock as an indispensable pre-treatment step, which adds to the energy cost of the overall process.

1.4 Hydrothermal Carbonization

The first scientist to introduce Hydrothermal Carbonization was the German chemist, Friedrich Bergius in the city of Hannover, Germany in 1913, as he attempted to simulate the process of natural coalification (Rebling, 2016). Ever since that date, hydrothermal carbonization has been gaining increasing focus as a feasible and developed technique for thermochemical treatment of biomass.

Hydrothermal Carbonization is defined as the thermochemical conversion of organic biomass into a carbon-rich solid, called hydrochar, in the presence of water and under mild operating conditions (S. Zhang, Huang, & Liu, 2018). Unlike previous thermochemical treatment processes, hydrothermal carbonization occurs in a wet medium, where water plays the role of a catalyst for the decomposition reactions. Thus, the need for a drying pre-treatment step is eliminated (Antero, Alves, de Oliveira, Ojala, & Brum, 2020). By eliminating the drying step, HTC allows for the treatment of biomass with moisture content up to 90%, while ensuring acceptable results (Lucian & Fiori, 2017).

1.4.1 Advantages of HTC

In addition to eliminating the need for drying, HTC provides a set of advantages that prioritizes its position among the different thermochemical conversion techniques. The first and most important advantage of HTC is its capacity to treat a wide variety of biowastes particularly sludges. Numerous studies have been performed on different sources of biomass (animal waste, plant waste, algal biomass, municipal solid waste, sewage sludge and wood residues), and results have confirmed the feasibility and applicability of HTC(Fakkaew, 2016). This advantage is mainly due to the operating conditions of HTC. In terms of pressure, HTC operates under autogenous pressures that are generated by the effect of water temperature and the sealed framework of the reaction. Furthermore, HTC operates at moderate temperatures that do not exceed 250℃, which reduces the energy cost of operation in comparison to other treatment techniques such as pyrolysis and gasification. Another advantage of HTC is that it occurs in a reactive aqueous medium where water which acts as a solvent and a catalyst for hydrolysis and decomposition reactions(Román et al., 2018). In addition, HTC allows for high yields of carbon-rich hydrochar while using lower energy input. The high concentration of carbon in the solid phase is another advantage of HTC, as well as the increase in the energy densification of the products(Toptas Tag et al., 2018). In terms of nutrient recovery, studies have shown that HTC facilitates the concentration of valuable nutrients such as phosphorous in the solid, which aids in the process of nutrient recovery (Bashir M. Ghanim, Kwapinski, & Leahy, 2018; C. Song et al., 2018). Finally, HTC allows for the concentration of carbon in the solid product, while hydrogen and oxygen migrate towards the liquid phase, which reduces the smoke and energy losses embedded in the process (Toptas Tag et al., 2018). For this reason, the application of HTC to biowaste counts as a promising and eco-friendly technique, but controlling the operating conditions and medium for the reactions is essential for defining the product streams(Antero et al., 2020).

1.4.2 Process Conditions

In general, HTC proceeds under mild operating conditions, which play a key role in determining the yield and characteristics of the final products. HTC results in three major products: a carbon-rich solid phase hydrochar, a liquid mixture of acids and bio-oil solutions, and traces of gases such as CO2, CO, H2 and CH4(Nakason et al., 2017). Hydrochar stands as the most valuable and available product resulting from HTC, and the efficiency of the treatment is widely connected to the yield of hydrochar and its energy density(M. T. Reza, Becker, Sachsenheimer, & Mumme, 2014).

$$Product\ Yield = \frac{Mass\ of\ Dry\ Hydrochar}{Mass\ of\ Initial\ Dry\ Feedstock} \tag{1}$$

$$Energy\ Density = \frac{Calorific\ Value\ of\ Hydrochar}{Calorific\ Value\ of\ Initial\ Feedstock} \tag{2}$$

For this reason, understanding the conditions of the reaction allows for a sustainable and improved production of hydrochar for nutrient recovery.

The major conditions that influence the mechanisms and outcome of hydrothermal carbonization are temperature, pressure, residence time and biomass/water ratio, along with other minor factors. HTC usually occurs inside a sealed reactor within a range of moderate temperatures (180℃-250℃) under an autogenous pressure that ranges between 2-6 MPa. The residence time of the reaction varies from 5 minutes to 72 hours, depending on the scale of application and the characteristics of the desired products, whereas the biomass/water ratio of the input feedstock ranges between 0.025-0.25 (C. Song et al., 2018). Table 1 includes a summary of the conditions and yields of several HTC experiments performed on biowaste recently.

Table 10: HTC Conditions and Yields for different feedstock (A stands for Autogenous Pressure)

Feedstock	T (℃)	P (MPa)	Residence Time (min)	B/W	Yield	Reference
Dairy Manure	200-280	1.8-7.6	240	0.05	43.48%-58.34%	(C. Song et al., 2018)
Dairy Manure	180,220, 260	2-5	5, 30	0.2	50.8%-93.6%	(Toufiq Reza et al., 2016)
Dairy Manure	150,180, 210,240, 270	A	30,60, 120,240, 360	0.025, 0.05,0.075, 0.1, 0.125	51%-74%	(C. Song et al., 2018)
Coconut Fiber	150-300	A	30 min	0.1	35%-92%	(Liu & Balasubramanian, 2012)

Eucalyptus Leaves	300-375	A	30 min	0.1	28%-92%	(Liu & Balasubramanian, 2012)
Rice Husk	300	A	360	0.2	66%	(Kalderis, Kotti, Méndez, & Gascó, 2014)
Eucalyptus bark	220	4.4-6	120	0.1	46.4%	(Gao et al., 2016)
Sewage Sludge	170	A	240	0.04	74%	(Danso-Boateng et al., 2013)
Poultry Manure	220	A	240	0.15	53%	(Oliveira, Blohse, & Ramke, 2013)
Poultry Litter	150	0.75	30	0.2	87.17%	(B. M. Ghanim, Pandey, Kwapinski, & Leahy, 2016)
Polyvinyl Chloride	220	A	60	0.1	41.3%	(Ning et al., 2020)
Water Hyacinth	180	A	10	0.1	53.7%	(C. Zhang et al., 2020)
Green Waste	150	A	40	0.125	78%	(Shao et al., 2020)
Spent Coffee Grounds	216	A	60	0.1	64%	(Afolabi, Sohail, & Cheng, 2020)

Urban Sludge	180	0.6	33	0.2	92.04%	(X. Xu & Jiang, 2017)
Kraft Pulp	220	A	10	0.07	77%	(Wikberg et al., 2016)
Grape Pomace	225	A	30	0.25	60%	(Pala, Kantarli, Buyukisik, & Yanik, 2014)
Opuntia ficus-indica cladodes	180	A	30	0.2	71.36%	(Volpe, Goldfarb, & Fiori, 2018)

Based on the data provided in Table 1, it can be observed that HTC provides a feasible option for the production of carbon-rich char products. It is also clear that the initial feedstock plays a significant role in determining the yield of HTC; however, different parameters have various effects on the outcome of HTC.

1.4.3 Effect of Parameters on HTC

Several studies have been performed to assess the effect of varying process parameters on the outcome of hydrothermal carbonization.

Temperature

The major parameter affecting the yield and characteristic of hydrochar is temperature. As mentioned previously, HTC proceeds under average temperatures ranging between 180°C-250°C. Temperatures above 260°C divert the treatment process into hydrothermal liquefaction (HTL), which aims at producing bio-oil as a major compound(Kambo & Dutta, 2015). Therefore, it is essential to define the range of temperatures within which hydrothermal carbonization occurs to ensure the production of hydrochar as the major product. Furthermore, temperature impacts negatively on hydrothermal carbonization, since an increase in temperature leads to a decrease in hydrochar yield. Toptas Tag et al. (2018) performed HTC on three different types of feedstock, with varying temperature conditions, and the results showed a decrease in the yield of hydrochar for the three biomass types(Toptas Tag et al., 2018) . Similarly, Oktiavananda et al. (2017) varied the temperature for HTC of sawdust and reported a decrease in hydrochar yield from 54.44% to 38.82% within a temperature increase from 200°C to 340°C (Oktaviananda et al., 2017).

An increase in temperature facilitates the decomposition of biomass constituents at early stages, favoring gasification reactions and the dissolution of carbonaceous products into the liquid product, thus lowering the content of the solid hydrochar (Sabio, Álvarez-Murillo, Román, & Ledesma, 2016). On the other hand, an increase in temperature leads to an increase in the calorific value of the hydro char product. Yan et al. (2014) executed a series of HTC experiments on loblolly pine biomass under the same biomass/water ratio, residence time and pressure, while varying temperature. The results recorded an increase of higher heating value (HHV), which reflects the calorific value of the fuel, from 21.41 MJ/kg to 22.12 MJ/kg as a result of an increase in temperature from 200°C to 230°C(Yan, Hoekman, Broch, & Coronella, 2014). The increase in HHV values reflects an increase in carbon content in the final products, which leads to the enhancement of reactions such as decarboxylation with increasing temperature. This proposition is supported by the observation of a decrease in H/C and O/C ratios in produced hydrochars, which reflects the increase in carbon content versus the elimination of hydrogen and oxygen in the liquid streams(Toptas Tag et al., 2018).

Residence Time

The residence time of HTC affects the yield and characteristics of the hydrochar, mainly due to the effect of time on the reactions occurring within HTC. It has been reported that the relation between residence time and yield is negative; that is, an increase in residence time decreases the hydrochar yield (Smith & Ross, 2019). Chen et al. (2018) studied the effect of residence time on the characteristics of hydrochar. The study shows that at fixed temperature and biomass/water ratio, increasing the residence time of HTC inside the reactor from 0 to 120 min results a decrease in hydrochar yield from 60.38% to 53.45%(Chen, Ma, Peng, Lin, & Yao, 2018). These results are further supported by a study performed by Nizamuddin et al. (2016), which records a decrease in hydrochar yield produced from palm shell biomass from 57% to 51% as a response to an increase of residence time from 30 min to 120 min (Nizamuddin et al., 2016). The increase in residence time drives the carbonization reactions and enhances the decomposition reactions of cellulose and hemicellulose, which release lighter components such as organic acids which catalyze further hydrolysis and reduces the content of the solid product. However, Atallah et al. (2020) reported an opposing effect of residence time on hydrochar produced from the HTC of dairy manure. The increase in residence time at temperatures ranging from 200°C-250°C led to further increase in hydrochar yield(Atallah et al., 2020). Furthermore, the effect of residence time on the calorific value of hydrochar was studied by Zhang et al. (2015) through the hydrothermal carbonization of corn cob residues, and the results show that an increase in residence time leads to a slight increase in the HHV of hydrochar until a certain time, after which no significant increase is recorded(L. Zhang et al., 2015). Similar results were reported by Atallah et al., where the intensification of HTC process parameters led to an increase in energy yields from 56% to 96% (Atallah et al., 2020).

However, the inconsistency in results between different studies suggests that the effect of residence time on hydrochar yield does not follow a single trend. Sabio et al.(2016) suggested that the effect of residence time on hydrochar is highly dependent on temperature, and therefore, the impact of residence time on hydrochar yield and calorific value can vary(Sabio et al., 2016). Similarly, the type of feedstock plays a role in the nature of the effect of residence time on hydrochar yield.

Biomass/Water Ratio

A third factor that has significant effect on the outcome of hydrothermal carbonization is the biomass/water ratio of the input feedstock in the reactor. As mentioned previously, the presence of excess water facilitates the reactions accompanying hydrothermal carbonization. However, the loading of biomass mixed with water into the reactor varies with regard to the different operating conditions. In general, studies have shown than an increase in biomass/water ratio leads to an increase in hydrochar yield. Oktaviananda et al. (2017) performed HTC experiments on sawdust biomass to track the effect of biomass/water ratio on the yield and energy densification of solid products. The results show that an increase in biomass/water ratio from 0.05 to 0.25 leads to an increase in hydrochar yield from 63.11% to 69.57%(Oktaviananda et al., 2017). Similar results were reported by Heilmann et al. (2010) for the HTC of algal biomass, where hydrochar yield experienced an increase from 28.4% to 45.7% at constant conditions of 190℃ and residence time of 30 minutes (Steven M. Heilmann et al., 2010) . This observation is compatible with the results obtained from a study performed by Li et al. (2018) on a series of different biomass feedstock, where the hydrochar yield showed an increase in response to an increase in initial solid concentration. (Li et al., 2018) The reason behind this phenomenon lies in the fact that increasing the ratio of water in the mixture drives the hydrolysis reaction, which reduces the solid content in the final stream(Kladisios P, 2018). However, recent studies suggest that the positive influence of biomass/water ratio on hydrochar yield is restricted to an upper limit. According to Li et al. (2020), the increase in hydrochar yield and total energy of product stream becomes negligible above a biomass/water ratio of 0.2 for several biomass feedstock(Antero et al., 2020). Therefore, increasing the biomass/water ratio enhances the production of hydrochar with higher energy densification ratio, yet this increase should satisfy the need for presence of excess water to preserve the catalytic value of water.

1.4.4 Products

As the definition proceeds, hydrothermal carbonization transforms biomass into valuable products with enhanced qualities. The outcome of HTC consists of 3 phases: a carbon-rich solid phase, called hydrochar, a liquid phase mixture of water, organic acids, furfural-like compounds and phenol, and a stream of gases including CO2, CH4 and CO (Fakkaew, 2016). The distribution of these products is dependent on the type of feedstock and the operating conditions. However, the general product stream of HTC consists of the following:

Solid Phase (45%-75%): Hydrochar is the main product of the conversion. It is a carbonaceous structure with a chemical structure similar to coal (Kantakanit, Tippayawong, Koonaphapdeelert, & Pattiya, 2018). As an upgrade to the initial biomass, hydrochar has higher concentrations of aromatic C, and lower concentrations of H and O, which are eliminated to the liquid product. Furthermore, the ash content in hydrochar is lower than that in biomass, which suggests the dissolution of inorganic elements into the liquid product(S. Zhang et al., 2018). In addition, hydrochar shows high calorific values when compared to initial biomass on a dry basis.

Liquid Phase (5-25%): The liquid product of HTC consists mainly of sugars, acids and phenolic compounds. Organic acids such as acetic acid, levulenic acid, formic acid and lactic acid are the dominant constituent of the stream. However, intermediate furfural derivatives and phenolic compounds such as phenol and cresol are detected in the liquid product of HTC (M. T. Reza, Wirth, Luder, & Werner, 2014) . Organic acids have a potential catalytic role in the different reactions in HTC, while intermediate compounds act as precursors for a wide range of industrial applications(M. T. Reza, B. Wirth, et al., 2014).

Gases (2-5%): The main constituents of the gaseous phase of the product stream is CO2, which consists more than 90% of the total gas yield (Lin, Ma, Peng, & Yu, 2017) . The majority of studies report no direct use of these gases in the overall process due to their minor percentages, yet further research might look into the integration of these gases into a cyclic version of HTC.

1.5 Applications of Hydrochar

The major product of HTC of biomass is hydrochar, which offers a wide range of applications, some of which are listed below in Figure 22(Kang, Li, Fan, & Chang, 2012) . The major applications of hydrochar are related to the agricultural sector, where soil fertility and removal of heavy metals from soil are frequent applications. Several studies have confirmed that hydrochars derived from animal biowaste have suitable sorption capacities to remove heavy metals from soils(Han et al., 2016) . Furthermore, Khoshbouy et al. (2019) successfully applied hydrochar derived from wastewater sludge for the removal of basic dye from aqueous solutions (Khoshbouy, Takahashi, & Yoshikawa, 2019) . Also, enhancing the carbon content in hydrochar makes it suitable for use as an electrode for supercapacitors, which was tested and confirmed by Susanti et al. (2019) in their study of hydrochar derived from HTC of Salacca peel for lithium ion capacitors. (Susanti et al., 2019) However, one of the most promising applications of hydrochar that does not receive a lot of attention is the recovery of nutrients such as phosphorous to tackle the growing demand of this critical resource.

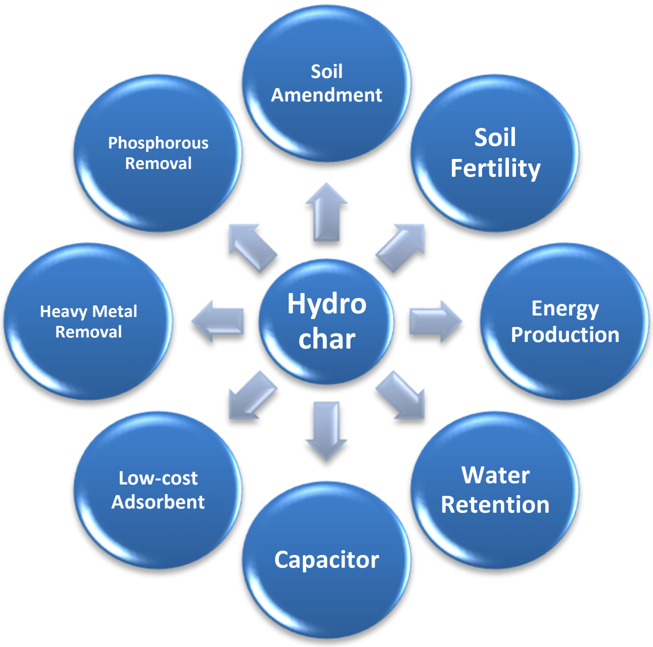


Figure 22:Common Applications of hydrochar

1.6 HTC Reactions and Mechanism

HTC involves a series of reactions that allow the transformation of raw biomass into carbon-rich solid products. Understanding the reactions of HTC provides insight to the mechanisms of carbon and nutrient deposition and concentration in the products. Different mechanisms were proposed to explain the reactions of HTC, yet the widely accepted version is the multi-step degradation process adopted for lignocellulosic biomass. Lignocellulosic biomass is used as a reference for biomass due to its applicable structure and composition that presents a wide range of biomass feedstock Reza et al. (2014). defined HTC through five major reactions, and they are: hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization(M. Toufiq Reza, Uddin, Lynam, Hoekman, & Coronella, 2014) .

Hydrolysis: As mentioned previously, hydrothermal carbonization proceeds in the presence of water, which acts both as a solvent and a catalyst. Hydrolysis of cellulose and hemicellulose proceeds at specific temperatures, as water reacts with the glycosidic groups of both components. In general, the hydrolysis of hemicellulose is initiated at temperatures of 160°C-180°C, whereas cellulose is hydrolyzed at higher temperatures such as 230°C (Aoyama, Seki, & Saito, 1995; Garrote, Dominguez, & Parajo, 1999). The reaction results in the formation of glucose, which undergoes isomerization into fructose, in addition to a set of oligomers such as cellobiose, cellotriose and cellotetraose(Sasaki, Fang, Fukushima, Adschiri, & Arai, 2000). The reaction proceeds by the reaction of C5 and C6 sugar polymers with water, which results in the cleavage of the β-glycosidic bonds to form hexoses such as glucose(Girisuta, Dussan, Haverty, Leahy, & Hayes, 2013). Similarly, hemicellulose undergoes cleavage of its glycosidic bonds to produce pentoses such as xylose. Furthermore, glucose and fructose undergo further decomposition to produce organic acids such as acetic, lactic, propenoic, levulinic and formic acids, which increase the pH of the resulting products. Hydrolysis is highly influenced by operating temperatures and pH, and it presents the major step towards carbon concentration in the products.

Dehydration: After hydrolysis, product oligomers undergo dehydration and their monomers undergo C-C bond breaking and ring opening, also known as fragmentation. Dehydration involves the ejection of bound water from the components of biomass, in addition to the elimination of hydroxyl groups (M. Toufiq Reza et al., 2014). The removal of hydroxyl groups leads to a reduction in H/C ratio, whereas a reduction in O/C ratio is observed due to the loss of carboxyl groups from cellulose and hemicellulose. The products of dehydration and fragmentation are furfural-like compounds including HMF, furfural, 5-methylfurfural and aldehydes, which are open to further decomposition to produce organic acids and phenols. Dussan et al. (2015) proposed a study on the kinetics of hemicellulose dehydration to produce furfural, and the results suggest that the production of acids such as formic acid enhances the dehydration process and drives the reaction towards more selectivity of desired products(Dussan, Girisuta, Lopes, Leahy, & Hayes, 2015).

Decarboxylation: In parallel with dehydration, decarboxylation of cellulose and hemicellulose occur. Decarboxylation involves the removal of carboxyl groups, and it is mainly detected by the release of CO2, which has been found to present a major portion of gases released by HTC(Yan, Hastings, Acharjee, Coronella, & Vásquez, 2010). Parshetti et al. (2013) deduced the presence of decarboxylation as a reaction in HTC due to the change in functional groups accompanied with the increase in fixed carbon percentages(Parshetti, Kent Hoekman, & Balasubramanian, 2013). Decarboxylation promotes the formation of carboxylic acids such acetic and formic acids, in addition to the release of CO2 and CO from the degradation of furfurals. Temperature plays a significant role in enhancing decarboxylation, which can be deduced from the reduction in pH values (increase in acid concentration) upon increasing HTC temperatures.

Condensation Polymerization: The highly reactive compounds produced by dehydration and decarboxylation undergo polymerization to produce soluble polymers. Monomers of furfural-like compounds and aldehydes combine to form polymers, which condense in the presence of lignin to form polymer chains. Polymerization can occur via aldol condensation or as a result of intermolecular dehydration, and it results in the initial formation of hydrochar (M. Toufiq Reza et al., 2014).

Aromatization: At hydrothermal conditions, linear polymer chains resulting from the condensation of cellulose and hemicellulose undergo aromatization, which refers to the formation of C-double bonds. As temperatures increase, linear polymers tend to form aromatic structures having high stability, thus presenting an upgrade towards the formation of hydrochar(Hoffmann et al., 2019) .

It is understood that carbon and nutrient concentration from the initial cellulose and hemicellulose towards the end products is affected by the operating conditions. Reactions such as hydrolysis, dehydration and decarboxylation play a significant role in the transformation of nutrients such as phosphorous, thus determining their solubility and destination on the path to recovery.

2 Phosphorous in Hydrothermal Carbonization

One of the major applications offered by hydrothermal carbonization of biomass is the recovery of valuable nutrients. In addition to satisfying market needs, the recovery and recycling of nutrients such as phosphorous allows for a circular economy that benefits the environment as well as the market.

Phosphorous recovery can be achieved from the two major products of hydrothermal carbonization. The major concentration of phosphorous lies in the solid product (hydrochar), yet the liquor of HTC possesses recoverable amounts of phosphorous(S. M. Heilmann et al., 2014) . The recovery of phosphorous from the treatment of biomass has proven to be a feasible green technology for nutrient recovery, whether on the level of lignocellulosic feedstock or P-rich biowaste such as animal wastes(Robinson et al., 2018) .

2.1 Phosphorous Quantities in Biomass: Feasibility of P-recovery

Different biomass types offer various potentials for phosphorous recovery, yet the majority of lignocellulosic biomass, as well as animal sludge are considered secondary resources of phosphorous. This observation has been supported by several studies on various feedstock types. Ntuli et al. (2012) studied the extraction of phosphorous from sewage sludge having a molar concentration of 14.25% phosphorous(Ntuli, Falayi, Mhlungu, & Thifhelimbilu, 2013) . Similarly, Adam et al. (2009) had previously recorded a phosphorous content in different samples of sewage sludge, with a range of 14%-25% phosphorous(Adam, Peplinski, Michaelis, Kley, & Simon, 2009) . Heilmann et al. (2014) revealed that the annual amount of phosphorous present in US Farm Animal Manures reaches 46.26 million kg for poultry, 405 million kg for swine and 791 million kg for cows(S. M. Heilmann et al., 2014). Similarly, Havukainen et al. (2016) reported the phosphorous contents for several feedstock types, and the results showed that sewage sludge contains 66 kg phosphate/tonne of solids, whereas cattle liquid manure contains 26 kg/tonne of solids (Havukainen et al., 2016) . Furthermore, Lee et al. (2016) studied the nutrient content in different biowaste, manure waste and industrial organic wastes, with emphasis on the extractable quantities of nitrogen and phosphorous, which were measured using Olsen and Mehlich-3 extraction methods. The results showed that dairy sludge contained 6.1 g of P/ kg of waste, from which the extractable amount was up to 313 mg/L. Similarly, chicken manure included 13.8 g of P/kg of waste, from which 127 mg/L were extractable (Lee, 2016). Among organic wastes, sewage sludge contains the second largest quantity of phosphorous, which nominates it as a feasible and potential source for phosphorous recovery. Therefore, the recovery of phosphorous from sludge offers economic advantages, in addition to its environmental impact.

2.2 Recovery Rates

The following section provides an overview on the phosphorous content present in the products of different experiments of HTC performed on different biomass feedstock.

Table 11: Phosphorous Recovery from HTC of different feedstock

Feedstock	HTC Conditions	Recovery Method	Phosphorous Recovery	Reference
Hydrocotyle verticillata (HV)	220°C 1:10	Chemical Extraction (NaOH)	86.98%	(Cui et al., 2020)
Myriophyllum spicatum (MS)	200°C 1:10	Chemical Extraction (NaOH)	93.61%	(Cui et al., 2020)
Canna indica (CI)	240° 1:10	Chemical Extraction (NaOH)	54.86%	(Cui et al., 2020)
Sewage Sludge	230°C 1:9	Molybdenum Blue Method	97.74%	(T. Wang et al., 2017)
Digestate from Sewage Sludge	210°C 4:25	Acid Extraction	82%	(Marin-Batista, Mohedano, Rodriguez, & de la Rubia, 2020)
Cow Manure	220°C 1:5	NA	90%	(Axel Funke, 2015)
Wheat straw Digestate	190°C 1:20	Kjeldahl digestion methods	77-80%	(A. Funke, Mumme, Koon, & Diakité, 2013)
Sewage Sludge	220°C 7:50	NA	90-93%	(Sumida H & Sumida H, 2013)

Sewage Sludge	200°C NA	NA	92.53%	(Smith, Singh, & Ross, 2016)
Swine Manure	200°C 11:100	Acid Extraction	80%	(Ekpo, Ross, Camargo-Valero, & Fletcher, 2016)
Seaweed	150 °C	Chemical Extraction	70%	(Løes, Sandquist, & Meyer, 2017)
Sewage Sludge	170° 12:25	Struvite Precipitation	98.73%	(Shi, Luo, Rao, Chen, & Zhang, 2019)
Orange Pomace	225°C 1:8		86-91%	(Erdogan et al., 2015)
Sewage Sludge	200°C 1:100	Acid Extraction	93.55%	(E. Song, Park, & Kim, 2019)
Poultry Litter	150°C	Chemical Extraction	80.67%	(Bashir M. Ghanim et al., 2018)

The above table reflects the feasibility of HTC as an intermediate process for phosphorous recovery. Increased efficiency in recovery is an effect of several factors, including the increase in solid product, the transformation in solubility of phosphorous and its immobilization in the solid hydrochar. Different feedstock of biomass experienced similar recovery rates, which reflects the main advantage of HTC over other thermal treatment processes; that is, its ability to treat and upgrade a wide variety of biomass feedstock with consistent efficiency.

2.3 Forms (Types) of Phosphorous

Phosphorous speciation in biomass provides insight into the forms through which the element exists, which aids in specifying the proper technique for removal. In general, phosphorous in sludge falls under two categories: organic and inorganic P, each of which possesses different characteristics of bioavailability and mobility. Organic phosphorous (OP) exists as a mixture of compounds including phospholipids and simple phosphate monoesters, whereas inorganic phosphorous (IP) includes a variety of forms such as non-apatite P (NaOH- P) and apatite P (HCl-P) (Dai et al., 2015) . Non-Apatite P is usually bound to Ca, whereas Apatite P can be related to metal concentrations of Fe, Mg and Al (Houben et al., 2019). Among different feedstock, the distribution and solubility of each type of phosphorous varies. In terms of distribution, inorganic phosphorous presents the major form of P in biomass wastes, with a mean abundance of 60-80% of Total Phosphorous, whereas organic phosphorous occupies the minor portion, with higher solubility. Shi et al. (2019) performed a study on the phosphorous content in sewage sludge before hydrothermal carbonization, and the results showed that Organic P counted for 16.24% of the total P content in the raw sludge material. (Shi et al., 2019) These results comply with the findings of Dai et al. (2015) in their study of HTC on cow manure, where the amount of Organic P accounted for 24.88% of the Total Phosphorous Content(Dai et al., 2015).

Furthermore, within the inorganic portion, the distribution of apatite and non-apatite P varies among different feedstocks. Assessing the distribution of each type allows for an estimation of the phosphorous solubility, as well as providing an insight into the migration of phosphorous between the solid and liquid products of thermal treatment. In general, the inorganic portion of phosphorous is dominated by non-apatite P (NAP), which is more soluble than apatite P. Shi et al. (2019) revealed that 82% of inorganic phosphorous in sewage sludge is present as non-apatite P (Shi et al., 2019). Similarly, Meng et al. (2018) reported that 67% of the inorganic phosphorous present in dried sewage sludge is in the form of non-apatite P (NAP) (Meng, Huang, Gao, Tay, & Yan, 2018). Also, He et al. (2017) measured the different fractions of phosphorous present in waste activated sludge, and the results showed that non-apatite P counts for 75% of total inorganic phosphorous(He et al., 2017). These results are in conformity with the results of Yu et al. (2018), who studied the phosphorous content of granular sludge, and the non-apatite P accounted for 78.97% of the total inorganic phosphorous in the raw feedstock (Yu et al., 2018). On the other hand, Dai et al. (2015) studied the phosphorous content of dairy manure and the results showed that apatite P counts for 57.35% of total phosphorous content, whereas the non-apatite P contributed to 17.78% of Total P (Dai et al., 2015). The difference in distribution of apatite and non-apatite phosphorous can be attributed to the initial type of feedstock, where cow manure is expected to have less solubility than sewage sludge, which justifies the higher concentration of apatite P.

Hydrothermal carbonization provides several advantages for phosphorous recovery from biowaste. In terms of abundance, HTC allows for the concentration of phosphorous in the solid hydrochar, thus increasing the amount of recoverable phosphorous. Cui et al. (2020) performed HTC on wetland biomass wastes, and the results showed a significant increase in P content from the initial feedstock to the solid hydrochar. For H. verticillate, total P content increased from 7.77 mg/g in raw biomass to 16.45 mg/g in hydrochar at 220°C. Similarly, the total P content in M. spicatum increased from 8.91 mg/g in raw biomass to 22.99 mg/g in hydrochar (Cui et al., 2020) . Meng et al. (2018) reported an increase in phosphorous content from 60 mg/g in raw dry sludge to 82 mg/g in hydrochar(Meng et al., 2018). Similar results were observed by Dai et al. (2015) where total phosphorous increased from 13 mg/g in cow manure to reach 17 mg/g in solid hydrochar (Dai et al., 2015). By concentrating the phosphorous in the solid product, HTC increases the chances for the recovery of phosphorous.

2.4 The Fate of Phosphorous in HTC

In general, it is understood that phosphorous resides in the solid product of HTC, which offers higher availability of phosphorous (Axel Funke, 2015). However, the liquid product also contains minor quantities of phosphorous that can be retrieved using technologies such as struvite precipitation, which are capable of extracting up to 80% of phosphorous(Wu, Zhang, & Yuan, 2018). The phosphorous content in the liquor of HTC is observed to increase as the operating temperature increases, where the process approaches liquefaction. In general, it is observed that organic P (OP) migrates towards the liquid product of HTC, whereas the inorganic portion of phosphorous is concentrated in the solid hydrochar. At higher temperatures, a portion of organic phosphorous migrates towards the gaseous phase (Huang, Fang, Lu, Jiang, & Tang, 2017). On the other hand, inorganic phosphorous is distributed among the solid and liquid products, and its distribution is affected by the biowaste feedstock and HTC conditions. The concentration of inorganic P in hydrochar varies among apatite and non-apatite P, which defines the solubility and mobility of the nutrient. Finally, it is worth noting that HTC promotes the transformation of organic phosphorous into inorganic forms, as well as cross-sectional transformations from non-apatite to apatite P, which reflects the immobilization of P in HTC products. Figure 23 presents a general outline for the fate of phosphorous during HTC, yet the transformations of phosphorous remain subject to the initial feedstock type and HTC process conditions.

2.5 HTC immobilization of phosphorous

In addition to concentrating the nutrient, HTC enhances the immobilization of phosphorous in the solid product. Immobilization refers to the decrease in solubility of phosphorous, which reflects the transformation of P from soluble forms into more stable fractions(C. Song et al., 2018). However, the immobilization of phosphorous is controlled by several factors, the main of which is the pH of the medium of HTC. Ghanim et al. (2018) studied the migration of phosphorous during the HTC of poultry biomass in a slightly basic medium, and the results showed a significant increase in apatite P (AP) from 3.29 mg/g in raw biomass to 16.96 mg/g in solid hydrochar (Bashir M. Ghanim et al., 2018). Similarly, Wang et al. (2018) performed HTC on different samples of sewage sludge in basic medium, and the hydrochar recorded an increase in apatite P (AP) versus a significant decrease in non-apatite P (NAP) (L. Wang, Chang, & Liu, 2019). These results were validated by the experiments performed by Marin Batista et al. (2020), where the percentage of AP increased slightly upon hydrothermal carbonization (Marin-Batista et al., 2020). This observation is supported by the findings of Cui et al. (2020), where the hydrochars derived from wetland plant biomass experienced an increase in apatite P (AP) from 0.16 mg/g to 18.85 mg/g (Cui et al., 2020). Similar results were observed by Dai et al. (2015) and Shi et al. (2019), where the increase in apatite P was significant (Dai et al., 2015; Shi et al., 2019). Also, Yu et al. (2018) studied the phosphorous content in hydrochar derived from the HTC of granular sludge performed in a slightly acidic medium, and the results showed a gradual decrease of apatite P, in parallel with an increase in non-apatite P(Yu et al., 2018). The above results validate the hypothesis that the pH of HTC affects the fate of phosphorous in the products. HTC in an alkaline medium promotes the concentration of apatite P rather than non-apatite P, whereas an acidic medium imposes the opposite transformation. Since the solubility of P and its mobility are mainly related to the apatite portion, a reduction in phosphorous solubility can be observed through the HTC of biomass, and this reduction reflects the immobilization of P through hydrothermal carbonization of biomass.

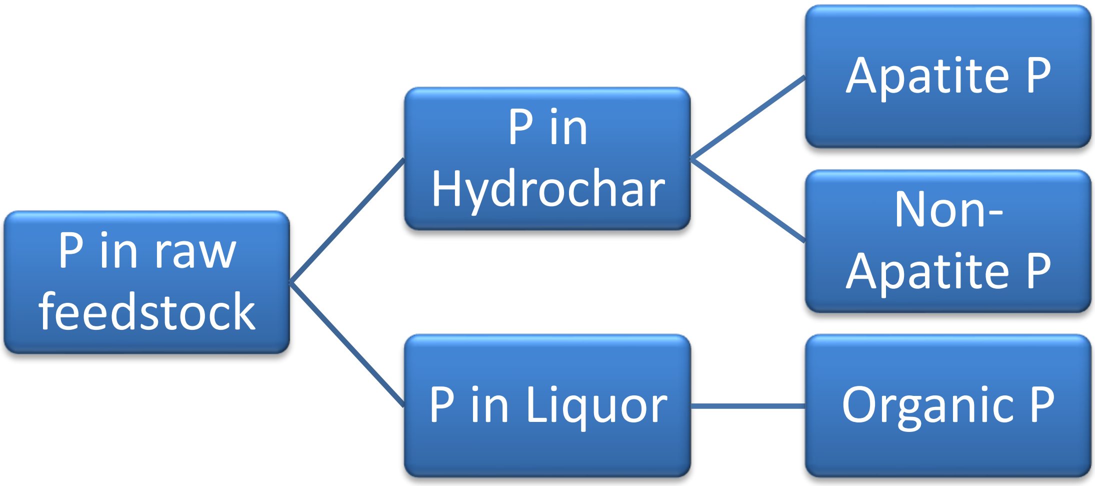


Figure 23: Fate of P in HTC of Biomass

To optimize the recovery of phosphorous, it is essential to understand the parameters of the process, mainly the destination of phosphorous, its form and solubility.

2.6 Effects of Parameters on P-recovery and destination

The fate and recovery rate of phosphorous are subject to different factors governing the process of HTC, yet the most significant parameters that affect P-recovery are temperature, pH and residence time.

Temperature As mentioned previously, defining a temperature range for operation is essential for HTC, in order to avoid the transformation into hydrothermal liquefaction, and thus, studying the effect of temperature must take into consideration the applicable range for HTC. Regarding recovery, an increase in temperature while fixing all other parameters leads to an increase in phosphorous recovery. This was observed by Wang et al. (2017) in their study on the HTC of sewage sludge, where the results show that an increase in HTC temperature from 200°C to 230°C leads to an increase in in phosphorous recovery from 87.34% to 97.74% (T. Wang et al., 2017). Ghanim et al. (2018) reported similar results during HTC of poultry litter, where an increase in temperature from 150°C to 175°C led to an increase in phosphorous recovery from 50.63% to 63.89% (Bashir M. Ghanim et al., 2018). Similarly, Hielmann et al.(2014) studied the relation between temperature and phosphorous recovery from swine and dairy cattle manures, and the results indicated a strong positive impact (S. M. Heilmann et al., 2014). The positive impact of temperature on phosphorous recovery can be explained by the increase in the yields of solid hydrochar, which is the main destination for phosphorous. Furthermore, the reactions involved within HTC increase the recoverable forms of phosphorous, facilitating the reclamation process.

However, it is also observed that the effect of temperature is limited to optimum range of values beyond which the effect of temperature on phosphorous recovery is reversed. This was demonstrated by Stutzenstein et al. (2018), where the increase in temperature of HTC of anaerobic digestate from 180°C to 200°C led to an increase in phosphorous recovery from 31% to 44%, yet the increase from 200°C to 220°C imposed a significant reduction in phosphorous recovery from 44% to 22%(Stutzenstein, Bacher, Rosenau, & Pfeifer, 2017). Similar observations were reported by Ekpo et al. (2016). The reason behind this observation relates mainly to the decrease in hydrochar yield at higher temperatures beyond HTC range, in addition to the decrease in the recoverable phosphorous content. Furthermore, the assumption that other parameters such as pH are not alternating may not be very accurate due to the interrelation between the parameters of HTC.

HTC reactions such as dehydration and decarboxylation involve the hydrolysis of organic matter, including organic phosphorous (OP), which is transformed into inorganic phosphorous (IP). Ismail et al. (2019) report an increase in IP over OP as temperature of HTC increases, especially at lower temperatures, where an increase in temperature led to a 63% in IP recovery(Ismail et al., 2019). Similarly, Shi et al. (2019) recorded a reduction in OP due to HTC, where an increase in temperature led to higher IP values and reduced OP values (Shi et al., 2019). These observations confirm the hypothesis that HTC enhances the transformation of organic phosphorous into inorganic phosphorous, which is more available to reclaim.

Furthermore, the effect of HTC temperature extends to defining the dominant form of IP in the products. As mentioned previously, the distribution of apatite and non-apatite P depends mainly on the type of feedstock and its solubility. However, HTC increases the abundance of apatite P (AP), which can be detected by the increase in concentration of Mg, Fe and Al ions in the hydrochar. Huang & Tang (2016) studied P speciation in hydrochar resulting from the HTC of sewage sludge, and they recorded an increase in apatite P in the form of Fe-bound phosphorous(Huang & Tang, 2016). Furthermore, Yu et al. (2019) performed a series of HTC experiments on sewage sludge, and the results reveal a significant increase of apatite P (AP) abundance from 11.62% in raw feedstock to 44.93% in the hydrochar(Yu et al., 2019). Similar observations were reported by Zhao et al. (2018) on digestate slurry, where HTC increased the fraction of apatite P (AP) to 81.5% in hydrochar (Zhao et al., 2017). Based on these results, it can be deduced that increasing HTC temperature enhances the transformation of organic P into inorganic P, as well as the concentration of apatite P in the inorganic phase. The reason behind this transformation lies in the dynamics of HTC reactions that include the hydrolysis of organic compounds and the dissolution of non-apatite compounds (Huang & Tang, 2015).

pH: In addition to temperature, the pH of the medium in which HTC occurs plays an important role in defining the fate and forms of P in the products. To begin with, the pH of HTC products is usually higher than that of raw biomass, and that is mainly due to the formation of organic acids yet controlling the pH of HTC defines the efficiency of P-recovery. In general, an increase in pH of HTC of biomass leads to an increase in phosphorous recovery. This is mainly due to the increased dissolution of biomass in acidic conditions, which reduces the solid product, whereas at higher pH values, more solid hydrochar can be attained, thus increasing the chances for phosphorous recovery. This observation is supported by Stutzeinstein et al. (2018), where an increase in the pH of HTC of anaerobic digestate from 3.3 to 8 led to an increase in phosphorous recovery from 22% to 39%(Stutzenstein et al., 2017). Similar results were obtained by Ekpo et al. (2016) during the HTC of swine manure(Ekpo et al., 2016). Also, Ghanim et al. (2018) reported a decrease in total phosphorous (TP) content in both products of HTC of poultry litter that reached 24% in acidic medium (Bashir M. Ghanim et al., 2018). Therefore, it is safe to conclude that initial slightly alkaline conditions of HTC promote the concentration of phosphorous in the solid and liquid products. On the other hand, initial acidic media enhance the hydrolysis and transformation of raw biomass into more soluble forms, thus reducing the range of immobilization of phosphorous. Furthermore, Ghanim et al. (2018) observed that initial acidic media led to a decrease in all forms of phosphorous in both products, with significant reduction in apatite P (AP) (Bashir M. Ghanim et al., 2018).

However, the impact of pH on the extraction of phosphorous follows an opposing trend. The impact of pH on phosphorous release can be observed by its influence on properties such as solubility, absorption and desorption (Y. Xu et al., 2015). It has been shown that extracting phosphorous from HTC products in acidic medium offers higher efficiency. Heilmann et al. (2014) reported an 80% recovery of phosphorous from hydrochar treated with HCl (S. M. Heilmann et al., 2014). Similarly, Ekpo et al. (2016) showed that treatment of hydrochar with H2SO4 led to an increase in P-recovery to 79% compared to an 11% recovery upon treatment with NaOH(Ekpo et al., 2016). Shi et al. (2019) proposed an explanation for this phenomenon, relating it to the dissolution of inorganic phosphorous into the liquor of HTC upon treatment with strong acids, which is followed by easier recovery techniques such as struvite precipitation (Shi et al., 2019).

Residence Time:As mentioned previously, the relation between residence time and hydrochar yield is negative; that is an increase in residence time reduces the solid quantities retrieved from HTC. This is due to the degradation of cellulose and hemicellulose, which increases the contents of the liquid product. However, the effect of residence time on phosphorous recovery does not follow a definitive path, and it is dependent mainly on the type of feedstock undergoing treatment. In general, the decrease in solid yield dictates a decrease in nutrient recovery, since the major portion of phosphorous is held in the hydrochar. However, studies have shown that increasing residence time within certain temperatures can enhance the phosphorous content in hydrochar, thus increasing the chances of phosphorous recovery. Ghanim et al. (2018) reported an increase in total phosphorous (TP) in hydrochar upon an increase in residence time from 30 min to 120 min, beyond which total phosphorous content starts decreasing(Bashir M. Ghanim et al., 2018). Similar results were obtained by Tu et al. (2016) in their study on the effects of parameters on HTC of several biowastes such as chicken manure. The results showed an increase in total phosphorous content (TP) upon an increase in residence time until an optimum residence time of 2 hr was reached, beyond which phosphorous content started decreasing(Tu et al., 2016). This observation can be explained by the increase in the extent of hydrolysis and decarboxylation reactions, which enhances the transformation of organic phosphorous into inorganic forms. This result was observed by Ghanim et al. (2018), where the increase in inorganic phosphorous content in hydrochar as a response to increase in residence time was the only stable trend among all phosphorous transformations (Bashir M. Ghanim et al., 2018). All in all, the effect of residence time on phosphorous recovery is linked to the effect of other parameters such as temperature and pH.

Therefore, it can be observed that phosphorous recovery is subject to the effects of temperature, pH and residence time. The first two factors are partially dependent on each other, and this is manifested by the effect of temperature on pH, which affects the extent of phosphorous recovery. Understanding the interdependence of the two factors is associated with the reaction mechanisms, where an increase in temperature enhances the degradation step and the production of organic acids, thus increasing the pH of the product stream. Similarly, the effect of residence time follows various paths depending on the temperature and initial pH of HTC, which emphasizes the importance of a collective assessment of parameter effects on phosphorous recovery through HTC. Hence optimizing the recovery of phosphorous from hydrochar and liquor of HTC must take into consideration a specific combination of temperature, initial pH and the transformation of each factor throughout the process.

3 Conclusion

The paper above provides an overview on phosphorous recovery from the products of hydrothermal carbonization of biomass. Biowaste represents an available and economic secondary resource for phosphorous. Different biowaste feedstock include different quantities of phosphorous, yet the treatment of biomass presents a viable route for the recovery of phosphorous. The advantages and mechanisms of HTC are assessed for the sake of understanding the fate and distribution of phosphorous. HTC allows for the concentration of P in the solid and liquid products, whereas the immobilization of P by decreasing its solubility allows for enhanced recovery. The efficiency of HTC has been demonstrated based on previous literature, and the factors that affect the recovery of phosphorous have been studied. Furthermore, the different forms of phosphorous present in the raw biomass and the products are studied in order to understand the transformations of phosphorous during HTC.

It is therefore concluded that HTC allows for the concentration and immobilization of phosphorous in the solid and liquid products. The distribution of P among the hydrochar and liquor of HTC is influenced by biomass type, temperature and initial pH of the process. Assessing the phosphorous content and types in the hydrochar and liquor is key to further understanding of the mechanisms of P deposition and speciation through HTC. Further research should be conducted on the kinetics of phosphorous disposition into each product, depending on the form of phosphorous present. In addition to that, it is necessary to shed light on the recovery of phosphorous through HTC on the industrial scale in order to overcome the challenges of scaling.

Effects of temperature and stoichiometric oxygen on the mineralisation of P-rich organic biosolids (ESR4)

Phosphorus presents a limited, irreplaceable and essential nutrient necessary for the growth of organisms. There is an increasing effort to recover phosphorus from production waste streams. Sewage sludge presents an important source of phosphorus but also contains organic pollutants and heavy metals. Thermal treatment technologies seem to be a promising option to treat sewage sludge and obtain ash/char from which high recovery rate of phosphorus can be reached. In this review, sewage sludge management options are first reviewed. Follows, an overview of sewage sludge thermal treatment technologies for the purpose of phosphorus recapture. A summary follows of recent advances in thermal treatment processes of sewage sludge and phosphorus recovery, identifying challenges and knowledge gaps. The review provides the foundation for future research aimed at achieving efficient, economic and environmentally sustainable recapture of phosphorus from sludge thermal treatment products.

Introduction

Phosphorus (P) is a limited, non-renewable resource, but is a vital nutrient for the growth of organisms, and cannot be replaced by other elements [1]. Nowadays it is generally applied to soils and is fortified in foods in quantities vastly in excess what can be uptaken so is largely wasted although it is a limited resource on Earth. This was confirmed by European Commission (EC) which added the phosphate rock to its list of critical raw materials in 2014 (EC website). Demand for P fertilizer has increased with an increase of population. The intensity of global fertiliser application amounts on average to 10 kg P/ha/year but this varies significantly between regions and countries. In 2017, 1.34 million tonnes of phosphorus fertilizer was used in EU agriculture, which is 34% higher compared to year 2009, presented in the Figure 24.

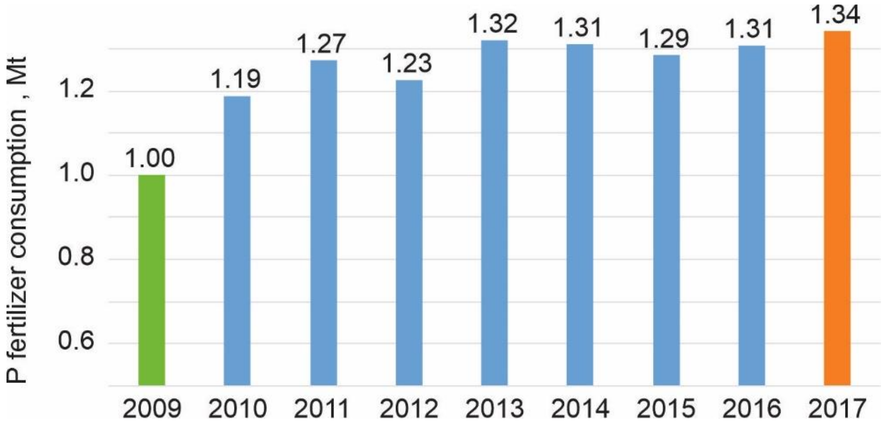


Figure 24. P fertilizer consumption by agriculture in EU-28 from 2007 to 2017 (source data based on: Eurostat, 2019)

From the global perspective, the distribution of the increase in P fertilizer consumption for the period 2014 to 2018 is summarized in Figure 25. The highest increase in consumption of P fertilizer for the stated period was in South Asia, while the lowest was in West Europe (FAO, 2018).

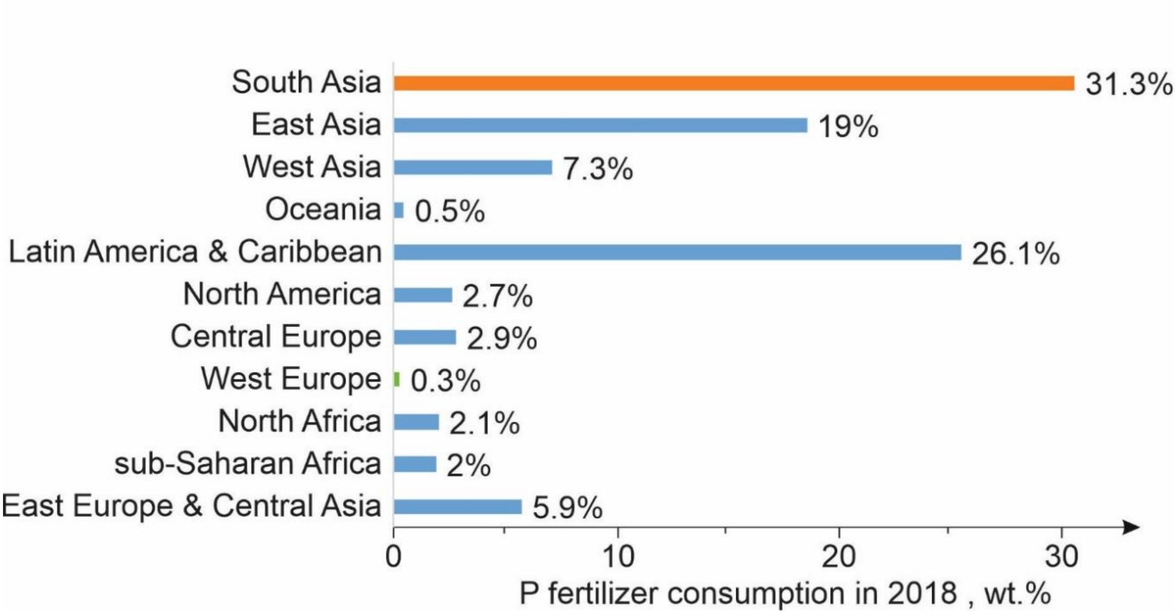


Figure 25. Share of world increase in P fertilizer consumption, 2014-2018 (source data based on: FAO, 2018)

Based on data provided by Heffer et al [2] only five countries, Morocco (74%), China (5.5%), Algeria (3.2%), Syria (2.7%) and Jordan (2.2%) control 85 to 90% of world's remaining reserves, as presented in Figure 26.

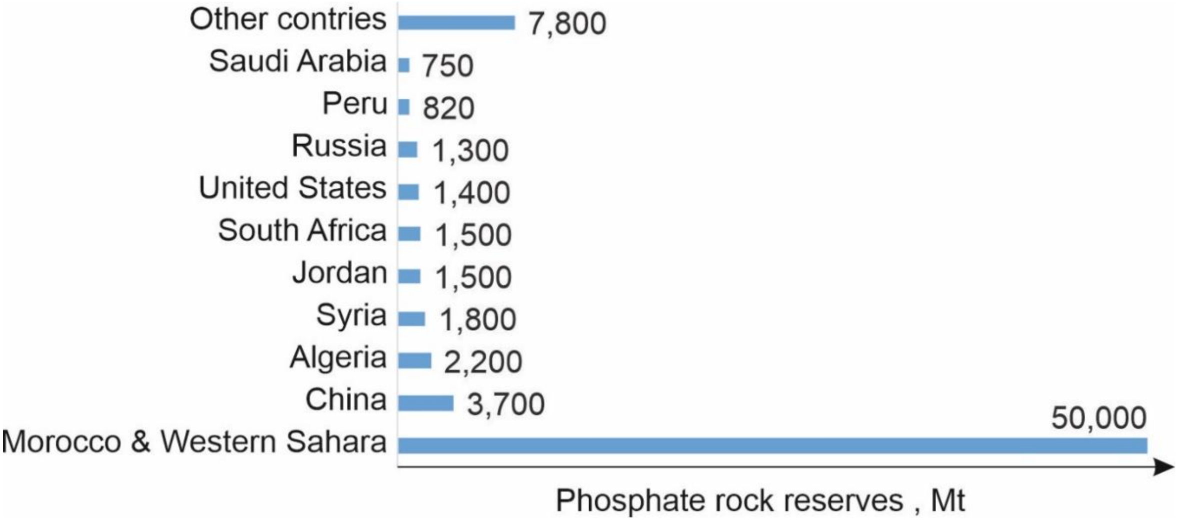
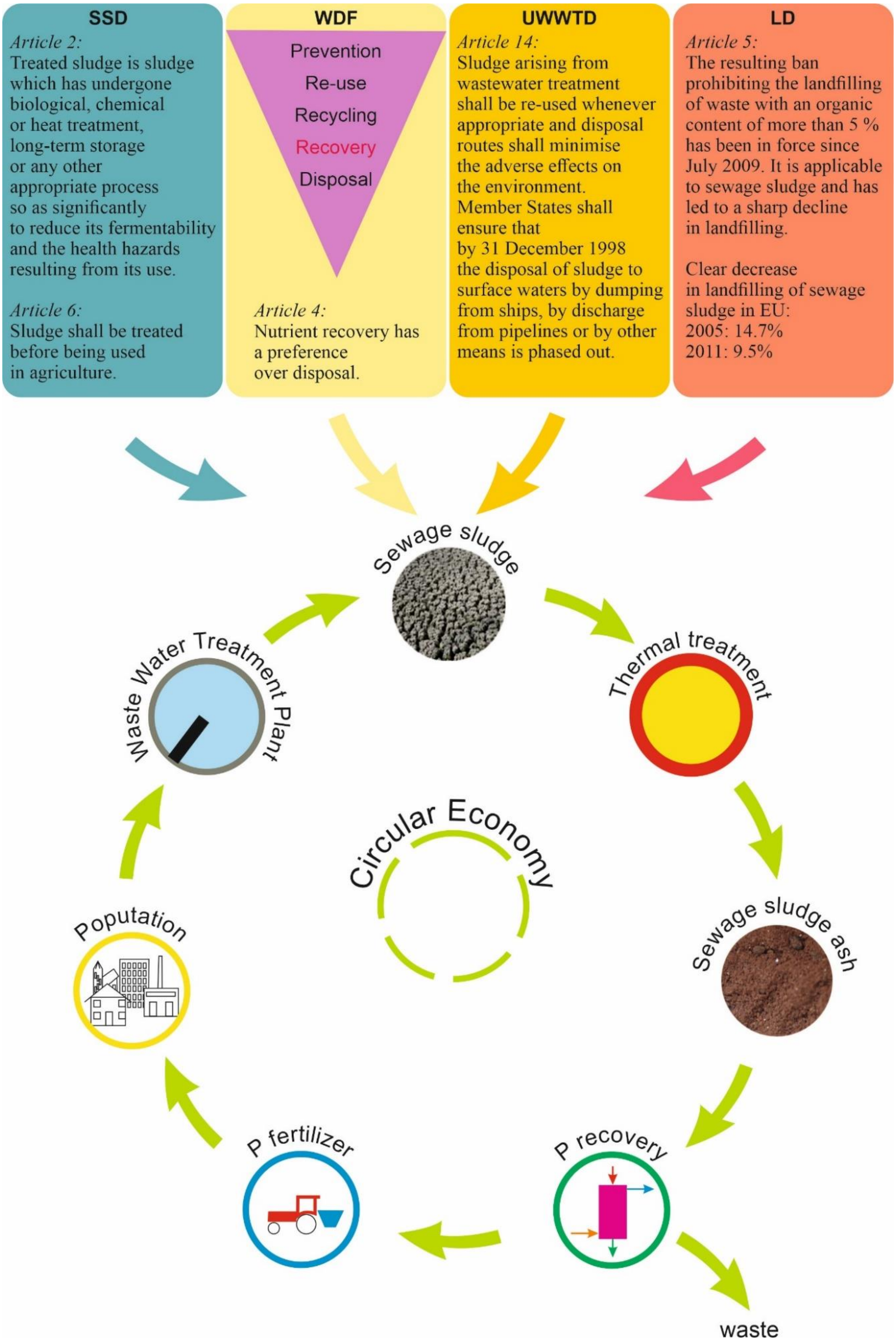


Figure 26. Phosphate rock reserves (in millions of tonnes)

Environmental issue related to sewage sludge (SS) disposal, supported by environmental legislation and the EU circular economy initiative present key drivers to accelerate the recycling and recovery of P from SS. Sewage sludge is rich in nutrients such as nitrogen and phosphorus, however it contains heavy metals and poorly biodegradable trace organic compounds, as well as potentially pathogenic organisms. Sewage sludge is the second largest source of P. The only organic waste containing more P is bone meal, but on a global scale, it is produced in much smaller quantities than sludge. Moreover, the content of P in SS is much higher compared to many other kinds of biomass [3]. While, Pradel and Aissani [4] concluded in their research that production of 1 kg P from the phosphate rock is more environmentally friendly approach than production of 1 kg P from sewage sludge where large amount of energy and reactants are needed, their analysis did not include the potential deleterious environmental and health effects of disposing of SS on land used for food production. The market for P recovery from waste and SS in particular within the EU will be largely driven by regulatory instruments. Those EU directives that considerably influence the recovery of P from SS are:

- Waste Framework Directive (WFD),
- Sewage Sludge Directive (SSD),
- Urban Wastewater Treatment Directive (UWWTD),
- Landfill Directive (LD).



SSD

Article 2:
Treated sludge is sludge which has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as significantly to reduce its fermentability and the health hazards resulting from its use.

Article 6:
Sludge shall be treated before being used in agriculture.

WDF

Article 4:
Nutrient recovery has a preference over disposal.

UWWTD

Article 14:
Sludge arising from wastewater treatment shall be re-used whenever appropriate and disposal routes shall minimise the adverse effects on the environment. Member States shall ensure that by 31 December 1998 the disposal of sludge to surface waters by dumping from ships, by discharge from pipelines or by other means is phased out.

LD

Article 5:
The resulting ban prohibiting the landfilling of waste with an organic content of more than 5 % has been in force since July 2009. It is applicable to sewage sludge and has led to a sharp decline in landfilling.

Clear decrease in landfilling of sewage sludge in EU:
2005: 14.7%
2011: 9.5%

Figure 27. Legal Framework for Sewage Sludge Management and the concept of Circular Economy

Due to the legal requirements summarised in Figure 27, SS thermal treatment processes have gained greater importance for sludge management. In EU countries, from 2005 to 2014 a considerable increase of 16.3% in the use of incineration technologies for SS disposal can be observed, Figure 28. A considerable decrease in landfilling from 2005 (14.7%) to 2014 (5.6%) and decline in use of sludge in agriculture in 2014 (25.1%) compared to 2011 (47.4%) are most probably the result of legal restrictions imposed in EU member states. Bianchini et al. [5] also reported that the EU management system for SS data lacks homogeneity and reliability. A better knowledge of the entire SS cycle dynamics is needed to allow EU countries to achieve their sustainability and efficiency goals.

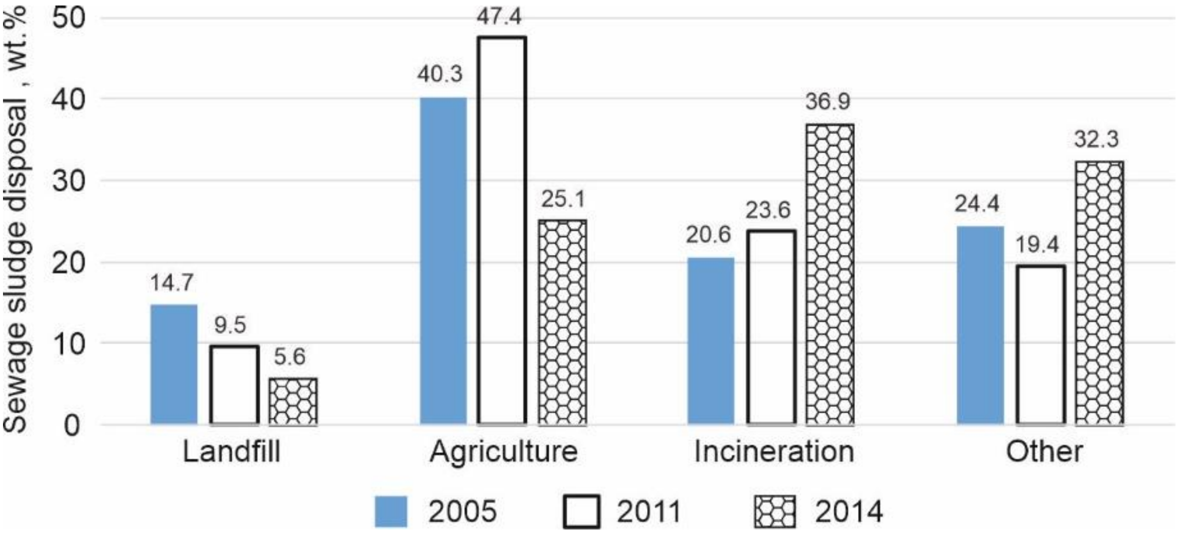


Figure 28. Sewage sludge (dry matter) disposal routes in EU-27 in 2005, 2011 and 2014 (source data based on: Eurostat 2018)

1 Phosphorus in sewage sludge

Phosphorous speciation presents a fundamental influencing factor for P recovery as it determines an element’s mobility, bioavailability and its recovery efficiency to a considerable extent [6]. Activated sewage sludge contains around 1.4 wt% P, while digested (stabilized) sludge has a P content of around 0.48–0.77 wt% [7]. Phosphorus in sewage sludge may occur in the form of univalent, divalent and trivalent metal species, mainly as magnesium, calcium, iron and aluminium salts. Phosphate salts show good solubility in water, while in case of the second- and third row salts, only the phosphates of alkali metals (except for lithium) are highly soluble in water. In SS, phosphorus can be present in the form of phosphates adsorbed on organic and inorganic matter and phosphates characterized by labile bonds with coordination complexes [8]. Total phosphorus (Ptot) present in SS consists of organic phosphorus (Po) and inorganic phosphorus (Pi) (eq.1) [8].

$$Ptot = Po + Pi \qquad (1)$$

Inorganic P (Pi), is Phosphorus bonded with hydroxides of iron, aluminium and manganese or bonded with carbonates. Pi is further classified into non-apatite inorganic P (NAIP) and apatite P (AP). NAIP is the P fraction associated with oxides and hydroxides of Al, Fe and Mn, while AP is the P fraction associated with Ca [9].

Organic P (Po), is Phosphorus associated with organic matter through soluble bonds and phosphorus bonded with aluminosilicates [9].

In SS, Pi accounts for ~ 90% while Po amounts to ~ 10% of Ptot [8]. The inorganic portion of phosphorus in SS is targeted as that form that is bioavailable. Orthophosphates are typical inorganic P components [10] and interact strongly with paramagnetic metals such as Fe and Mn [11]. Polyphosphates can occur in ring and branched structures meta- and ultraphosphates, respectively, although the linear structures are the most common form in nature. Polyphosphates can be organic (e.g., adenosine triphosphate (ATP) and other nucleotide triphosphates), or inorganic [11]. The main metals present in the raw sludge are Ca, Fe, Mg and Al and they are important components that are connected with phosphorus recovery [12].

Li et al. [13] carried out the extraction of P from SS with H2O, NaHCO3, HCl and NaOH and concluded that P is predominantly soluble in NaOH and that P can be substantially extracted by both NaOH and HCl.

The amount of P and the species present in SS depends also on the sludge quality and degree of treatment. It varies between primary, secondary and digested form of SS, which represent the three main types of sludge from waste water treatment plants (WWTP), as presented in Figure 29.

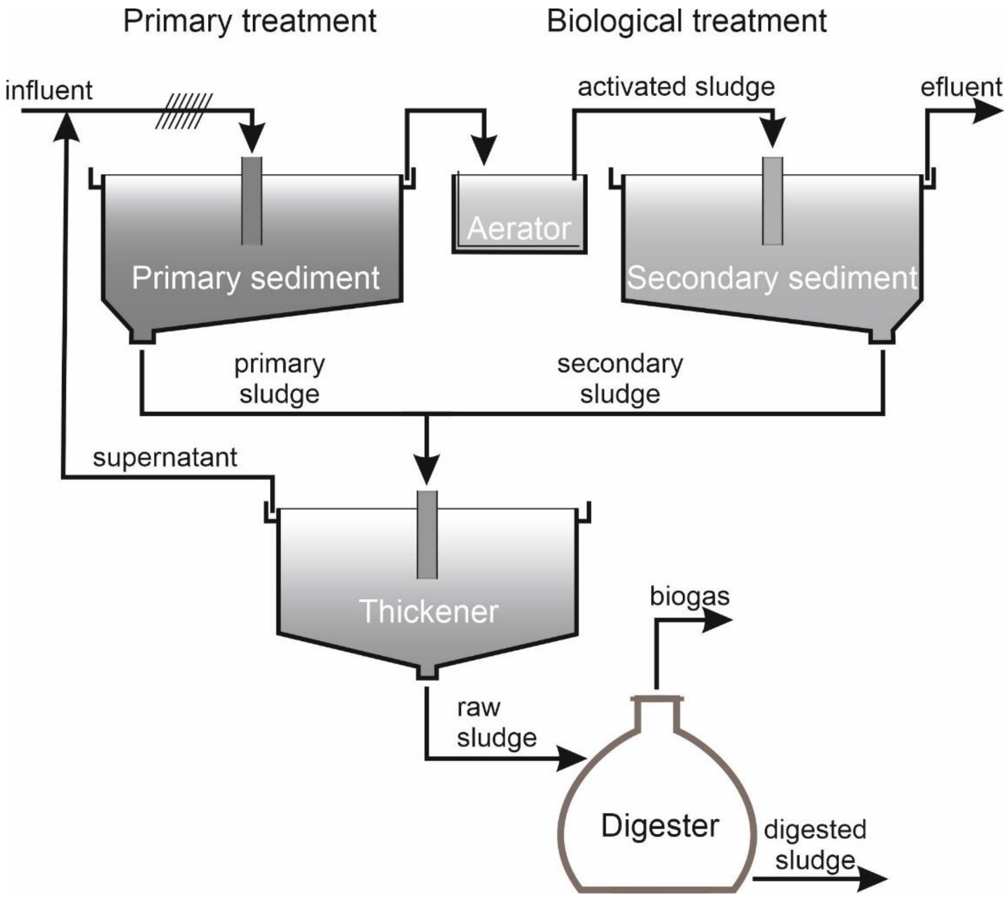


Figure 29. Sewage sludge streams from WWTP

Primary sludge is produced during the primary treatment, i.e. screening, grit removal, flotation, precipitation and sedimentation, when heavy solids, grease and oils are separated from raw wastewater [14]. Secondary sludge is produced during biological treatment, when microorganisms decompose the biodegradable organic content from wastewater [15]. Digested sludge is sludge stabilised by aerobic or anaerobic treatment methods [16]. The percentage of organic and inorganic P in each type of sludge are presented in Table 1.

Table 12. P species in sewage sludge at different stages of treatment (source data based on: Czechowska-Kosacka, 2016)

Fraction of P	Primary sewage sludge wt.%	Secondary sewage sludge wt.%	Digested sewage sludge wt.%
Pi	~ 46	~ 55	~ 66
Po	~ 53	~ 45	~ 34

With an increase of the degree of SS treatment, the proportion of inorganic, mobile fraction increases. This trend can be explained by increased mineralization of SS as the wastewater treatment progresses [17]. Higher percentage of inorganic P fraction, especially orthophosphate in digested sludge compared to activated sludge can be explained by the fact that polyphosphate is possibly released from bacterial cells and hydrolysed into orthophosphate during anaerobic digestion [11]. Sludge that underwent treatment had orthophosphate as the primary P entity [18]. Particular attention should be paid to a SS retention time in the secondary sedimentation tank, as if is too long, anaerobic conditions can be created which would result in P release into wastewater [17] [11].

2 Drying

Drying of SS is carried out in order to reduce sludge volume and make it easier to transport, increase its calorific value, makes it hygienic, stabilize and if combusted enable efficient incineration [19, 20]. Based on the sludge application, there exist different requirements for sludge dry solids (DS) content. Figure 29b shows the change of DS content with sludge treatment.

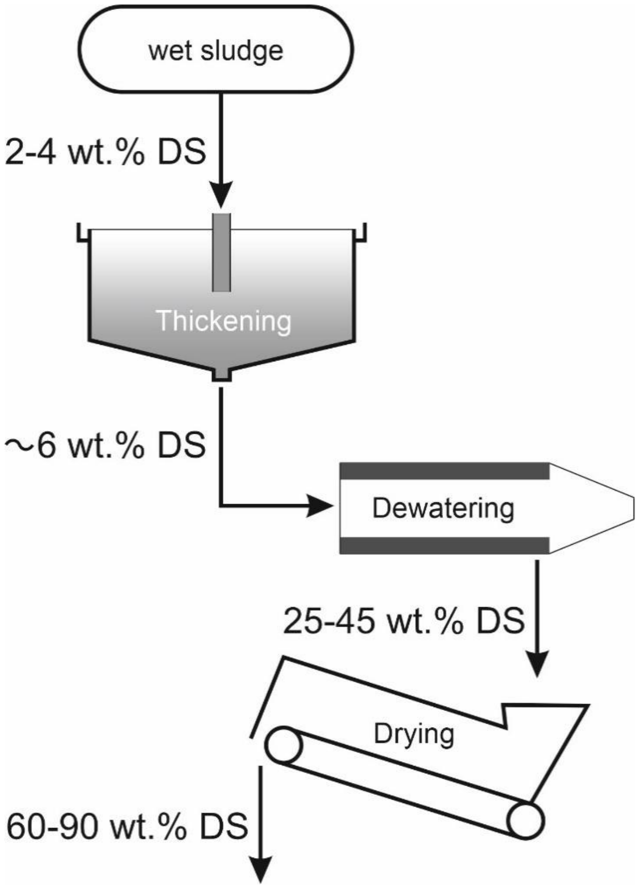


Figure 29b. Content of DS in sewage sludge at different stages of a treatment

If sludge is to be used for agriculture, the suggested degree of drying is 60% of DS and more. The same value applies to sludge co-incineration with waste. For sludge incineration, the suggested degree of sludge drying is 35-45% of DS (partial drying) or above 90% of DS (if dried sludge is going to be mixed with sludge of 35-45% of DS before it is directed to the incineration facility) [21].

During oven-drying of SS, P extracted with HCl increases by 23%, with NaHCO3 by 33% while that with NaOH is reduced by 19% compared to the fresh sample. The amount of P extracted with deionised water and residual P after drying remain almost unchanged as presented in Figure 30.

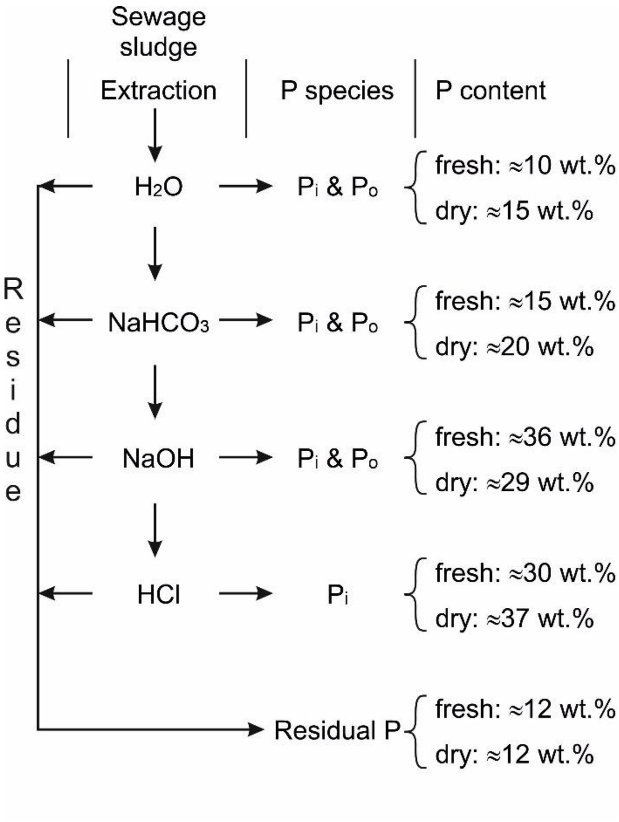


Figure 30. P species in fresh and dried sewage sludge (adapted from Ajiboye et al., 2004)

Most of the P in the fresh as well as in the dry sample is inorganic, Pi. In the fresh sample, the Pi amounts to around 55–77%, while in the oven-dried sample, the proportion of inorganic P is around 75-89% [22]. Li et al. [23] confirmed in his experiments that the organic fraction of P was converted to the inorganic form as the temperature increased during drying of SS and the bioavailability of P increased as well.

3 Thermal treatment technologies

Thermal processes make it possible to burn almost every waste regardless of type and composition. Thermal conversion of sludge into ash is a viable method to concentrate P and produce a pure, high quality, reliable product [24]. Sewage sludge thermal treatment technologies would decrease waste disposal cost, allow energy recovery, conserve natural resources and provide new sources of P, which is an essential, non-renewable element whose shortage poses a significant problem on earth [25] [26]. However, the main problem concerning thermal processes includes the excessive energy necessary to reach high temperatures, high capital costs, the need for extensive air pollution prevention equipment [27]. Moreover, SS has a high-water content and therefore some drying or the addition of supplementary fuels is required to ensure efficient thermal treatment [1]. Table 2 depicts sludge utilization methods.

Table 2. Sewage sludge utilisation methods

Agricultural use	Co-incineration	Mono-incineration
Recovery rate of P from sludge < 60%	Extraction of nutrients and P-recovery from ash not possible!	Recovery rate of P from sludge ash >90%

Spreading sludge on agricultural land, although cost-efficient, is in most aspects the least preferable option from an environmental point of view. Also energy is required for transportation, pasteurisation and spreading of sludge. In co-incineration, sludge is mixed with incombustible residues from the main firing which results in sewage sludge ash (SSA) that is unusable for P recycling. Only mono-incineration of SS in conjunction with P recovery is a safe and reliable technique that can be regarded as the best technology currently available for sludge utilisation [28]. Moreover, the recovery of P from wastewater or sewage sludge is possible, but the recovery rate is less than 50 %, while the recovery potential of phosphorus from ash is around 90%. There are also thermal treatment processes other than mono-incineration, such as hydro-thermal carbonisation (HTC), gasification and pyrolysis. Solid product from those processes (hydrochar, char and ash) applied for SS treatment also contains a valuable amount of P. The other thermal processes enable the removal of organic pollutants and pathogens, leading to a considerable reduction of waste, allowing for the recovery of energy and nutrients [29] and have advantages over combustion in terms of the flue gas volume and its cleaning and ash treatment [30].

This review paper focuses on thermal treatment processes such as combustion, HTC, pyrolysis and gasification of SS as a pre-treatment for P recovery. Brief comparison of the main process parameters and products are presented in Table 3.

Table 3. Sewage sludge thermal treatment processes

Process	HTC	Pyrolysis	Gasification	Combustion
	Endothermic	Endothermic	Exothermic/ Endothermic	Exothermic
	Batch	Batch or continuous	Continuous	Continuous
Atmosphere	in water	oxygen free	N2, limited oxygen/ addition of water steam	air (excess oxygen)
Temperature	180-250°C	250-900°C	500-1800°C	800-1450°C
Pressure	autogenous pressure	atmospheric	usually higher pressure	atm. or higher pressure
Products: liquid	water with small CxHyOz content (mainly phenols)	Bio-oil, tar	tar	no liquid product
gas	CO2, small CxHy content	H2, CO, CO2, short CxHy	syngas (H2, CO), CO2, H2O, N2, short CxHy	CO2, H2O, O2, N2
solid	hydrochar	biochar	char, ash	ash

Since phosphorus does not volatilize easily, after thermal treatment its majority remains in char/ash. For volatilization of P, high temperatures over 900-1200°C are needed, and even then, only 10% of P can be lost by volatilization [31]. Temperature also exerts a considerable influence on speciation of phosphorus during the thermochemical treatment of SS. Furthermore, P in SSA/char is more stable than P in SS [32].

In order to improve P availability which is very low in ash/char, various methods for P recovery from SSA/char have been developed. When applying wet chemical methods, P is recovered from SSA by leaching with acidic or alkaline solutions, or sequentially with acidic and alkaline solutions [33] [34]. During thermochemical treatment, a chemical is added to SSA which is than heated to a high temperature of around 500°C up to 1000°C leading to destruction of organic compounds and the resulting ash is than treated for P recovery [35]. Thermochemical methods proved to have many advantages over wet methods for P recovery, as presented in Table 4.

Table 4. Methods for P recovery from sewage sludge ash

Wet chemical methods		Thermal treatment methods	
Advantages	Disadvantages	Advantages	Disadvantages
Less expensive; Retrofitting easily possible; Good phytoavailability of phosphorus.	Only 40% recovery; Compatibility only with biological phosphorus installations.	90% recovery rate; Material and energy recovery at the same time; Suitable for all types of sewage sludge; All organic pollutants are destroyed; Considerable reduction of waste volume.	High investment costs; Cost intensive.

3.1 Combustion

Combustion is the best-known waste treatment processes in general [36]. Combustion has been used as a wastewater residual management process since the early 20th century. It is used not only for energy but also material recovery. Sewage sludge combustion was first carried out in the US in the early 1960's, and is now a well proven technology with hundreds of plants installed worldwide. Sludge combustion has numerous advantages that do not exist in other treatment alternatives, such as reduction of sludge volume to a small, stabilized ash, which accounts for only about 10% of the volume of mechanically dewatered sludge [37] [38] [30]. Combustion of SS requires previous dewatering to at least 28% dry solids for the process to be self-sustaining, i.e. without need for external heat input [39]. Furthermore, all organic compounds are destroyed, while phosphorus and heavy metals are transferred to ash [40] [41]. The main components of incinerated sewage sludge ash (ISSA) are SiO2, CaO, Al2O3, Fe2O3, MgO and P2O5 while the precise composition varies depending on the wastewater quality, applied treatment and other conditions [42]. The use of ISSA as a fertilizer is limited due to its heavy metal content and reduced P availability and is one of crucial reasons why the recovery of P from ISSA is gaining interest. ISSA contains a significant amount of P as stated earlier [43] [44]. It contains approximately 22.5% of P2O5, which is close to the content of P2O5 in natural phosphate rocks (28.05%) [45]. Most of the P is concentrated in fly ash which contains high amount of phosphorus, typically 10% to 20% mass as P2O5 [46]. In ISSA produced at a temperature over 700°C water insoluble hydroxyapatites are formed [47], and the phosphorous compounds can be unsuitable for agriculture use as they are bio-unavailable [48, 49]. However, recently Wang et al. (2018) [50] published a method which allows the extraction of about 80% of P from ISSA recovered as struvite. Herzel et al. (2016) [33] also showed a high recovery potential of P. Combustion of SS is often conducted at a temperature of about 850°C since at this temperature, P forms volatile oxides, which then condense upon cooling, forming P2O5 that is a component of fly ash retained by filters [7].

Commonly used reactors for SS combustion are fluidized bed reactors which provide reliable process conditions for mono-combustion [51]. Nevertheless, it is a technology with high capital and operating costs and with limited energy recovery, but also with a high P recovery potential [52]. Fluidized bed technology has been used since 1922, when Fritz Winkler patented its application for gasification at BASF in Ludwigshafen, Germany. Since then it has received wide applications, especially in combustion, as it represents an efficient combustion system, able to burn not only coals but also low-quality fuels and wastes [52]. Fluidized bed technology has been successfully used for sludge combustion due to many advantages such as:

- the fluidization of the bed material and the fuel particles have a three-dimensional motion of the solids provides good mixing conditions in both horizontal and vertical directions. This effective mixing behaviour results in even temperature and fuel distributions within the combustion chamber which is a significant advantage compared to grate furnaces and pulverized fuel combustors [39];
- FBC have high heat transfer rates due to the even temperature distribution and temperature levels (typically 850°C) so no thermal NOx is produced [53];
- the large surface area of an inert bed material that allows efficient heat transfer and results in complete combustion at relatively low temperatures and excess air levels (25–50%);
- the residence time of the large amounts of sewage sludge in a hot bed is long enough to ensure sufficient burn-out of the sludge [54];
- the freeboard, which acts like a post-combustion chamber, provides complete thermal destruction of the organic substances [55];
- the large inventory of hot inert bed material prevents a sudden temperature changes, since any short-term major variations in the sludge composition or water contents are stabilized by the large heat reservoir [56];
- a very low inventory of fuel or carbon in the bed which permits start-up and shutdown in a matter of minutes when the combustor is near its operating temperature and the slow rate of bed cooling allows for intermittent operation, when desirable [56];
- maintenance costs which are mostly due to refractory replacement are considerably lower since the large inventory of the bed material acts as a thermal flywheel thus eliminating thermal shock and damage to the refractory [52].

Fluidized bed furnaces are usually suitable for the combustion of low-grade fuels which are rich in moisture and ash or fuels with variable properties, which are typical properties of SS [39]. For combustion of SS, both circulating fluidized bed (CFB) and bubbling fluidized bed (BFB) based technologies can be applied. BFB furnaces are used for mono-combustion of SS, while CFB technology is mainly considered for co-combustion of the sludge with coal, biomass, or other fuels [57]. Compared to CFB, a BFB may retain a larger part of the total ash in the bed ash fraction and separates volatile ash components into the flue gas better than a CFB, thus providing a higher degree of ash fractionation [58]. The efficiency of a CFB is 98% to 99.5% and is higher than that of a BFB, as a result of higher gas velocity, thus better gas-solid mixing and recirculation of unburnt carbon particles back to the furnace [59]. Li et al. (2017) [60] reported that after fluidized bed combustion of SS, 89.3% of the P was enriched in SS bottom ash and 5.6% was distributed in fly ash. Cammarota et al. [61] reported that the SS palletisation plays an important role in fuel conversion and results in a stable and efficient combustion behaviour in fluidized bed combustors in terms of low elutriation of unburnt species. Nevertheless, cleaning processes are necessary to reduce gaseous and particulate emissions.

A high recovery rate of P from ISSA has been reported in many studies. Krüger et al. [62] investigated the composition of 252 ISSA samples collected from 24 mono-thermal treatment facilities for SS in Germany and found that the mean content of P in ISSA amounted to 7.9%, highlighting its important recovery potential. Takahashi et al. [63] reported a high rate of P recovery from combustion ash of SS, by mixing the ash with sodium hydroxide or sodium carbonate and treating the mixture at 750°C to 900°C under aerobic conditions. The P was successfully recovered as an alkali metal phosphate from the treated ash through water extraction with the recovery rate of the P reaching 78%. A P recovery rate of 99% from combustion ash can be achieved using a 10 minute extraction by 14% H2SO4 and a solid to liquid ratio of 2 [46]. P recovery from SS can be also conducted by electrodialytic separation. The negative side of this process is that it is time-consuming, but the big advantage is that it removes heavy metals simultaneously from ash [41]. Additional treatment of ashes is needed to increase the bioavailability of P and remove heavy metals in order to use the ash as a fertilizer [43] [64]. Gorazda et al. [65] reported a combustion temperature of 950°C as the best condition for downstream phosphorus extraction from ash. Acid leaching resulted in nearly 85% recovery of P with both sulphuric acid and oxalic acid for sludge combusted at 900°C [66]. Kasina et al. [67] investigated the chemical and mineralogical characteristics of ISSA obtained from Veolia's fluidized bed incinerator for SS (Pyrofluid) at 850-900°C and concluded that elements which are characterized by high melting temperatures concentrate in the ISSA, while elements that are characterized by lower melting temperatures (e.g. Sn and Hg) concentrate in the air pollution control (APC) residues. Moreover, over 17 wt% of P2O5 accumulated on average in the ISSA, resulting in a considerable amount of P that can be that can be recovered. Franz [44] analysed SSA obtained from two fluidized bed incinerators in Switzerland when sludge with 30% dry solids was incinerated with oil at a temperature of 830-850°C. The ISSA contained between 9% and 21% P2O5 and extraction with H2SO4 12-14% by weight for 10 min with L:S ratio of 2 showed it to be the most favourable condition for P recovery. Moreover, extraction of P from ISSA with sulphuric acid results in the lowest amount of heavy metals, compared with other acids [68]. The sampling period also appears to influence the P content in ISSA. P content is seen to decline during the summer months with a minimum reached around June, July, and August. The P content increased toward February and March. However, the reason for such a trend is yet unclear. A possible explanation can be found in varying food habits and leisure time behaviour during different seasons, however this requires further investigated [62]. Combustion of SS is a well-known and controllable process, but due to emissions of nitrogen oxides, heavy metals, and other harmful compounds, it raises many concerns and requires large investments for the cleaning of flue gases [69].

3.2 Pyrolysis

Pyrolysis is a process where the decomposition of organic material occurs in an inert atmosphere at moderate temperatures [70]. It also represents the first step in gasification and combustion processes, which is followed by cracking and/or oxidation of gaseous products and oxidation of char [71] [72] [73]. Pyrolysis can be used effectively to recover both energy and the P present in SS [74]. For pyrolysis sludge moisture content must be around 15% [16]. The proportion of all three products, i.e. gas, liquid and biochar, depends considerably on the pyrolysis method and reaction parameters [75]. A considerable amount of P is present in the solid process residue, char/biochar [76]. With an increase of temperature, the yield of char decreases [77] [76], as the pyrolysis temperature rises from 500°C to 900°C, the yield of char reduces from 63 wt.% to 53 wt.% [1]. That was also concluded by Jin et al. [78] and Park et al. [79] who reported the highest SS char yield at a temperature of 400℃ and a decrease with further increase of temperature. Lu et al. [80] found that the surface area of char from SS pyrolysis increases with temperature and that the P remains in solid phase (char) while partitioning into the other phases, i.e. liquid and gas is to a much lower extent. Different types of pyrolysis processes exist depending on the product selected [81], as presented in Table 5.

Table 5. Different types of pyrolysis processes

Pyrolysis type	Residence time (for vapour)	Residence time (for solids)	Heating rate °C/min	Temperature °C	Main product
Flash, fast	< 2 s	Short	High	900-1300	Liquid (single phase) or vapour
Intermediate	10 – 30 s	From s to min	Medium	400-600	Liquid (two phases: water and tar phase), solid (char) and gas
Slow	minutes	From min to h	Low	300-550	Solid (biochar)

For P recovery from SS, slow pyrolysis plays an important role and should be taken into consideration. Barry et al. [82] concluded that slow pyrolysis of SS produced the best char in terms of yield, heating value (on a dry basis), and stability. Hossain et al. [76] conducted pyrolysis of digested SS in fixed bed horizontal tubular reactor at four different temperatures 300°C, 40 °C, 500°C and 700°C. The P present in the pyrolysis char was the highest at 400°C and decreased with temperature. Moreover, the usage of pyrolysis technology and its formed products could potentially reduce environmental pollution [83, 84].

3.3 Hydrothermal carbonisation

Hydrothermal carbonisation (HTC) is a wet thermochemical process in a closed system that operates under autogenic pressure and relatively low temperature compared to the other thermal processes mentioned [85]. HTC does not require a specific atmosphere [86] [87, 88]. Reactions in HTC mostly occur in the liquid phase with hydrolysis considered to be the first step [89, 90]. Since the HTC process proceeds in a closed system, the phase change of the moisture does not occur so consequently the latent heat of vaporisation is not utilized in the process [91]. It requires less energy compared to other thermochemical treatment processes, and results in a stable solid product [92]. The hydrothermal process is characterized by high liquid yields, as its content is very high at the start of the process and almost does not change. During the reactions a small amount of CO2 is emitted as the main gas product, and the ratio of solid product to liquid is much lower than in pyrolysis [87, 93]. Moreover, the ignition temperature of the hydrochar is higher and is safer for handling, transportation and storage than dry SS [94]. HTC represents an attractive technique for the conversion of SS to valuable products [95]. The process accumulates significant amounts of P from the SS within the hydrochar [96]. Takahashi et al. [97] reported 58-71% P recovery from carbonized SS by hydrothermal treatment when an NaOH solution was added. Schneider and Haderlein [98] estimated that total P in SS hydrochar was around 46.5 mg P g− 1.

3.4 Gasification

Gasification at high temperatures converts carbonaceous materials by partial oxidation in some cases in the presence of steam to synthesis gas (syngas), ash and eventually char [99]. This process offers a sustainable method for SS management that takes into account the concept of a circular economy (CE) [45]. Gasification of SS has not been as widely applied as combustion, due to the complexity of the technology and its higher investment and operational costs [100]. Nevertheless, it can be assuming that this process is a successful solution for P recovery, since due to reductive atmosphere during the process, inorganic compounds are moved into the solid phase, which presents a promising source of phosphorus [45]. Gasification can operate with SS with 75% moisture content [16]. The solid fraction obtained from the gasification of SS contains around 20 wt.% P2O5 [101]. Furthermore, direct application of the gasification char as a fertilizer is limited due to presence of heavy metals, as well as due to the low plant availability of the P. For these reasons, the investigation of P recovery from gasification char has increased in importance [102]. Among the different reactors that exist for gasification of SS, fixed and fluidized bed are mainly used. Fixed bed gasifiers have simple construction and show good thermal efficiency. With fluidized bed reactors, higher gasification efficiency can be achieved compared to fixed bed, due to better mass and heat transfer, but on the other hand sintering of SS and bed material can occur [103]. Atienza et al. [104] studied the extraction of P from SS char combustion and char gasification ash by means of acid leaching. 90% of the P present in char combustion ash and in char gasification ash can be recovered using sulphuric and oxalic acid. P recovery rate using oxalic acid is higher compared to sulphuric acid, especially for char combustion ash obtained at 600°C to 750°C. When using sulphuric acid, P recovery from char combustion ash obtained at 900°C is higher than from ash obtained at lower temperature, under the same extraction conditions. Viader et al. [105] carried out a comparative analysis between an ISSA from sludge combustion in fluidized bed combustor (FBC) and a SSA from gasification in low-temperature fluidized bed gasifier. They reported that the content of P was little higher in gasification ash compared to that produced from the incineration process.

4 Transformation of P in sewage sludge during thermal treatment

Water-soluble phosphorus (PWS) in SS presents good indicator to test the runoff P (RWSP) in treated SS. Its proportion in SSA from char (SSA/C) can be calculated using the equation (2).

$$RWSP = \frac{Pws}{Ptot} 100\% \qquad (2)$$

where PWS is the amount of P extracted by water (mg/g) from SSA/C, and Ptot is the theoretical P content (mg/g) in SSA/C. RWSP in SSA/C amounts to no more than 2.5%, while RWSP in SS is higher and it is around 20%. PWS in SSA/C decreases with an increase of temperature which leads to conclusion that thermal treatment increases the stability of P in SSC/A [32].

P in SS consists of organic and inorganic P as mentioned earlier. Organic P is usually transformed into ortho-P and pyro-P during thermal treatment [106]. A high importance should be attached to the transformation of ortho-P as it comprises around 75 wt% of total P [32]. The thermal treatment process and temperature are two critical factors for the speciation evolution of P. At lower temperature, i.e. 400°C, pyro-P is produced due to dehydration of $M2(HPO4)x$ or $M(H2PO4)x$ and transformation of organic P in the sludge. With an increase of temperature, the proportion of pyro-P decreases to a considerable extent and its production within the temperature range of 700−800°C is inhibited [32] [11] [76]. Some soluble ortho- and pyro-P, which is rare in SSA/C can be easily dissolved in $NaHCO3$ - solution thus forming $NaHCO3$-P. Some Al, Fe−P compounds that are formed are insoluble and can be extracted by NaOH solution. At high temperature, reactions between inorganic P and metal ions can occur resulting in the formation of P-containing minerals [107] [108]. Nevertheless, the mechanism of transformation of P to minerals at higher temperatures remains unclear. These P minerals and other more stable species, such as insoluble Ca, Mg-P can only be extracted by HCl solution, thus forming HCl-P [32]. One study reported the influence of particle size of ISSA on transformation of P species. Namely, Li et al. [13] found out that AP was the primary component in the fly ash at 850°C. and increased with decreasing particle size, whereas NAIP exhibited the opposite tendency, and became stable when the particle size was less than 37.5 µm. Furthermore, the formation of calcium phosphate ($Ca3(PO4)2$), calcium pyrophosphate ($Ca2P2O7$), and hydroxyapatite ($Ca5(PO4)3(OH)$) at high temperatures during combustion was reported by Wang et al. [96]. Some studies reported the presence of $Ca9Fe(PO4)7$ in crystalline form in incinerated sewage sludge ash [109]. P present in ISSA is usually as insoluble calcium and aluminium phosphate minerals which are poorly bioavailable [110]. Gondek et al. [111] found that during the pyrolysis of SS, the contents of PWS decreased. Also, SSA from low temperature gasification contains very little P available to plants [112]. As reported by some researchers, metaphosphate and the P associated with C bridged by O were the main species in pyrolysis biochar [113]. Wang et al. [96] found that during HTC, an acidic feed water pH favoured the transformation of AP to NAIP and of Po to Pi, while an alkaline environment promoted transformation of NAIP to AP and a small portion of the Pi to Po. However, the available information on the above topics found in literature is limited and more investigations are needed.

5 Overview of some existing technologies with high recovery rate of P from SSA

The concentration of P in SSA depends on the sludge quality, process temperature and P recovery treatment method used. In Table 6 an overview of various technologies used for P recovery from sludge ash is presented. The Centre for Solar Energy and Hydrogen Research Baden-Württemberg in Germany is currently developing an innovative sustainable process for simultaneous SS fluidized bed combustion and recovery of phosphorus in a Ca reach bed.

Table 6. Technologies for recovery of P from SSA

Technology	Product	Recovery principle	P recovery rate	References
ASH DEC	Mg-SSA	Thermal	> 95%	[114] [115]
ASH DEC	Rhenanit (CaNaPO4)	Thermal	~ 98%	[116] [114] [115]
Mephrec	P- rich slag (5-10% P)	Thermal	~ 80.5%	[116] [117]
Kubota	P- rich slag (˜13% P)	Thermal	> 80%	[118]
RecoPhos	Ca- and Mg- phosphates	Wet chemical	~ 98%	[119]
Leachphos	Ca-phosphate or struvite	Wet chemical	70-90%	[120]
EcoPhos	Phosphoric acid, dicalcium phosphate	Wet-chemical	~ 97%	[116]
PASCH	Ca - phosphate	Wet-chemical	~ 80%	[120]
Sephos	Ca - phosphate	Wet chemical	~ 90%	[121]
SESAL-PHOS	Ca - phosphate	Wet chemical	74-78%	[122]

6 Conclusion

Sewage sludge thermal treatment technologies present a promising option for sewage sludge management which is in compliance with EU legal requirements and for phosphorus recovery whose reserves have been considerably depleted. Many technologies for the recovery of P from sewage sludge ash and char have been developed so far. However, relatively few studies on the P transformation during sewage sludge thermal treatment have been reported in a limited degree and more investigation is needed as it plays a crucial role in the development of suitable strategy for P recovery. Fluidised bed technology has a high P recovery potential. Depending on the process conditions during incineration a significant amount of P can be found in the bottom or fly ash. With an increase in the thermal treatment temperature the content of water soluble P from SS decreases. Some methods have been developed for the effective transformation of P from thermal process residue and with the addition of minerals a struvite crystals are formed.

Struvite precipitation from organic waste (ESR5)

Phosphorus recovery in form of struvite is highly influenced by mineral aspects, physical state of the waste and concentration. Phosphorus levels are different in liquid wastes, biosolids and ashes. Various wastes including biosolids, liquid wastes and waste treatment ashes have been reviewed for mineral concentration of total elemental composition of phosphorus, potassium, magnesium, calcium, zinc, copper, manganese and iron. This was reviewed in highlight of wastes treatment technologies able to concentrate P and minerals for prompt use as raw material in struvite production. The high mineral composition of ash suggests combustion as one of treatment process of organic rich wastes to concentrate phosphorus and microelements. However, the emission of greenhouse gases and micropollutants from incineration disqualifies it from green technologies. Thus, wet pyrolysis techniques, such as hydrothermal carbonization of organic waste are recommended for advanced study in mineralization and nutrient recovery. Struvite precipitation from ash needs prior extraction and counterions adjustment through either ion exchange or by additional amount of precipitating reagents in optimized molar ratio. The P recovery as struvite and micronutrient enriched fertilizer can be done from liquid and ash wastes through struvite precipitation and formulation. Biosolids should undergo further mineralization and extraction steps to enhance reactive P for struvite precipitation. The research works on P recovery from hydrochar and ash of dairy processing wastes are not yet available and make subsequent part of this review.

1 Introduction

Milk processing is one of the largest industry in the European agriculture sector and the EU is the second top global producer of milk-based products [1]. Industrial wastes are increasing with world population, economic growth and industrial development. Agro-food industry generates up to five million metric tons of wastes per year. Up to 39% come from food processing and manufacturing [2]. Food supply chain including animal derived food waste highlights their use in anaerobic digestion to produce heat fuel and bio-fertilizer [3]. Additionally, the wastes serve as a source of fats, fibers that are extracted and used for therapeutic purposes while the residue is used as fertilizer [3]. Another way of treatment involves thermochemical incineration of the waste into ash with high minerals content [4]. Along the wastewater treatment process, phosphorus (P) is susceptible to recovery from a fraction of treatment product either by concentrated stream, or by a sludge ash with more than 90% of P recovery [5]. The concept of EU directives and regulations regarding wastes recycling is to leave no waste from any production and ensure no risk of nuisance to humans, animals and ecosystem in general [6]. Phosphorus remains bound in nature as ores including phosphate rocks, as well as P2O5 [7,8]. About 82% of the mined phosphorus is used in agriculture, while 7% is used for the production of animal feed. The remaining 11% of the mined phosphorus is used in industry and medicine for the production of pharmaceuticals, oils, detergents, or even textiles [9]. The aforementioned multiple uses of phosphorus ending with its loss to sewage, effluents and run off from farms, the recovery of phosphorus from wastes is important in research and industrial sectors [9,10].

The P loss in environment is reported to cause P soil nutrient depletion inducing the decrease in crop production [11,12]; and root cause of water bodies eutrophication due to the excess of phosphates from industrial effluent [13]. High P exploitation without renew will cause a P price growth in near future and problem in P mining [14,15]. Along with nitrogen, phosphorus is a leading agent responsible for the bloom of micro and macrophytes in water bodies [16–19].The P recovery strategies mainly include precipitation as calcium phosphate, hydroxyapatite, and struvite [9]. Additionally, the existing P industries have shown interest and the ability to integrate sewage sludge ash to produce P materials [5]. The main product is magnesium-ammonium-phosphate (MAP) also known as struvite, as well as production of marketable products, such as mineral fertilizers, phosphoric acid, and even P in its pure form [5]. The mitigation measures of both soil P depletion and water pollution would obviously include phosphorus recovery and use of slow release phosphorus fertilizers, mainly struvite [20]. The latter is formed through precipitation reaction between magnesium, ammonium and phosphate under oversaturated solution [21]. Therefore, waste treatment enhancing P mineralization and concentration is important to increase struvite ion activity product and high saturation index [22]. Since phosphate can precipitate potentially with other cations than struvite [23,24], it is important to have a prior knowledge of mineral aspect of raw material including wastewater, bio-solids and ash. Previous reviews emphasized on process of phosphorus recovery and struvite precipitation from wastes [9,10,25–29]. The review on organic waste treatment to enhance P concentration and struvite precipitation are still limited. In addition, despite the influence by other elements on struvite precipitation, mineral screening of dairy and dairy processing wastes (DPW) for their use as raw material in struvite production was not previously reviewed. This work reviews wastewater and organic residues from dairy wastes treatment focusing on their use in P recycling and recovery as struvite enhanced by mineralization aspect of waste treatment technologies.

2 Phosphorus recovery through struvite precipitation

The P recovery needs much attention view its use, environmental concern and recycling regulations. Treated water for reuse should contain 2 mg/kg P at most, the range recommended by Food and Agriculture Organization (FAO) being 0-2 mg/kg [13]. The production of P rich biosolid is done through enhanced biological phosphorus removal (EBPR) on sludge under action of polyphosphate accumulating microorganisms yielding a P rich biomass [30]. However, the application of EBPR biosolid as a fertilizer is limited due to the lower level of P, lower P availability and possibility of contamination of agriculture land by micropollutants [31]. EU regulations limit the presence of micropollutants in organic fertilizer, with polyaromatic hydrocarbon (PAHs = n.a), which standard limit is 6 mg/kg in biochar [32]. The European Innovation Partnership Agricultural Productivity and Sustainability (EIP-AGRI) highlighted P precipitation for phosphorus recovery from wastes [33]. Calcium phosphate was reported to be recovered from manure while struvite is the recommended form for fertilizer use [33]. Struvite is a benefit in agriculture due to its content in nitrogen and phosphorus in forms efficiently available to plant [34,35]. Phosphorus can exist in matrix as particulate and dissolved species both involving organic and inorganic forms [36]. The inorganic phosphorus species include mainly orthophosphate which is the main available form for plant nutrition thus important in soil fertility and problematic in water pollution [18].

2.1 Struvite precipitation mechanism

Struvite precipitation reaction is described by Eq. 2

$$Mg^{2+}(aq) + NH_4{}^{+}(aq) + H_nPO_4{}^{(3-n)-}(aq) + 6H_2O \rightleftharpoons MgNH_4PO_4 \cdot 6H_2O\,(s) + nH^{+}(aq) \qquad Eq.\ 2$$

Though the reaction is faster in aqueous solutions by which precipitation term is used, the mechanism of struvite crystallization involves mainly nucleation and crystal growth [37].
Nucleation is the stage when the first new crystalline nuclei are formed. It is divided into primary and secondary nucleation. Primary nucleation has further two categories. These are homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs in supersaturated solutions in the absence of crystals or other solid phases while heterogeneous nucleation needs additional particle material [38]. In secondary nucleation, previously formed crystals enhance the nucleation process. In contrast, crystal growth is a subsequent process of incorporating constituent ions into the crystal lattice to form detectable crystals.

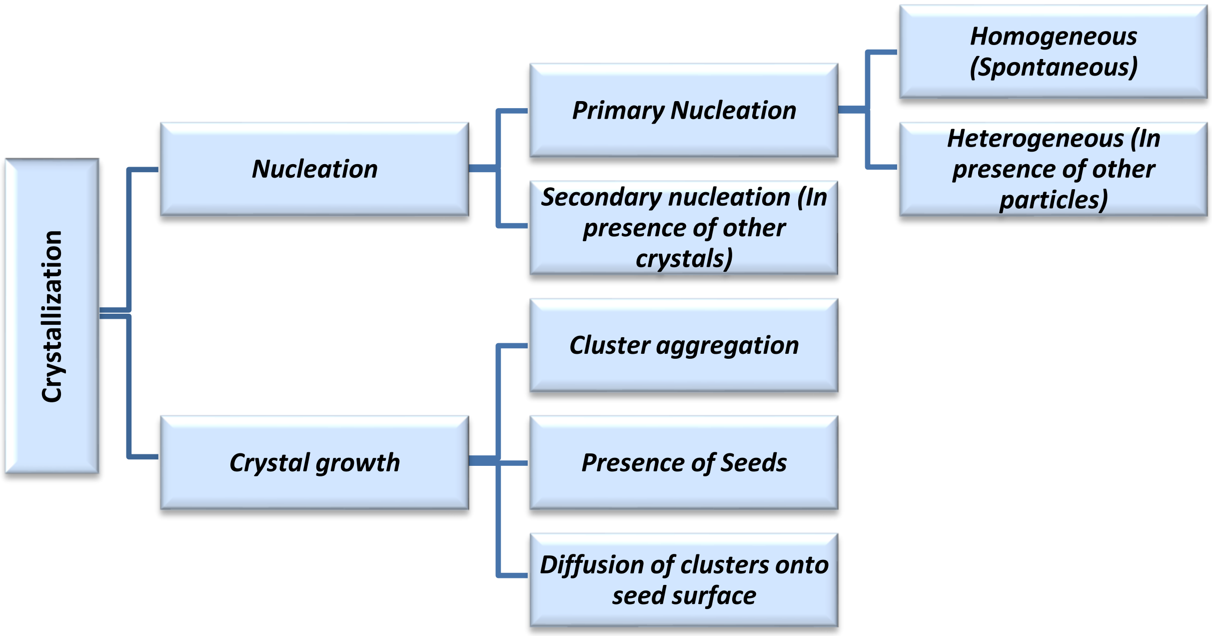


Figure 31. Crystallization stages

The theory of diffusion-reaction at a limited rate is used for advanced explanation of crystal growth where ions are transported from the supersaturated solution to the crystal surface, by diffusion, convection, or a combination of both mechanisms [39]. The grown crystals aggregate to form a solid-liquid phases equilibrium [34].

2.2 Factors affecting struvite precipitation.

Struvite precipitation is affected by various parameters including the concentration of chemical reagents, pH, temperature, and the presence of foreign ions.

2.2.1 The effect of concentration

Precipitation of a compound is generally expressed as heterogenic equilibrium between dissolved and solid species of a component.

$$A_a B_b \rightleftharpoons aA^{z+} + bB^{z-} \qquad \text{Eq. 3}$$

Equilibrium between solid solutions and aqueous phase is included in the models obtained through heterogeneous mass-action Eq. 4. In pure phase, the concentration of pure component is thermodynamically taken as unit. Thus the Eq. 4 becomes solubility product Ksp described by Eq. 5.

$$K = (\{A^{z+}\}^a \{B^{z-}\}^b)/\{A_a B_b\} \qquad \text{Eq. 4}$$

$$Kps = \{A^{z+}\}^a \{B^{z-}\}^b \qquad \text{Eq. 5}$$

Struvite solubility product corresponds to multiplication of concentration *(C_i)* of magnesium, ammonium and phosphate ions in saturated solution. Thus the Eq. 4 can be resumed for Struve as in Eq. 6

$$K_{struvite} = C_{Mg^{2+}} * C_{NH_4{}^+} * C_{PO_4{}^{3-}} \qquad \text{Eq. 6}$$

The system is explained as under-saturated, saturated and oversaturated in relation to solubility product (Ksp). A saturated aqueous solution has dissolved the maximum of solute. The precipitation of struvite cannot happen spontaneously if the product of Mg2+, NH4+ and PO43- concentrations is lower than Kspstruvite. In this case, the solution is under-saturated. The struvite precipitation is enhanced by species concentrations product higher than saturation Kspstruvite. [40]

2.2.2 Effect of Temperature

The concentration term is replaced by activity (ai) which coefficient (γ_i) is a thermodynamic parameter depending on a chemical potential [41]. The activity expression in relation to concentration is given by Eq. 7

$$a_i = C_i \gamma_i \qquad \text{Eq. 7}$$

The coefficient γ_i involves the interaction of other ions concentration (Ionic strength, I) and a temperature and dielectric constant term (A). Activity coefficient is calculated using Debye-Huckel relation Eq. 8 and extended to Davis expression Eq. 9 used at higher ionic strength (0-0.5 M) [42]

$$log\,\gamma_i = -AZ_i^2\sqrt{I} \qquad \text{Eq. 8}$$

$$\boldsymbol{log\,\gamma_i = -AZ_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} + 0.3I\right)} \qquad \text{Eq. 9}$$

With I, ionic strength, $I = \frac{1}{2}\sum_{i=1}^{n} Z_i^2 C_i$, while A is a factor dependent to dielectric constant, ε ,and temperature, T, calculated by $A = 1.82 * 10^6 * (\varepsilon T)^{-3/2}$. The dielectric constant was studied elsewhere in aqueous solutions in relation with temperature and contribute to activity of a species in solution by affecting term A of activity coefficient (Figure 32) [43]
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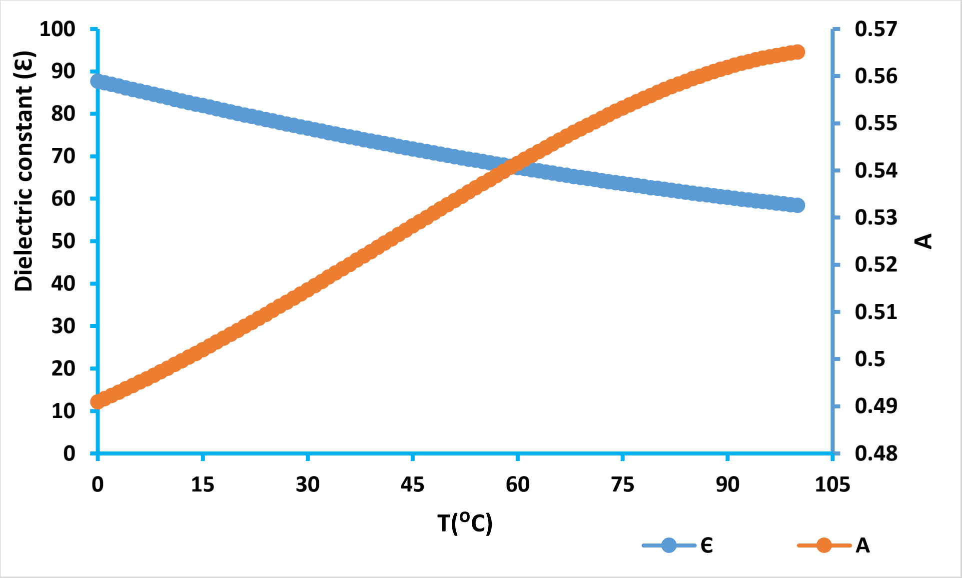

Figure 32. Contribution of Temperature effect on activity coefficient

The increase of temperature demonstrates an increasing effect on term A thus, decrease in activity coefficient and dissolved species activity.

Thermodynamically, the equilibrium expressions are rather in terms of activities than concentrations (Eq. 10). In general, for a compound that dissolves in heterogenic equilibrium, the expression Eq. 11 gives a product of ionic species activities exponent their stoichiometric coefficients

$$Kps' = a_{A^{z+}}^{a} * a_{B^{z-}}^{b} \qquad \text{Eq. 10}$$

$$\boldsymbol{Kps'} = \prod_{m}^{Meq} \boldsymbol{a}_{i}^{c_{m,i}} \qquad \text{Eq. 11}$$

With Ksp equilibrium expression of mass action as product of ion concentrations and Ksp′ its thermodynamic expression of product of ion activities ai of species of mass m to make a saturated phase exponent the mass coefficient of ionic species i.

The temperature effect on struvite precipitation was discussed elsewhere. Salsabili A et al, has found that the solubility of struvite was lower at temperature lower than 20 oC while it was increasing between 20-30 ° C and then decreasing from 30-60 ° C [44]. Aurélie Capdevielle et al found the temperature below 20 oC as optimum for struvite crystallization [45]. In other side, optimum temperature was found to be 25.23 oC [23].

Precipitation prediction. A solution trends to heterogenic equilibrium when the liquid phase is supersaturated thus contains more than the equilibrium soluble amount of species of a compound. Therefore, at any point of the system, the equilibrium status is estimated as ion activity product (IAP) Eq. 12. The saturation index (SI) is defined as the logarithm of normalized expression of IAP on Ksp (Eq. 13)

$$IAP = \prod_{m}^{Meq} a_{i}^{c_{m,i}} \qquad \text{Eq. 12}$$

$$SI = log\left(\frac{IAP}{Kps}\right) \quad \text{Eq. 13}$$

Thus the SI = 0 indicates an equilibrium, negative SI indicates low probability of solid phase formation, positive SI indicates probable formation of solid phase. The SI remains a governing parameter of precipitation potential and kinetics in multicomponent solution. The formation of concentration Xcst of crystalized compound in heterogenic system is directly proportional to its super-saturation (σ) with kinetic rate constant as proportionality coefficient and n, the order of precipitation reaction [46]. The supersaturation is SI dependent defining how far the component is from equilibrium

$$r_{cst} = k_{cst} X_{cst} \sigma_{crt}^{n} \quad \text{Eq. 14}$$

$$\sigma = \left(\frac{\prod_{m}^{Meq} a_i^{c_{m,i}}}{Kps}\right)^{1/m} - 1 \quad \text{Eq. 15}$$

In this regards, struvite and other salts precipitate kinetically according to their Ksp and IAP.

2.2.3 Effect of pH

Inorganic Phosphorus species are pH dependent. Thus, struvite saturation index is affected by phosphate, and ammonium acid base equilibria. To highlight the effect of pH, the proton based ionic speciation model (Eq. 16) is applied on the basis of solution components ordered increasingly in their equilibrium constants found in other works [47].

Table 13. Proton exchange for ionic equilibria and their constants

Ionic equilibrium	**pK**	**K**
$HCl \rightleftharpoons H^+ + Cl-$	-6	1000000
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	-1.98	94.9
$CO_2 + H_2O \rightleftharpoons H_2CO_3$	1.47	0.033884
$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$	1.55	0.0279
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	2.15	0.007112
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	6.35	$4.45 * 10^{-7}$
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	7.20	$6.34 * 10^{-8}$
$NH_4^+ \rightleftharpoons NH_3 + H^+$	9.25	$5.69 * 10^{-10}$
$HCO_3 \rightleftharpoons H^+ + CO_3^{2-}$	10.32	$4.74 * 10^{-11}$
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	12.02	$9.48 * 10^{-13}$
$H_2O \rightleftharpoons H^+ + OH^-$	14	10^{-14}

The molar fraction model for species in acid base equilibria is given by Eq. 16 and the results of phosphate availability in aqueous solution with multiple proton acceptors are shown in Figure 1 [47]

$$\alpha_{ij} = \frac{[H^+]^{n-i} K_0 \ldots K_i}{[H^+]^{n-0} K_0 + [H^+]^{n-1} K_1 + [H^+]^{n-2} K_1 K_2 + \cdots + [H^+]^{n-n} K_1 K_2 \ldots. K_n} \qquad \textit{Eq. 16}$$

The molar fraction of ionic species plotted against pH indicates high fraction of phosphate in alkaline pH.

The pH conditions favoring high fraction of PO_4^{3-} is above pH 10, however above that pH, ammonium acid base equilibrium is predominantly in form of ammonia gas (>60% of initial ammonium moles) evolving from the reactor. Therefore, struvite precipitation is likely to occur in optimum pH of high struvite ion activity product. The best conditions reportedly ranged from pH 8.5 and may not precipitate at pH above 11 [48,49].

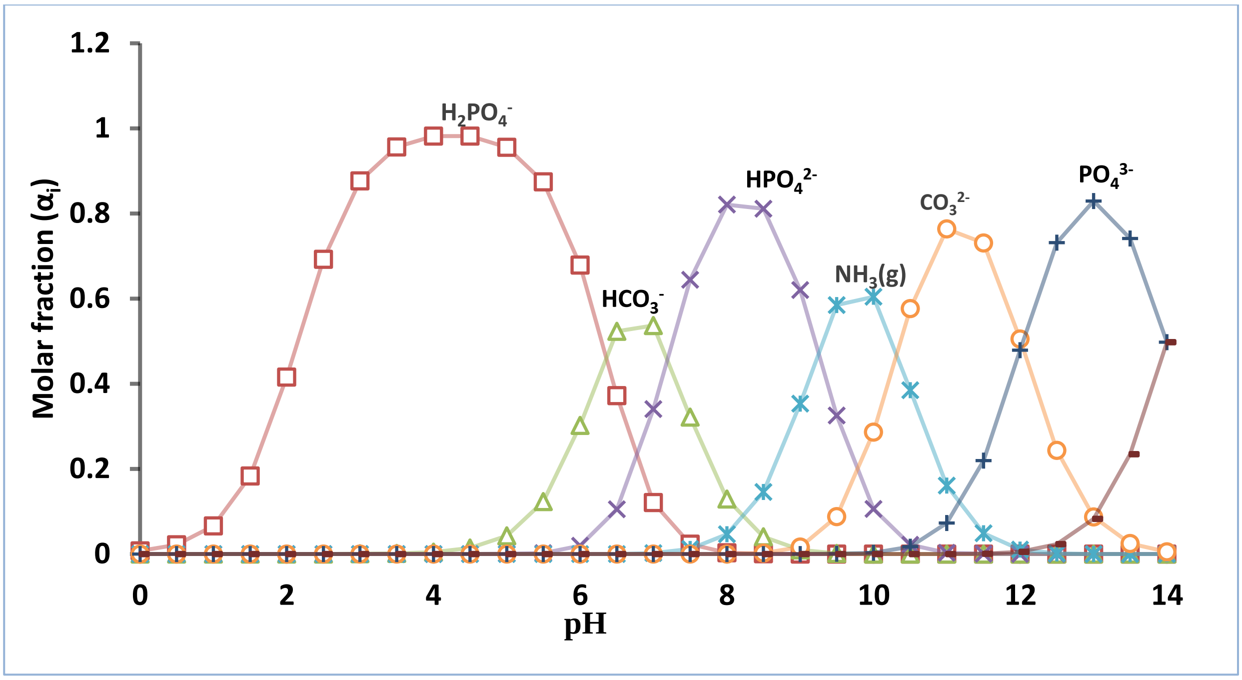

Figure 33. Molar fraction for proton acceptors in multicomponent aqueous solutions

2.2.4 The effect of foreign ions

Effect of foreign ions concentration is observed on ionic strength. The latter affects ion activity product thus saturation index (SI) Eq. 13. Anions can affect magnesium activity in solution where carbonate salts can potentially co-precipitate in form of huntite ($Mg_3CaCO_3)_2$) or hydromagnesite [50].

The precipitation of P is susceptible to happen with a number of cations forming less soluble salts with phosphate. The summary of typical examples of precipitation is described by Figure 34

Multi-component aqueous matrices contain more phosphate counterions which precipitation with phosphates form less soluble salts with a number of cations thus counter competition with magnesium and ammonium during struvite precipitation [51]. On the side of phosphate counterions, calcium effect was pointed out in several researches where its high level favors precipitation of calcium salts including calcium phosphate ($Ca_3(PO_4)_2$, hydroxyapatite ($Ca_5(PO_4)_3OH$, Ksp = 2.91 * 10^{-58}), octacalcium phosphate (($Ca_8H_2(PO_4)_6$.$5H_2O$), Ksp = 1.12 * 10^{-48}), and amorphous calcium phosphate [52–54]. In such multi-component solutions, the mass contribution balance of single ionic species is observed and enhances efficiency P removal through co-precipitation [42].

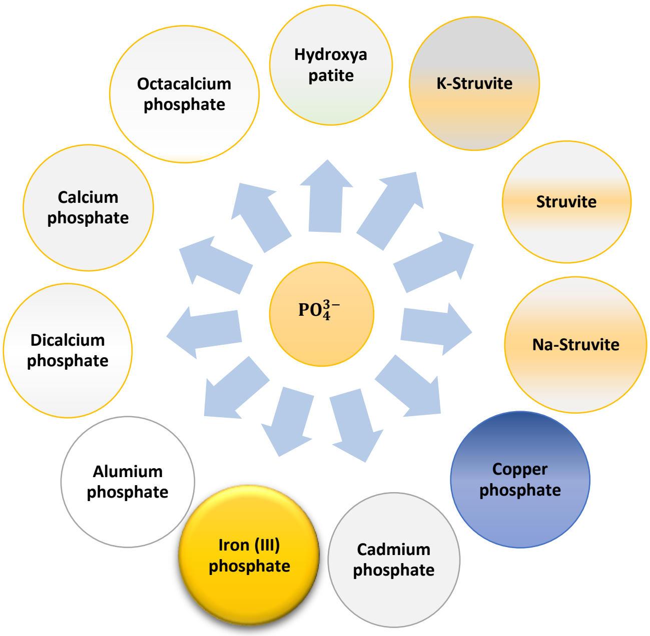

Figure 34. Phosphate counterions and possible phosphate salts precipitation

Though there are other phosphate counterions including silver, aluminum, copper, cadmium, iron and other transition metals, they are in trace concentrations. Since dairy products make one of groups of Ca functional foods, the waste from milk processing plants have high level of calcium and struvite precipitation from DPW needs advanced experimental design and optimization [55]. Calcium ions at higher molar concentration than magnesium exhibits high precipitation potential to inhibit struvite ($Ksp=10^{-13.6}$) in non-optimized conditions [56]. The solubility product Ksp is used to describe the product of electrolyte species concentration or activities of saturated solution. The higher Ksp, the higher is solubility otherwise the precipitation is enhanced with lower Ksp [57]. Water soluble inorganic phosphorus (PO_4^{3-}) can be precipitated in different form in the same solution and Ksp values are given in

Table 14. In light of Ksp as in the

Table 14 calcium phosphate salts are kinetically apt to inhibit struvite. Hydroxyapatite is likely to be the calcium phosphate form with high precipitation rate. To solve the problem of struvite inhibition, there is a need of chemometric models with experimental design and optimization of mineral ratios.

Table 14. *P precipitate and their solubility products (Ksp)*

Precipitate	formula	Ksp	Reference
Struvite	$MgNH_4PO_4$	$10^{-13.26}$	[58,59]
K-Struvite	$MgKPO_4$	10^{-11}	[59]
Octacalcium phosphate	$Ca_8H_2(PO4)_6$ 2H2O	$1*10^{-47.95}$	[46]
Hydroxyapatite	$Ca_5(PO4)_3(OH)$	$2.1*10^{-58}$	[54]
Alumninium phosphate	$AlPO_4$	$9.84 * 10^{-21}$	[60]
Silver phosphate (I)	Ag_3PO_4	$8.89*10^{-17}$	[60]
Cadmium phosphate	$Cd_3(PO4)_2$	$2.53*10^{-33}$	[60]
Calcium phosphate	$Ca_3(PO4)_2$	$2.07*10^{-33}$	[60]
Cobalt phosphate	$Co_3(PO4)_2$	$2.05*10^{-35}$	[60]
Iron (III) phosphate dihydrate	$FePO_4 .2H_2O$	$9.91 *10^{-16}$	[60]
Magnesium phosphate	$Mg_3(PO4)_2$	$1.04*10^{-24}$	[60]
Nickel (II) phosphate	$Ni_3(PO_4)_2$	$4.74*10^{-32}$	[60]
Copper (II) phosphate	$Cu_3(PO_4)_2$	$1.4 * 10^{-37}$	[60]
Bobierrite	$Mg_3(PO_4)_2 .8H_2O$	$1 * 10^{-25.2}$	[59]
Cattiite	$Mg_3(PO_4)_2 .22H_2O$	$1 * 10^{-23.10}$	[59]
Newberyite	$MgHPO_4 .3H_2O$	$1 * 10^{-23.10}$	[59]

In relation with ion pairing, rate expression for precipitation of calcium, magnesium, ammonium and phosphate are presented in Table 15

Table 15. *Typical rate expression for phosphorus precipitation*

Precipitate	Ionic species					Rate	Ksp
	Ca^{2+}	Mg^{2+}	NH_4^+	PO_4^{3-}	H^+		
Struvite		-1	-1	-1		$k_{str}X_{str}\left[\left(\frac{a_{Mg^{2+}} * a_{NH_4^+} * a_{PO_4^{3-}}}{Kps_{str}}\right)^{1/3} - 1\right]^3$	$10^{-13.26}$
Amorphous calcium phosphate	-2			-3		$k_{ACP}X_{ACP}\left[\left(\frac{(a_{Ca^{2+}})^3 * \left(a_{PO_4^{3-}}\right)^2}{Kps_{ACP}}\right)^{1/5} - 1\right]^2$	$10^{-25.46}$
Octacalcium phosphate (OCP)	-4			-3	-1	$k_{OCP}X_{OCP}\left[\left(\frac{a_{H^+} * (a_{Ca^{2+}})^4 * \left(a_{PO_4^{3-}}\right)^3}{Kps_{OCP}}\right)^{1/8} - 1\right]^3$	$10^{-47.95}$
Hydroxyapatite	-5			-3	+1	$k_{HA}X_{HA}\left[\left(\frac{a_{OH^-} * (a_{Ca^{2+}})^5 * \left(a_{PO_4^{3-}}\right)^3}{Kps_{HA}}\right)^{1/9} - 1\right]^3$	$2.1* 10^{-58}$

Though co-precipitation in struvite crystallization decreases its quality as fertilizer, the P removal efficiency is enhanced by contribution of different precipitant species. The mass balance contribution model used in multi-components solution for P precipitation is described by (Eq. 17). [42]

$$TOT_{PO_4^{3-}} = [PO_4^{3-}] + \sum_i^N v_{i,j} Z_j \qquad \text{Eq. 17}$$

Where $TOT_{PO_4^{3-}}$ is the total molar concentration of phosphate involved in the reaction system, while $[PO_4^{3-}]$ stands for phosphate concentration in solution and the sum of N molar concentrations (Z_j) of phosphate binding components with v_i, stoichiometric coefficient that equals to the number of moles of PO_4^{3-} present in one mole of j^{th} species. Previous works accounted on the molar ratio of Ca:P and Mg:P during struvite precipitation Table 16

Table 16. Ion molar ratios in previous works in struvite precipitation

Factor	**Literature**			
	[61]	[23]	[49]	[45]
pH	9.5	10.89	8.5, 9.5	7-10
Mg:P	4	2.25	5	2.25
Ca:P	0.05*	-	1.95	1
NH_4^+:P	12*	-	5	3.1
P recovery	92.6%	84.7%	84%,	>90%

*Calculated from the composition of used raw material

Prior knowledge of mineral concentration of raw material is important to have an idea of precipitation kinetics. In this review, mineral aspects of wastewater, biosolids and ash were reviewed.

3 Struvite precipitation from wastes

The process of phosphorus recovery requires the consideration of the raw material, environmental concerns and recycling regulations. The waste water could contain no more than 2 mg P/kg(FAO recommendation is 0-2 mg P/kg) [13]. In reference to the P products presented in

Table 14, the precipitation of phosphorus as struvite from multicomponent solutions requires a study of optimization and stoichiometric iterative matrices with accountability of both kinetic and thermodynamic conditions [25,62]. The compounds such as calcium phosphate, hydroxyapatite, magnesium phosphate, nickel phosphate, copper phosphate, iron (III) phosphate, cadmium (II) phosphate, silver phosphate, aluminum phosphate, amorphous calcium phosphate, and di-calcium phosphate hydrate, have lower water solubility products (Ksp) than struvite. Therefore, their co-precipitation inhibits the struvite formation [57,58,60,63].

Table 17. Available researches for P recovery as struvite from wastes

Wastes	**Reactor**	**TotP/PO4**	**TN/NH4**	**Ca**	**Mg source**	**Add. Reag.**	**pH**	**pH adj**	**P rec**	**NH4 rec**	**Reference**
					Wastewater						
Leather tanning wastewater	Closed stirred batch reactor	NR/12.3	2405	370	MgCl2	Na2HPO4	9	NaOH	90	85	
	Closed stirred batch reactor	NR/2.5-8	NR/119-1076	178–245	MgCl2	Na2HPO4	9	NaOH	NR	<89	[64]
Cochineal insects processing wastewater (Carmine Dye industry)	Agitated batch reactor	NR/3490	NR/2320	42	MgO	Na_2HPO_4	8.5–9	MgO	100	89	[65]
AD effluent of molasses-based industrial wastewater	Stirred batch reactor	NR/24	NR/1400	21	$MgCl_2$		8–9	NaOH/HCl		78–95	
Semiconductor wastewater	Jar test with paddle	NR/286	NR/100	5–12	$MgCl_2$	-	9	NaOH	70	98	[66]
Anaerobic effluent from potato processing industries	Continuous aerated stirred reactor	NR/43–127	NR/208–426	36–65	$MgCl_2$	-	8.5–8.7	NaOH	19–89	NR	[67]
Rare-earth wastewater	Stirred jar apparatus	7.8/NR	NR/4535	0.7	Brucite/ H_3PO_4		8.5–9.5	NaOH	97	95	[68]
Fertilizer production waste water	Tube Mixed type continuous crystalliser	NR/4.45%	NR/0.440%	-	$MgCl_2$ NH_4Cl		9–11	NaOH	99.5	NR	[69]
Beverages industrial waste water	Agitated glass batch reactor	NR/415	NR/NR	NR	$MgCl_2$ NH_4Cl		9.5	NaOH	97	NR	[70]

Yeast and anaerobic digestion leachates	Stirred batch reactor	22/17.4	354/161	25.6	$MgCl_2$	Na_2HPO_4	9.5	NaOH	83	81	[71]
	Stirred batch reactor	NR/10.8	595/528	258	$MgSO_4$	H_3PO_4	9	-		87.55	[72]
Dairy wastewater (synthetic)	Batch reactors	NR/570	NR/756	200	MgO		9.5	NaOH/H2SO4	93.5		[61]
Ash											
Sewage sludge ash		6.2%	-	6%	$MgCl_2$& NH_4Cl	-	10	NaOH	97%		[73]
Biosolids											
Sludge AnD	Batch reactors	37	32.5	101			9.5	NaOH	94		[49]

The influence of pH, temperature, chemical compositions, reaction period and stirring have been studied previously to optimize struvite precipitation [62]. Nevertheless, there are still limited researches of struvite precipitation from DPW. The previous researches on P recovery as struvite and key process parameters are summarized in Table 17

The recovery of P in form of struvite from waste needs the P in reactive form thus requires mineralization of organic matter to release bound P. The precipitation from ash is done by P species extraction, metal adjustment by experimental design of reactive salts molar ratio or metal removal by ion exchange materials followed by struvite precipitation [73].

3.1 Phosphorus speciation.

In addition on factors influencing struvite precipitation, other factors include P species, organic matter, and operating conditions such as aeration, stirring and reaction time have significant effect in struvite crystallization [74]. Elemental species as referred by International Union of Pure and Applied Chemistry (IUPAC) is the elemental form defined as specific isotopic composition, oxidation state, molecular or/and complex structures; while speciation is distribution of element among its chemical species in the system and speciation analysis, the activity of identifying qualitatively or/and quantitatively the species of elements in the system [75]. The common method for P speciation analysis is the reaction of molybdenum with orthophosphate in presence of potassium antimony tartrate in acid condition (pH<2) to form antimony-phosphomolybdate complex which is reduced to phosphomolybdenum blue by ascorbic acid or stannous chloride [76]. This blue complex favors spectrophotometric determination of phosphorus specifically reactive dissolved phosphorus (RDP) also called soluble reactive phosphorus (SRP). This method is criticized for overestimation of phosphorus. However it has been widely used in P speciation in different matrices including wastewater to find total reactive phosphorus, acid hydrolysable phosphorus, organic phosphorus and their soluble forms [77]. Sludge and biosolid phosphorus species are determined as fractions of sequential extractions with water, sodium bicarbonate, sodium hydroxide, hydrochloric acid that extract up to 88% of total phosphorus, the residual P being nearly 12% [78]. The P speciation[3] flow-chart is summarized on Figure 35.

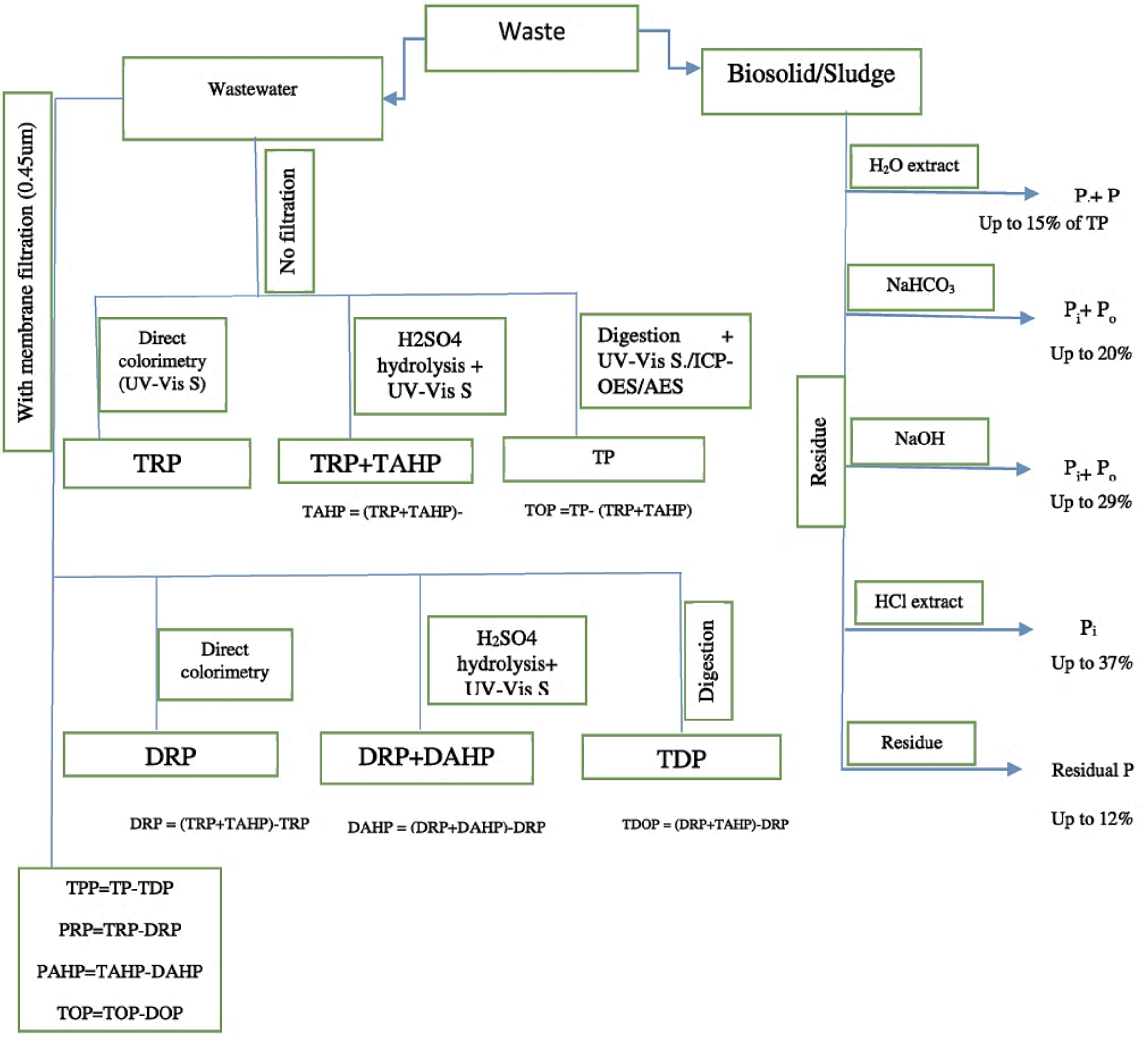

Figure 35. *Combined procedures for P speciation from wastes* [77,78]

Most of the P in dairy is found in the $NaHCO_3$ extract (35%). The rest consists H_2O (18%), NaOH (10%), HCl (8%) fractions, with the residual P up to 29% [78]. The inorganic species is mainly orthophosphate. More detailed species of organic phosphorus can be analysed using mass spectrometry hyphenated to chromatography to determine polyphosphate following suitable extraction [79].

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[3] TP: Total P; TRP: Total reactive P, TAHP: Total acid hydrolysable P, DRP: Dissolved reactive P; DAHP: Dissolved acidic hydrolysable P, DOP: Dissolved organic P, TDP: Total dissolved P; TPP: Total particulate P, PRP: Particulate reactive P; PAHP: Particulate acid hydrolysable P; TOP: Total organic P; TPOP: Total particulate organic P, Po: Organic P, Pi: Inorganic P.

3.2 Wastes treatment and mineral aspect

Different treatment technologies are used to reduce the volume and the mass of wastes including incineration and use of waste in material and energy recovery [80]. The latter is recommended to ensure the use of wastes as renewable resources to produce energy fuel including biogas, lipids, fertilizers, bioactive substances including enzymes, phytochemicals, nutraceuticals and other more added value products [3]. The used technologies include anaerobic digestion and thermochemical treatment.

3.2.1 Anaerobic digestion (AD)

This is a natural biological process that runs without oxygen in built systems referred to as anaerobic digesters. AD systems can minimize odors and vector attraction, reduce pathogens and waste volume, and produces gas, liquid, solid digestate [81,82]. Mineralization pathway derives from decomposition of organic matter. It transforms complex organic matter into small molecule stepwise to acetic acid and hydrogen also transformed into biogas. This involves major steps of hydrolysis of complex organic matter into high carbon organic matter. The latter are fermented to acetic acid and hydrogen, and finally biogas production [83]. The steps of hydrolysis, fermentation and methanogenesis are described in Figure 36.

Fatty acid and carbohydrates are degraded to acetic acid by acetobacteria and form biogas by methanogen activity. Inorganic species are dissolved and participate in chemical reactions involving precipitation and volatilization. Precipitation is enhanced by ferric or ferrous salts of chloride or sulfate, aluminum sulfate and calcium hydroxide added in feed of sludge to increase coagulation and chemical precipitation during wastewater treatment [84–87]**.** Protein are degraded by proteolytic microorganisms including yeasts [88] that decompose proteins into small molecules mainly ammonium which undergoes further mineralization steps to nitrates and nitrites by nitrobacteria [89]. The research indicates that soluble phosphorus increased from 41.6 mg/kg to 212 mg/kg during anaerobic digestion of cattle manure [90]. The ammonium (NH_4^+) and phosphorus ($PO_4^{3-)}$ produced by microbial activity can be trapped in the presence of magnesium to precipitate struvite under optimum conditions. The forward pathway reactions involve precipitation and possible electrochemical reactions described elsewhere [84].

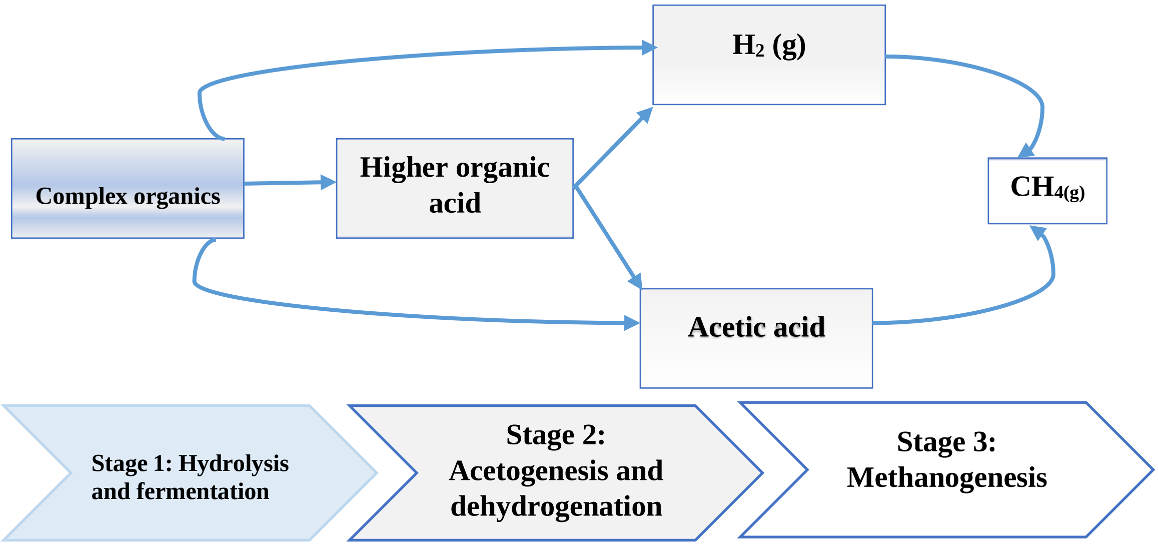

Figure 36 Organic matter decomposition in anaerobic digestion ([83]*)*

Nevertheless, other mineral phosphate can precipitate as iron phosphate following their addition as micronutrient to increase microbial growth [84]. In wastewater treatment, the inlet wastewater is treated through aerobic and anaerobic digestion resulting to wet sludge with lower percentage of dry matter. Dewatering process produce biosolids and sludge with 25-45% of dry matter. Further drying increases the dry matter content up to 90% in produced biosolids [91]. Mineral composition of biosolid depend on previous process. The biological process involving polyphosphate accumulating microorganisms produces biomass with high phosphorus concentration [92].

3.2.2 Thermochemical treatment.

A forecast of global municipal solid wastes (MSW) generation expects their increase to approximately 2.2 billion tons/year by 2025 [93]. The enhanced landfill waste management (ELWM) is disregarded as solution of MSW management. The enhanced waste management strategies support the reduction of waste volume thus landfill may be used as temporary waste management for further steps of use or waste treatment process [94]. Carlos Escobar Palacio J et al, (2019) has divided thermochemical process of municipal solid wastes into (i) incineration, (ii) gasification, and (iii) pyrolysis [93]. **Incineration** is a specific treatment that reduces the volume of waste and its level of dangerousness. It concentrates minerals and destroys the potentially harmful organic substances. Incineration processes can also offer the possibility of recovering the heat energy and minerals of waste by accumulation in ash [93,95]. From the mineralization point, incineration is considered as the effective way to reduce volume, mass and up to 0 organic matter, and then concentrate mineral phosphorus and microelements in the ash [31]. Nevertheless, European Environmental Agency has reported air pollution associated with incineration of industrial waste and sewage sludge. Greenhouse gases (NOx, and CO_2) are emitted, together with volatile toxic heavy metals including mercury (Hg), lead (Pb) [96]. Moreover, incineration process was discussed to use either of two processes: grate combustion can handle larger particle wastes while fluidized bed is a burning process that needs smaller particle [93,95,97]. **Gasification** is used to convert solid materials such as coal, coke, biomass and solid waste into a gas, mainly CO, Hydrogen, and CH_4. **Pyrolysis** is thermal treatment done in the absence of oxygen in closed system and produces oil, gas and char [98]. The char was defined as a product of decomposition of organic natural or synthetic material by dry or wet pyrolysis [99]. The benefits of pyrolysis is its environmental friendliness [98]. While charcoal is produced from wood as a dry pyrolysis, wet process is being used as state-of-the-art treatment technology to transform wet biomass into a high carbon biosolid (biochar) with multiple use in life sciences [42].

Hydrothermal carbonization (HTC). This is a wet pyrolysis, typical process of heating biomass together with water at a temperature between 180 °C and 250 °C in a pressure vessel for several hours [42]. The product is hydrochar composed by a high fraction of aliphatic organic compounds and makes it different from pyrolysis product (pyrochar) due to its high aromaticity [100]. The investigation of HTC process conditions extended to temperature higher than 250 ^{o}C suggested the decrease of organic carbon in aqueous phase thus can be a tool of mineralization of organic wastes [101]. However, the partioning of P in HTC products depend on presence of multivalent metals such as calcium, iron, and aluminium that precipitate mineralized P in hydrochar. Otherwise, high fraction of P can be found in liquor [102]. The mineralization of P from organic waste through HTC with temperature range 160-315 ^{o}C is interesting research for P recovery from HTC products through struvite precipitation.
Taking into account mineral aspect, municipal and industrial wastewater is a crude matrix with suspended and dissolved matter as well as emulsions [103]. Mineral elements are either dissolved, bound or present in the form of particulate matter in the effluent [104]. The concentration of total and dissolved species is dependent on the volume of the career system. Treatment technologies aim purification that involves process enhancing the dissolution and recovery of minerals [105]. Anaerobic and aerobic digestion degrade complex organic matter into organic biomass with smaller volume with increase of mineral concentration in liquid fraction and dry solid sludge [106]. Further steps of thermochemical process concentrate phosphorus and other minerals in ash thus can serve as raw material in P fertilizer production [4].

3.3 Mineral aspect of raw wastes

The mineral characteristics of bulk biosolids, ash and wastewater make important information on raw material for struvite precipitation and fertilizer formulation. The reviewed content in mineral parameters of interest were total phosphorus (TP), total potassium (TK), calcium (Ca), magnesium (Mg), zinc (Zn), copper (Cu), manganese (Mn) and iron (Fe). The bulk biosolid samples are considered as a group of organic wastes comprising farm yard manure (FYM), cow manure, vermicompost, biochar, digestate organic residues [107–120]. **Liquid wastes** include industrial effluents, anaerobic digestion leachates, hydrothermal carbonization liquor [90,121–124]. The ash includes sludge ashes, dairy wastes and wood ash [111,112,125–128].

General variability of mineral concentration in their waste categories including liquid, ash and biosolids make visible classes based on mineral content. The latter can be classification variables to demonstrate mineralization and concentration variability in waste at any stage of its resource management. Based on TP, TK, Mg, Ca, Zn, Cu, Mn, and Fe, the variability is explained up to 87% of variance with three principal components among liquid, ash and biosolids mineral content (Figure 37a). Furthermore, linear discrimination plot visualizes three segregated classes of waste matrices based on mineral aspect (Figure 37b) with up to 93% classification rate.

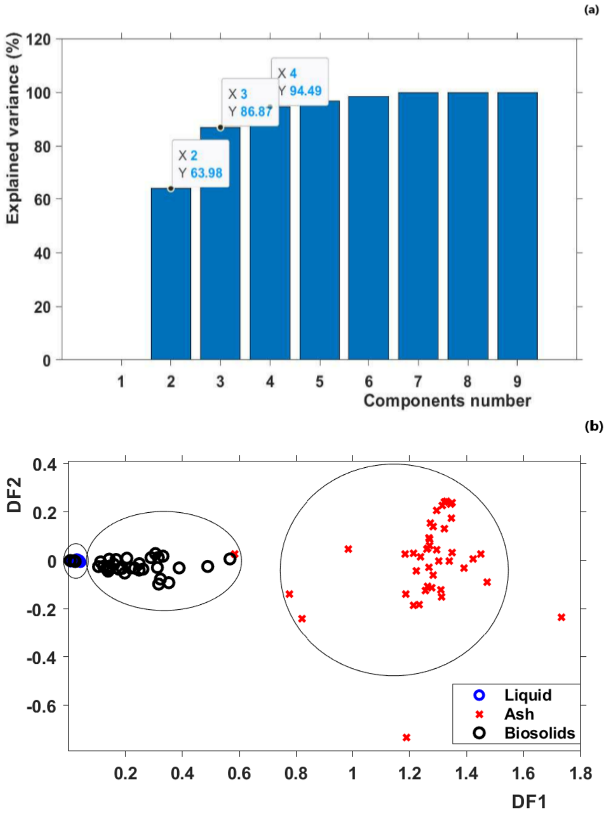

Figure 37: Mineral variance explanation by (a) PCA and (b) LDA classification

The high value of explained variance suggests the difference in mineral concentration of wastewater, bulky biosolids and ash. The mineral content in waste indicates high calcium concentration in wastewater, sludge and ash. And all studied minerals are more concentrated in ash *Figure 38*(a). The Figure 38 represent Z values for each found data in matrix in terms of reviewed mineral content.

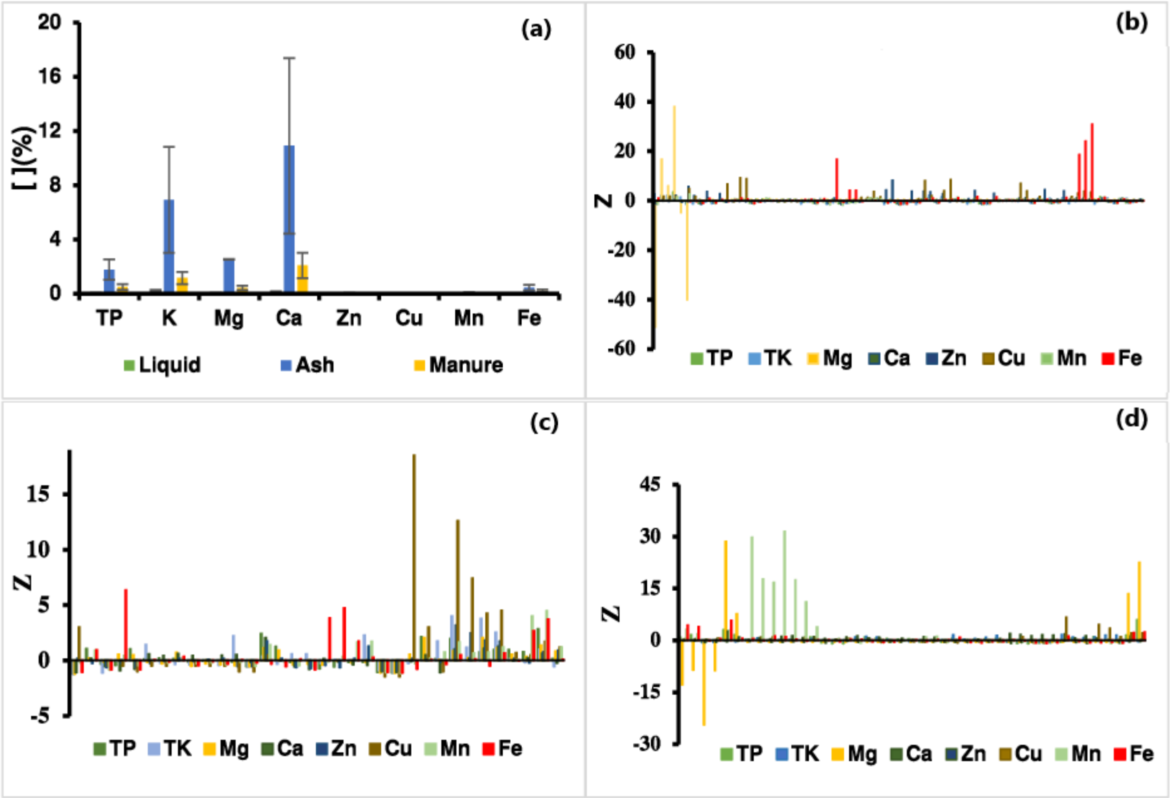

Figure 38.Distribution Z-values of concertation of mineral in different waste matrices

The mineral concentration is higher in ash than in wastewater and biosolids (Figure 38a) There is a pattern similarity of typical mineral distribution in the same class of wastes which can facilitate in robust method development for nutrients recovery. At 99.7 % confidence interval, the distribution of P is 100% similar in liquid waste, biosolids and ash. The similarity of other minerals is higher than 80% (Figure 38b-d). This can facilitate in robust method development for struvite production applicable to different wastes. The matrix influences the concentration due to its volume. The increase of phosphorus mean concentration is from 0.035, 0.5 to 1.76% in wastewater, biosolids and ash, respectively.

3.4 Mineral pre-adjustment for struvite precipitation

Different techniques have been used to overcome the effect of foreign ions. Phosphate counterions including calcium and other microelements as described in

Table 14 and Figure 34 are the main inhibitors of struvite precipitation.

3.4.1 Calcium removal

In previous works, [62] used chemical precipitation of calcium by oxalic acid and ammonium oxalate prior to struvite precipitation. On the other hand, Ethylene diamine tetra-acetic acid (EDTA) was used to chelate calcium and release phosphate from calcium phosphate salts [129]. The removal using EDTA may also decrease the activity of magnesium in the solution due to complexation. However the $MgEDTA^{2-}$ complex is less stable than $CaEDTA^{2-}$ by 2 orders of magnitude ($logK_{25^oC}^{Mg^{2+}} = 8.92\ and\ logK_{25^oC}^{Ca^{2+}} = 10.77$) [130]. Thus there is negligible effect of EDTA in Mg complexation for struvite enhancement.

3.4.2 Adjustment through ion exchange

The selective ion exchange materials were reported as effective in mineral adjustment applicable for either anion and cation removal in prior of precipitation [131]. Natural zeolite was reported to be a material with appropriate selectivity to remove cations including heavy metals and anions thus can be applied in mineral adjustment followed by struvite precipitation [132]. Clinoptilolite, phillipsite and chabazite can be used in ion exchange as well as strong acidic resin [73,133] The ion equilibrium reached with lower foreign ion molar ratio to P favors struvite crystallization.

3.4.3 Adjustment through additional P and Mg salts

The alternative way of overcoming foreign phosphate counterions is to add additional amount of P, magnesium and ammonium salts to increase struvite supersaturation and precipitation potential [21,62]. Calcium concentration higher than Ca : P > 0.5 molar ratio to P exhibits the progressive inhibition on struvite precipitation due to kinetic properties of calcium phosphate salts mainly hydroxyapatite [23]. Thus mineral adjustment is achieved using additional struvite precursor salts through design of experiments.

In general, phosphorus recovery from dairy organic and effluent wastes by struvite precipitation can be achieved after adequate mineralization, and concentration in aqueous solution. Foreign ions effect can be adjusted chemically by complexation with EDTA particularly calcium which can also be precipitated using oxalate solution. Other foreign phosphate counter ions are adjusted by ion exchange material such as clinoptilolite. Thermal technologies of combustion concentrate minerals in ash which can be used as raw material in P recovery as struvite. However, ash production is accompanied with emission of micropollutants such as volatile heavy metals as well as organic micropollutants. Thus wet pyrolysis technologies especially HTC at high temperature (>250 °C) decreases organic matter. Thus HTC can be studied for P mineralization from bulky matrix for further use in P recovery as struvite. Previously, no researches that were conducted on struvite precipitation from DPW sludge ash, nor HTC hydrochar or liquor. Besides that, research works on chemical characteristics of DPW based on mineral aspect are still limited.

Production of high purity Phosphoric acid from ash (ESR6)

Phosphorus is one of the critical elements in Europe. Currently, EU is focusing on recovering and recycling phosphorus from municipal wastewater, industries, agriculture and animal livestock. Several technologies have been developed which are on the cusp of becoming economically competitive. One of the routes to mitigate P losses that has not been thoroughly investigated is using dairy waste such as ash as a secondary raw material along with a low-grade phosphate rock to produce phosphoric acid. Mono-incinerated ash obtained via fluidized bed combustion retains most of the P and heavy metals. In this review, the different types of wastes, their processing and recent advances in processing of dairy wastes have been discussed. It also sheds light on the methodology adopted to recover phosphorus. Technologies based on P-rich ash are found to be promising in terms of recycling efficiency, further encouraging industries to find innovative waste management solutions to recover and recycle P, thereby decreasing their negative impact on the environment and contributing to circular economy.

1 Introduction

Phosphorous (P) was discovered by accident by alchemist Hennig Brandt by evaporating urine in 1669. It is a non-metal and originally means “Light-bringer” because in ancient Greek language, the planet Venus is called Phosphorous, hence the meaning. Due to its high reactivity, P does not occur freely in nature but is distributed in many minerals. It is also found in animals and plants [1]. Phosphorous has been extensively used in the production of chemical fertilizers for plant growth, in the metallurgical industry for surface treatments, in the food industry as an additive [2].

The driving force for sales of P, its compounds and the factor triggering the expansion of the phosphate rock (PR) market is the increasing demand of food, fertilizers, animal feed and metallurgical industries [3]. The global phosphate rock extraction for producing food is approximately 90% and the remaining portion is used for industrial applications such as for water treatment, pesticides production, metal finishing, etc., [4]. In 2018, China, which is the largest phosphate rock producer, produced almost 50% of the world production [5]. Forty-four and half million tonnes of phosphate rock were the world consumption in 2016 and by 2020, it is predicted to increase to 48.9 million tonnes. Phosphate rock reserves are estimated to be approximately 68 billion tonnes, which shows that the rock is still physically available in large quantities at least for a century and probably it will last for millennium. But for future generations to access these high-grade deposits and to reduce their costs, it is important to close the loop of the broken phosphorous cycle. Another reason to close the P-cycle is to increase the supply security via recycling [6].

For recovery of P from P-rich wastes such as ashes from animal meat, biowastes, manure and sewage sludges, there are methods, some of which are advanced with substantial state-of-the-art while others must be optimized in terms of technology and economy. The most important challenge is to close the gap between recovery and actual recycling to work with value chains because both recovery and recycling will have a major impact on improving resource efficiency and sustainable nutrient management [6].

One such P recovery routes currently being investigated is from dairy processing waste (DPW). The dairy industry has grown immensely over the years due to demand and production of milk and its products; for example, cheese, yogurt, ice cream and whey powders. Due to this rise in milk production rate in Europe, the dairy industry is perceived to generate huge amounts of wastewater, toxic gases and sludges containing both organic and inorganic pollutants which can cause severe damage to the environment if not treated carefully [7] . Since these effluents contain inorganic components like P and N, they can cause water bodies eutrophication. Similarly, emission of greenhouse gases like N_2O and CH_4 which are air pollutants and can affect climate change, also emerge from dairy wastes [8]. Several advanced technologies have been developed to mitigate the negative effects of these wastes. Better efficiency is achieved by physico-chemical treatment followed by biotechnological methods and the resulting products include biofuels, bioenergy, organic acids, whey-derived products; important for industries [9].

Europe imports about 92% of mineral P inputs such as phosphate rock, phosphoric acid (PA) and fertilizers while white phosphorous is 100% imported. Therefore, due to the rapidly changing political scenarios and lack of phosphate mines, the European Union, in 2014, included phosphorus in the list of EU critical raw materials. European waste streams such as sewage sludge, meat and bone meal, manure together incorporate over 500 kt P/a and this presents a great potential for recycling of P. Limited technological advancements have been a roadblock in finding a solution to recover and recycle P from DPW. NuReSys has developed a phosphate-recovery-system at Humana Milchunion, a subsidiary of Humana's corporate group in Germany, known for dairy products and baby food. It produces 600kg struvite per day [10]. However, as P is now considered to be a critical raw material, many industries and organizations have come forward to tackle this problem of processing P from DPW to ensure long-term environmental and economic sustainability [6].

To produce high purity H_3PO_4 from ash in this research, the following steps will be taken on laboratory scale and pilot scale:

Study properties of ash:

Ashes from mono-incineration have higher P-content than co-incinerated ashes as P content in co-incinerated ashes is highly diluted. The physical properties and the composition of ash will be analysed with different characterization techniques. Based on this, impurities present in the ash and their sources will be identified.

Processing of ash and purification:

The optimal conditions for processing a low-grade P-rock together with DPW ash in a hemihydrate-dihydrate process are found by analysing the effects of different temperatures and residence times. Several tests will be conducted for this and CHALMERS will provide support in selecting the best conditions for processing based on the most suitable environmentally sustainable option. Trials will also be conducted to check whether a continuous or batch process is better. As there will be some unreacted and co-crystallised P_2O_5 in the gypsum by-product due to variations within the feed ratio which can produce different filterable characteristics of gypsum cake, the operating conditions such as temperature, % P_2O_5, %SO_3 are varied to convert α-hemihydrate to dihydrate for further purification and to reduce the P_2O_5 losses. Based on the data obtained, heat and mass balance sheets will be prepared which are important for scaling up the process. The resulting H_3PO_4 obtained after processing will be tested for its purity and further purification may be achieved by use of ion-exchange materials.

Scaling up the process and preparing a business case:

The desirable parameters for DPW ash dissolution are selected based on the laboratory scale trials results and after achieving the required P_2O_5 content of 60% in the product acid, pilot scale tests are carried out. A study will also be carried out to estimate the availability of DPW ash in the future. Finally, a business case for potential commercialisation of produced H_3PO_4 from ash will be developed by using a techno-economic market dynamic model.

2 Phosphorus occurrence, deposits, reserves and applications

Phosphorus occurs in nature mainly in the oxidized state in the form of organic and inorganic phosphates (PO_4^{3-}) [1]. These phosphates amount to 0.10% of the earth's total surface and are found distributed in soil, oceans, rocks, living cells and in many foods. In mineral soil, the total average P concentration is 800 mg/kg, in sea water it is 0.09 mg/L and lake water 0.02 mg/kg respectively [10]. P is typically present in 3 types of rocks based on their chemical compositions viz., sedimentary, igneous, metamorphic rocks and apatite group minerals are commonly found in them. Apatite, $Ca_5(PO_4, CO_3)_3$ (Cl, F, OH), is composed of calcium phosphate together with either chloride, fluoride and hydroxide ion. It has low solubility in water, but higher solubility of apatite can be achieved by incorporating rather hydroxide than fluoride, chloride and halides in general. [6]. The composition of phosphate rock is shown in Table 18.

Table 18: Phosphate rock composition (after beneficiation) based on dry material in wt % [12]

Phosphate rock	**P_2O_5**	**CaO**	**F**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CO_2**	**SO_3**
Kola (Russiaa)	39.1	51.5	3.4	2.0	1.2	0.7	0.0	0.0
Phalaborwa (South Africa)	38.4	52.5	2.3	1.9	0.2	0.4	1.3	0.1
Florida (USA)	31.6	47.7	3.9	9.0	1.0	1.6	3.7	1.4
Khouribga (Morocco)	34.8	52.5	4.2	0.9	0.5	0.1	4.1	1.5
Togo (Togo)	29.7	40.3	3.9	10.2	4.4	5.3	1.6	0.1

More than 80% of the phosphate rock production is from sedimentary deposits. This type of rock normally contains more than 7.8% P_2O_5, if it contains phosphate in the range of 7.8-19.5%, it is called phosphatic sedimentary rock and for concentrations above 19.5% phosphate, it is called phosphorite. China, USA and Northern Africa have the largest sedimentary deposits in the world. The typical P concentrations in igneous rock vary from 0.05-0.4%. However, igneous rocks which consist of low silica contents and show strong alkalinity have 1.5-2.0% P_2O_5. Beneficiation of igneous deposits can lead to rocks with 35-40% P_2O_5. Some of the igneous deposit regions are Brazil, Finland, Canada and Russia. Both sedimentary and igneous deposits can be found in metamorphic rock deposits and this type of rock has P contents ranging from 0.01-1.3%. They are found in India and China. These deposits when compared to sedimentary and igneous deposits, are formed due to high temperatures and pressures and hence have their crystals tightly packed with little porous texture in the rock. Therefore, it is currently not economically feasible to exploit metamorphic deposits [12]. Many phosphate deposits comprise of silica (quartz), calcite, dolomite, iron oxides and clay minerals. Zeolite may also be found in some deposits [6].

Figure 39: Phosphate deposits in the world **[**13**]**

The total global phosphate rock (PR) reserves were approximately 68 billion tonnes and the global production of PR from mines was approximately 176 million tonnes in 2010 (Figure 40) [6, 14]. Out of the 33 countries producing PR, only 16 countries are major PR producers; some of which are Morocco, China, USA, South Africa, Jordan, Syria and Algeria. These countries contribute to about 95% of the total world PR [15].

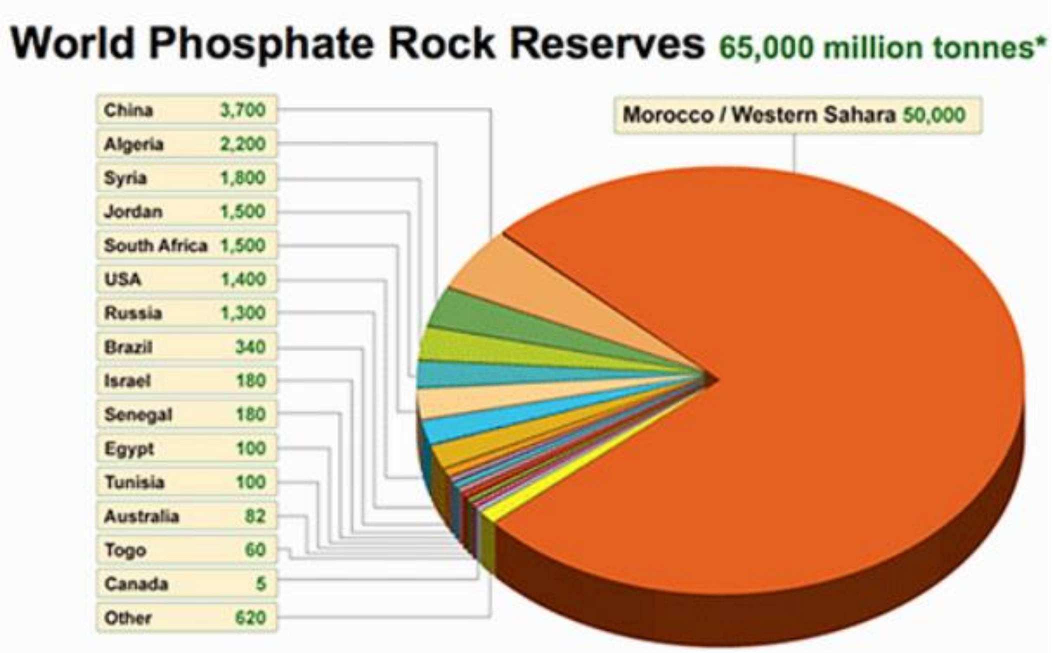

Figure 40: World PR reserves in 2010 [4]

The leading global consumers of PR are China, Morocco, USA, India and Russia [15].

Phosphorus containing derivates are largely used in fertilizers. Phosphoric acid is used in industries ranging from metallurgy to the food industry. It is primarily used for the removal of rust and as an additive in the food industry to acidify foods and beverages. In dentistry, it is used as a temporary cement powder (by mixing it with zinc powder to form zinc phosphate), as an etching solution and in many teeth whitening solutions. It is also used in the cosmetics as a pH adjuster, as an electrolyte in phosphoric acid fuel cells and copper electro-polishing [16].

3 Why phosphorus recycling

Phosphorus is a non-renewable, finite raw material and is an important element for food production, in industries, in agriculture, etc. The supply of phosphorus in the coming decades is considered to be at risk for regional and national economies. The ever-increasing population has resulted in PR mining and conversion into soluble P compounds for use in industries which has hampered the natural P cycle [17]. The P losses in the supply chain take place during the P mining, beneficiation and processing stages, crop harvesting and majorly due to humans. Because of the excessive availability of highly reactive P in the environment, unwanted problems which damage the quality of soil, aquatic and human life occur [18]. This happens mainly due to the inefficiency to control P (mined P dissipates into low grade PRs, manures, by-products and residues which are not re-used). The production of P from PR also results in pollution as the PR is contaminated with toxic heavy metals and radioactive elements. In order to use P efficiently and sustainably, proper P management strategies must be developed in the future to help protect future security of food, water and energy [17].

Emerging countries like India and China have their own P story. While India is heavily dependent on imports (85%), China has its own P reserves and mainly exports P to other countries. But again, to satisfy their growing population, there is a possibility that China might not be able to export P in the future which poses a critical problem for all of Asia. By year 2050, it is estimated that the virtual phosphorus demand required in India in terms of amount of food would be twice that of China while in comparison to India, it is predicated that China would triple their per capita consumption. Therefore, countries relying on other countries for P should promote recovery and recycling by analyzing the bottlenecks involved in P production. The major problem for these countries, however, is having improper environmental regulations and underdeveloped infrastructure which are required for collection and treatment of wastes rich in P. Therefore, for sustainable P management, technology transfer related to P recovery and recycling is needed [6].

The only PR mine located in Europe is in Finland. EU included P in the list of its critical raw materials due to its heavy import dependency (> 90%) [19]. Although the supply of PR in the present time is not scarce, the European Union has taken the steps to mitigate the economic and supply risk of P including :

- Due to the increase in P fertilizer prices during 2007/2008 and also due to presence of PR reserves in geopolitical regions, the EU has referred to recycling of P as a future potential solution.

- At the 1992 United Nations Rio Convention, the EU concurred with the principle of intergenerational justice to provide future generations, access to high grade P deposits and to reduce the opportunity costs.
- For competitive economic development, it is important to follow the ideas of circular economy [6].

In general, the important factors for P recovery and reuse are the increasing costs of P, its scarcity and overabundance. Many types of wastes have been identified as P recovery sources (Figure 41). These sources arise from agriculture, animals, municipal and other industries and are discussed in following section**Error! Reference source not found.**. Before P recycling was considered an option, these wastes were disposed by either landscaping, incineration or landfilling [20].

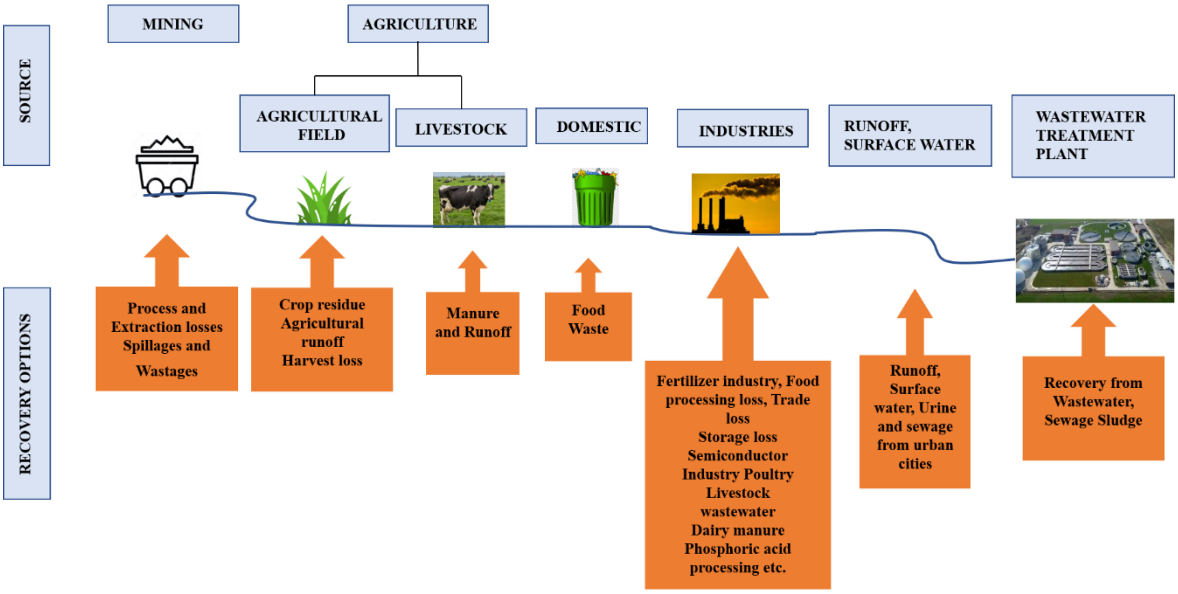

Figure 41: Alternatives for P recovery [20]

As most of the P recycling technologies in use are currently in their infancy stage, in order to close the P loop and to achieve long term objectives of P recycling, it is necessary to pressurize authorities to find integrated and viable innovative, economic, societal, environmental and legal solutions in nutrient management, water processing and recycling and waste disposal. In comparison to conventional recycling of sludge, recycled phosphorus reduces risks caused by impurities and can be easily transported to long distances, thus reducing the costs considerably [20].

4 Wastes for phosphorus recovery

P is widely dispersed in the Technosphere and the large variabilities of P flows across sectors suggests that some of the P is lost. These secondary materials originate from agricultural wastes, animal wastes, municipal water, biosolids, industrial wastes [17] and consist of a range of accessible resources from which P can be recovered for re-use, thereby avoiding depletion of natural phosphate deposits. DPW comes under agricultural wastes but it will be separately discussed. Table 3: Potential quantities of wastes produced in selected countries is shown in **Table 25** [21].

4.1 Dairy Processing Waste

Amongst the food industries in the world, dairy industry is one of the largest water consumer and wastewater producer. A dairy plant consumes 2-5 liters of water per liter of milk processed, in cleaning and washing operations (Table 19). They incorporate different systems, technologies, operational methods and final products; hence the flow and characteristics of wastewater vary with different plants [22]. According to Indiana Department of Environment Management, "*dairy wastes include milk, milk products and all dairy processing wastes that do not meet applicable standards, have become contaminated, or otherwise have become unusable for human consumption, animal feed, or any other beneficial use*." [23] Dairy wastewaters contain high concentrations of organic materials (proteins, lipids, etc.), suspended solids, high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand), nutrients such as phosphorus and nitrogen, oil and grease [24]. In the Food Harvest 2020 highlights in Ireland, it was found that untreated milk wastes have BOD of ~2700 mg/L, poultry processing wastes have BOD of 1306 mg/L and meat packing waste has BOD of 1433 mg/L. These high BOD values indicate the pollution risks associated with dairy products. [25]. Due to the complexity of these effluents, they cannot be used for irrigation purposes or be discharged in public sewers. Therefore, regulatory agencies in many countries have placed restrictions to nutrient discharge through effluents. In order to reduce severe biological and chemical contaminations factors, dairy industries are developing efficient and economic waste management systems. Characterization of wastewater, planning of appropriate units, treatments and processes are necessary in order to have a properly functioning effluent treatment plant [22].

Table 19: Sources from which wastewaters arise in dairy industries [26]

Losses	Reason
Spillage	Leaks, overflow, boiling over, freezing-on, careless handling
Processing	Sludge discharge from settling tank, discharges from bottles and washers, splashing and container breakage in automatic packaging equipment
Washing and cleaning	Wastewater/product remaining in tanks, truck, cans, piping and other equipment
Other	Detergents and other compounds used in washing and sanitizing solution discharged as wastes

Cleaning waters in dairy industries can alter the pH of wastewaters significantly depending on the cleaning strategy used because they may contain various sterilizing agents, acids and alkaline detergents [7, 27]

Depending on the quantity of milk produced and type of product manufactured, dairy wastewaters have characteristics that contain BOD, COD, pH, dissolved solids, suspended solids, color, temperature, chlorides, sulfates, oil and grease [28]. Characteristics of dairy industry wastewaters are shown in [28].

Table 20: Characteristics of dairy industry wastewater as reported by several authors [28]

(In Table below, TSS – Total Sediment Solids; TS – Total Solids)

Waste type	**COD (mg/L)**	**BOD (mg/L)**	**pH**	**TSS (mg/L)**	**TS (mg/L)**
Milk and dairy products factory	10251.2	4840.6	8.34	5802.6	-
Dairy effluent	1900-2700	1200-1800	7.2-8.8	500-740	900-1350
Dairy wastewater	2500-3000	1300-1600	7.2-7.5	72,000-80,000	8000-10,000
Cheese whey pressed	80,000-90,000	120,000-135,000	6	8000-11,000	1

Total sediment solids (TSS) can build up sludge deposits in surface waters and contribute to benthic enrichment (by depriving oxygen to macroinvertebrates and fish eggs), toxicity and sediment oxygen demand. Highly turbid water can harm aquatic plants by blocking sunlight, thereby decreasing their ability to increase dissolved oxygen in the water column [29].

The quantity of oxygen consumed by microorganisms in decomposing the organics from wastewater at a temperature of 20°C is referred to as oxygen demand [30]. Biological Oxygen Demand (BOD) measures the content of biodegradable substances in wastewater. Microorganisms break down these substances by consuming oxygen and consequently create anoxic conditions harmful to aquatic life. Taste and odor of drinking water can change due to oxygen-reducing conditions [29].

The quantity of pollutants in wastewater which can be oxidized by a chemical oxidant such as a strongly acidic solution (potassium permanganate/ potassium dichromate) at high temperature is indicated by the Chemical Oxygen Demand (COD). The oxidant is converted to corresponding amount of oxygen and through oxidant consumption, the content of organic substance is measured [30].

The wastewaters biodegradability is indicated by the COD/BOD ratio. Relatively easily degradable substances are indicated by values of less than 2, while high values indicate the contrary [30].

Excessive nitrogen and phosphorus can lead to eutrophication and reduce dissolved oxygen in surface waters. Nitrogen excess also causes blood disorder in infants and pregnancy problems in women [29]. Dissolved inorganics like boron, chlorides, sulfates, sodium and other solutes limit the reuse options (ex: irrigation) of treated wastewater. Soil structure can be harmed by the presence of excessive sodium and to a lesser extent potassium [29].

Table 21 shows emission levels of dairy processing wastewaters to water bodies achievable with the application of BAT (Best Available Technique) in Ireland [31]

Table 21: Emission levels of dairy processing wastewaters to water bodies in Ireland

Parameter	Emission Level
pH	6 - 9
BOD_5	20 - 40 mg/L (or > 90% reduction of influent load)
COD	125 – 250 mg/L (or > 75% reduction of influent load)
TSS	50 mg/L
Total Ammonia	10 mg/L
Total Phosphorus	2 – 5 mg/L (or 80% reduction of influent load)
Total Nitrogen	5 – 25 mg/L (or 80% reduction of influent load)

Pollutants in dairy effluents can be reduced by some of the following mentioned steps:

- Avoiding solid materials to enter the effluent system by fitting drains with traps/screens
- Avoiding spillage from vessels and tanks by using level controls and automatic shut-off systems
- Spilled solid materials such as cheese curd and powders can be collected for reprocessing or use as stock feed
- Prior to the internal cleaning of tanks, the product can be recovered from the pipes by using starch plugs or pigs
- Using dry cleaning techniques wherever possible
- Both product and water losses can be minimized by installing in-line optical sensors and diverters that distinguish between them. [32]

Dairy industries should be checked for their environmental impact as many of the pollutants arising originate from organics. Several good, economic and cost-effective effluent management systems have been developed to reduce pollutants. Depending on the area, environmental regulations have been placed in order to determine the level of treatment. As dairy industries use and generate high volumes of water, the wastewater can be treated and reused [33].

Treatments for processing dairy wastes can be divided into 3 categories:

1. Primary treatment to get rid off debris by screening/sedimentation, to achieve steady flow and concentration in wastewater, for pH control and to remove oil, grease and fat by dissolved air flotation.
2. Secondary treatment mainly involves biological methods to remove organic components, suspended solids and partial removal of organic phosphorus and nitrogen. Aerobic (uses dissolved oxygen), anaerobic (without oxygen) and anoxic (uses biological reduction of oxygen donors) treatments are the 3 options in secondary treatment that can be used by themselves or in combination with other processes.
3. Chemicals (Ferric sulphate/ Aluminium chloride) are used in tertiary treatment for removal of phosphorus before the treated wastewater is released into municipal wastewater treatment plants or lakes, rivers, etc. [25]

4.2 Agricultural Wastes

Farming activities produce many unwanted wastes in the form of unused or excess fertilizers, pesticides, manure, etc. Application of pesticides and herbicides continuously ends up accumulating in the soil and damages the pollinators and beneficial microbes. Effluents used in agriculture also pose various risks such as heavy metal pollution, surplus nutrients concentration causing problems with water quality, pharmaceutical disruptors, pathogens from human and animals causing water contamination. The major source of farming wastes are fertilizers which contain N, P, K and are important for plant growth. When they are released in the environment, for example, when it rains, the rainwater takes these nutrient rich fertilizers along with it into rivers and lakes, they lead to aquatic eutrophication. Eutrophication can be recognized by the turbid and greenish color of water bodies as shown in Figure **42** [34]. The global agricultural wastes generated yearly are estimated to be 998 Mt [35].

Figure 42: Water body before and after eutrophication [34]

4.3 Animal Wastes

Such wastes include manure, organic materials from slaughterhouses and rendering plants, wastewaters arising from bathing animals, washing cages and slaughterhouses, animal urine, pungent odors and air pollutants (CH_4, H_2S). These pollutants, if left untreated, can generate greenhouse gases, cause water pollution and are harmful for soil fertility. The volume of water generated from livestock wastes is approximately 75-95% of the total volume. Organic, inorganic materials and several species of microorganisms comprise the rest of the volume [35]. Massive quantities of manure are generated annually by the world's livestock population (65 billion). These huge amounts contain P which equals 10 times the global agricultural demand of P. In India, about 346kt, 274kt and 62kt of P are supplied by 173Mt cattle manure, 10Mt poultry manure and 12Mt of sheep manure produced. The chemical composition of manures can vary and depends on animal species, types of feed, bedding materials and housing, quantity of water used by animals, climatic conditions and waste management systems. It is necessary to process the animal manure at the origin because unprocessed manure contains high levels of Cd, Pb, Escherichia coli above allowable limits. Farmers are tempted to dispose these wastes to nearby fields due to higher transportation costs involved in transporting bulk manure. This leads to increase in P-carrying capacity which in turn leads to transport of nutrients, finally causing eutrophication of water bodies [21].

4.4 Municipal and Industrial Wastes

Municipal waste waters (return liquor) produced by anaerobic digestion of activated sludge in the dewatering stage are characterized by high concentration of nutrients and organics. Singapore with a population of 4 million, yearly supplies 13300 tons of nitrogen and 5700 tons of phosphorus [36]. Almost 3 Mt of P in wastes were released by the world population in year 2000 [37]. In one of the studies, the chemical composition of municipal wastewater contained 31.8-202.4 mg/L N, 4.9-106.2 mg/L P and 299-4294 COD mg/L. Wastewater contains human excreta, household detergents, medical wastes, small amounts of industrial effluents and precipitation run offs which carry P. The different sources of P in wastewaters entering and leaving households in Austria (dish-wash detergents and not P-free detergents are used) are shown in Figure **43**. [38].

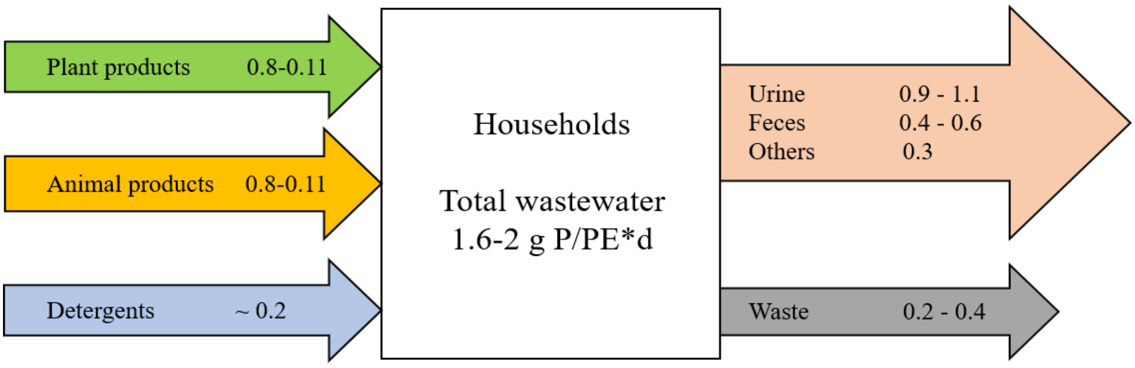

Figure 43: Entry and exit sources of P in wastewaters in Austria [38]

In municipal wastewaters, the typical concentration of P ranges from 6-8 mg/L. However, if a 24- hour period is considered, the P concentration at treatment plants can vary from 2-16 mg/L [39].

Breweries, food-processing industries, paper and pulp industries, sugar industries are few amongst the industries that generate massive quantities of effluents. The amount of organics in the total industrial effluents generated is approximately 65-70% and this amount is contributed together by the food products and agro-based industries [40]. The effluents have a strong odor and are difficult to be applied directly as volatile compounds and organics are present. A high BOD and COD is one of the characteristics of industrial effluents. Environmental laws demand the P content in effluents to be less than 1 mg/L [21].

4.5 Biosolids

Biosolids, also known as treated sewage sludge from wastewater plants, are loaded with organics and plant nutrients and are used to improve soil quality. On an average about 13500 mg/kg of total P, 174000 mg/kg organic C and 17700 mg/kg of total N are found in biosolids. They also include heavy metals, pathogens, toxic residues and greenhouse gas emissions [21]. Distribution of various substances found in biosolids is shown in Figure 44.

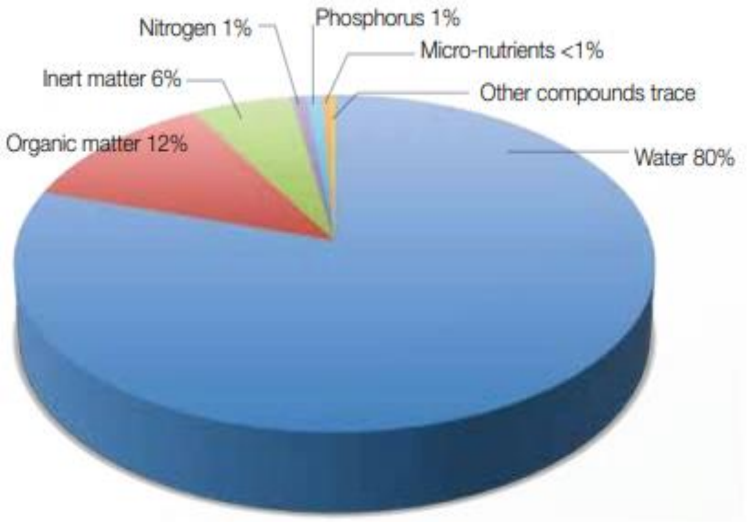

Figure 44: Components in a typical biosolid **[**41**]**

P to Fe and Al molar ratio is used to determine the P availability in biosolids and biosolid/soil mixtures. A ratio of less than 1 means that there is very low P available. The yearly generation of biosolids in a few countries is listed in Table 22. They are disposed by either applying to land or via incineration.

Table 22: Annual generation of biosolids in few countries

Country	Biosolids generated in tonnes of kt of dry matter	References
USA	7100	[42]
Canada	388.7	[43]
Australia	300	[41]
China	24691	[21]
Europe	9866.7	[44]

5 Technologies for producing phosphoric acid

There are two well-known commercial processes of producing phosphoric acid viz., wet process and dry/thermal process. The latter takes place at higher temperatures and is suited to manufacture high grade chemicals for food and industrial applications where high purity is essential while phosphate fertilizers are commonly manufactured by the wet process. As the name suggests, in the wet process, strong mineral acids (H_2SO_4, HCl, HNO_3) are used to undergo reaction with the phosphate rock and the product obtained has impurities higher than those produced by the dry process which almost has no impurities. However, the dry process requires high energy and may also require hazardous chemicals like chlorine as intermediates to produce various compounds [6] [45]. Other thermal processes to recover energy from sewage sludge such as incineration, pyrolysis and gasification are also gaining importance [46].

5.1 Wet Process

This process produces approximately 95% of all the phosphoric acid which is used for the fabrication of fertilizers. The type and quality of the final product obtained depends on the type of acid added in the wet process, purification steps and other macronutrients addition for producing fertilizers. Sulfuric acid is commonly used and, in a few cases, HCl and HNO_3 can be used [6].

In a dihydrate process, naturally available phosphate rock (fluorapatite) is first decomposed in the reactor by using sulfuric acid and the calcium ions from the rock react with sulfate ions from the acid to form calcium sulfate (phosphogypsum) which is separated by filtration. The outer surface of the rock can become covered by an insoluble layer of gypsum when direct acidification with sulfuric acid is carried out thereby covering and hampering reaction on the inner surface of the rock. To avoid this, the rock is treated with the recirculated phosphoric acid first to form calcium dihydrogen phosphate and then sulfuric acid is added. The wet process (Figure 45) is demonstrated by reactions (1) and (2) [47, 48, 6].

$$2\ Ca_5(PO_4)_3F + 12\ H_3PO_4 \longrightarrow 9\ Ca(H_2PO_4)_2 + CaF_2 \quad \text{------------------ (1)}$$

$$9\ Ca(H_2PO_4)_2 + CaF_2 + 10\ H_2SO_4 + 20\ H_2O \longrightarrow 18\ H_3PO_4 + 2\ HF + 10\ CaSO_4 .2H_2O \quad \text{------ (2)}$$

93% sulfuric acid is used to get stronger acid concentrations and to reduce evaporation costs. Gypsum crystals are hence precipitated and filtered out from the acid. After the phosphogypsum slurry is filtered in partial vacuum, a P_2O_5 concentration of 28-31 wt% is obtained. This concentration is not adequate to be used as a fertilizer and has to be concentrated to 40-55%. To achieve a yield recovery of more than 99% of the filtered phosphoric acid, the separated crystals are thoroughly washed and after washing, the gypsum is transferred for storage. Water used in the process is recycled to the phosphoric acid process through a surge cooling pond and similarly, vacuum flash cools part of the slurry so that the heat generated in the reactor is recycled. 2-3 vacuum evaporators are required to concentrate the phosphoric acid to 40-55% P_2O_5 to usually produce fertilizers of different grades. About 5 tonnes of gypsum is produced for every tonne of phosphoric acid produced. Since the phosphoric acid produced by the wet process has many impurities such as Ca, F, Si, sulfites, etc., the purification is performed via ion-exchange, precipitation, membrane technologies, reverse osmosis, adsorption and extraction processes [6] [45].

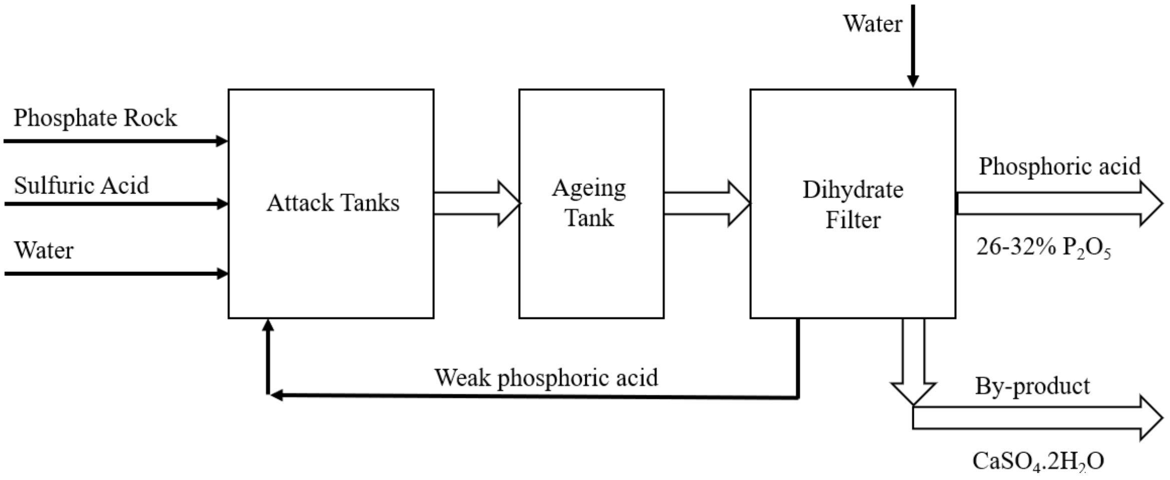

Figure 45: Wet (Dihydrate) process for phosphoric acid production [48]

The wet digestion processes are further classified into dihydrate (DH), hemihydrate (HH) and the combinations of DH and HH as DH/HH and HH/DH [49].

Only the DH-HH CPP or the Central Prayon Process is discussed as this process operates at Prayon, Engis, Belgium. The process was developed with a goal to produce a purer phosphogypsum that can replace natural gypsum. It gives a high yield (98.5%), relatively strong acid (approx. 36% P_2O_5) and dry gypsum (< 8% humidity). Rehydration by natural rehydration of hemihydrate which takes place in this process, lowers the energy costs for drying gypsum.

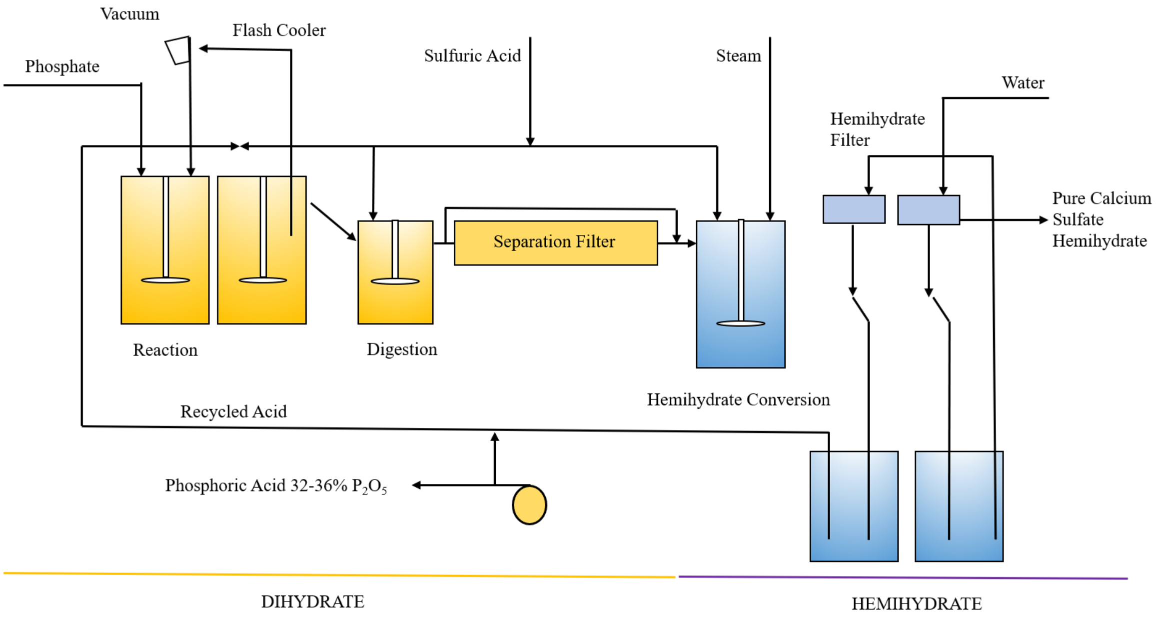

Figure 46: Central Prayon Process [50]

Phosphate rock, sulfuric acid (98%), water are the starting materials in this process. Dihydrate crystals slurry is formed in the first reaction. The slurry is filtered and the quantity equivalent to the acid to be produced is separated and sent to storage while the solids and the remaining slurry are transported to the conversion tank. In this tank, the dihydrate crystals change to hemihydrate crystals after the addition of sulfuric acid and steam. The produced slurry is then filtered, and the cake is washed. The solids can be used as a raw material for other gypsum products after neutralization and the filtrates from the second filter can be recycled back to the attack tank [50].

A brief comparison of the types of wet processes is shown in Table 23.

Table 23: Comparison of types of wet processes [50]

(In Table below: C1 – Crystallization 1, C2 – Crystallization 2, F1 – Filtration 1, F2 – Filtration 2)

Process	C1	F1	C2	F2	P_2O_5 (%)	Efficiency (%)
DH	DH	DH	-	-	28-30	95-96
HH	HH	HH	-	-	40-48	92-95
DHH (CPP)	DH	DH	HH	HH	32-36	> 98.5
HDH	HH	HH	DH	DH	40-52	> 98.5

5.2 Dry/Thermal process

In the thermal process, elemental (yellow) phosphorous, water and air are used as raw materials for producing phosphoric acid. While producing white phosphorus on an industrial scale, phosphate rock, coke and silica are used as starting raw materials and their mix is heated by electrodes. This is known as the Woehler process and it follows the reaction [6]:

$$4\ Ca_5(PO_4)_3F + 18\ SiO_2 + 30\ C \longrightarrow 3\ P_4 + 30\ CO + 18\ CaSiO_3 + 2\ CaF_2 \text{ -----------(3)}$$

In the first step of the dry process i.e., during combustion, elemental phosphorus oxidizes in a combustion chamber with ambient air and at a temperature range of 1650-2760°C, phosphorus pentoxide (P_4O_{10}) is formed.

$$P_4 + 5\ O_2 \longrightarrow P_4O_{10} \text{ ---------------- (4)}$$

Either water or dilute phosphoric acid is used to hydrate the formed P_4O_{10} to produce strong phosphoric acid.

Finally, during the demisting step, with the help of high pressure-drop demisters, the phosphoric acid mist from the combustion gas stream is separated and released to the atmosphere, provided it is clean and free from pollutants.

$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$ -------------- (5)

As elemental phosphorus is used as the starting raw material in the dry process, the phosphoric acid obtained is highly concentrated, concentration normally ranges from 75-85% (v/v) and barely contains few impurities. The burned elemental phosphorus is also recovered (99.9% w/w) by plants working efficiently. The highly concentrated acid is used to manufacture high-grade chemicals and other non-fertilizer products [45].

6 Thermo-chemical waste treatments

6.1 Incineration

Combustion of organic material to CO_2, trace gases and evaporation of water occurs during incineration. It takes place at high temperature, in excess of oxygen and involves heat recovery [46]. There are two methods of incineration: mono-incineration and con-incineration. In mono-incineration, dewatered sewage sludge is subjected to high temperatures in dedicated incineration plants wherein steam and residues are produced. Steam can be reused in the plant and residue/fly ash (phosphorus content: 2-6%) can be used as a substrate for recovering P. Dedicated incinerators take wastes with high variability. Sewage sludge, municipal solid wastes or industrial wastes can also be co-incinerated together for energy production in general purpose incineration plants. The P concentration in co-incinerated ashes is lower than those obtained during mono-incineration and contains other substances, thereby increasing the difficulty for nutrient recovery [8]. Co-incineration of wastes at industrial facilities usually involves selection and pre-treatment of wastes they handle to reduce variability and optimize its behavior in the process [51].

Different types of incineration include multiple hearth, electric, rotary kiln and fluidized bed. As grate furnaces operate with only 30-40% excess air they are less advantageous than fluidized beds in terms of efficiency for energy recovery. Fluidized beds for incinerating wastes operate at temperatures typically ranging from 750 - 850°C. It incorporates a sand bed kept in fluid motion by hot air flowing upwards through it. In Europe, bubbling fluidized beds and circulating fluidized beds are used for combustion of wastes. The difference between the two is that in bubbling beds, the air velocity is held close to the maximum above which bed material is carried away whereas in circulating beds, air velocity is high enough to entrain part of the bed material which is then captured and returned to the bed [51].

Incineration of sludge in fluidized bed sludge incinerators leads to char formation and mineral residue. At small enough particle size, it is mostly retained from the bed as fly ash. An electrostatic precipitator or a fabric filter collects the fly ash particles from the flue gas [52].

6.2 Pyrolysis

It takes place in the absence of oxygen, typically at moderate heating rates (200-700°C) and involves thermochemical decomposition of organic material using long heating times [53]. Pyrolysis of a substance leads to formation of 3 products in solid (high in carbon content, heavy metals), liquid (water: 15-35% and organic chemicals) and gas (CO_2, CO, CH_4, H_2, C_2H_6 and other compounds) phases [54]. The products after treatment yield saleable by-products.

Pyrolysis can be divided into slow and fast pyrolysis. Slow pyrolysis involves a slow heating rate and long residence time and has been used to produce biochar whereas fast pyrolysis is characterized by rapid heating rates (around 100°C/min) to produce gas and liquid fractions for energy recovery [54].

Disadvantages: Fuel gases and/or liquids when pyrolyzed produce gases containing harmful compounds and when compared to incineration, the volume of reduction of solid residues is lower in pyrolysis [55]. Pyrolysis is still in the infancy stage and more research is required to study recovery of P from pyrolyzed sewage sludge char using techniques generally applied to incinerated sewage sludge chars such as acid leaching [46].

6.3 Gasification

It is a process that treats organic materials at high temperatures ($>700^{o}C$) with controlled amounts of oxygen. The organics are converted into an ash-rich solid char and a mixture of gases (H_2, CO and CH_4) which can be used as fuel [53, 56] . Due to its complexity of technology, investment and operational costs, gasification of sewage sludge (SS) has not been extended as much as incineration [57].

6.4 Hydrothermal carbonization (HTC)

HTC process is suitable for waste biomass with high moisture and organic content such as municipal solid wastes, sewage sludge, algae and other types of biomass. It converts organic wastes into energy in a closed system, at moderate temperatures ($180\text{-}350^{o}C$) and an approximate pressure of 10 bar over an aqueous solution, resulting in hydrochar production. Some P is released in the liquid phase or adsorbed in the solid phase when the concentration of oxonium ion (H_3O^+) increases which creates an acidic environment during hydrochar production [53, 58]

Previous research on this process was concentrated on HTC of sewage sludge or biomass for soil amendment, char characterization and combustion behavior of biofuel. Investigations are still being carried out to understand the economic feasibility and energy recycling of the char obtained from sewage sludge by HTC [58].

6.5 Thermo-chemical/Metallurgical treatment

Thermo-chemical treatment involves heating of organic residues to high temperatures ($800\text{-}1500^{o}C$) to increase plant P availability by forming soluble P-bearing mineral phases [53, 59].

Organic pollutants are destroyed the first step of sludge mono-incineration. Although the ashes obtained have a high P content, they still contain heavy metal compounds above the limits for agriculture use. Thermo-chemical treatment allows separation of these heavy metals via the gas phase [59, 60].

Compared to wet chemical processes, thermo-chemical processes have often been associated with high specific energy demands in the past. However, recent advances in integrating different processes, which facilitate the direct transfer of hot sewage sludge ash (SSA) obtained from incineration to the subsequent calcination and advanced heat recovery, promise a reduction of energy consumption [60].

Recent P-recycling technologies from wastes

Phosphorus enters the processing chains in the form of wastes at several entry points. Different projects are being undertaken currently to recover and recycle P from wastes, some of which have been developed on the industrial scale while some on pilot scale and their comparison is shown in Table **24**.

Table 24: P-recovery technologies from wastes

Process	Recovery principle	Feed	Scale	P-output form	P-recovery rate (%)	Ref.
LeachPhos	Wet-chemical	SSA	Pilot	Ca-phosphates	70 - 90	[61]
EcoPhos	Wet-chemical	SS	Full	H_3PO_4 /Ca-phosphates	> 95	[53]
Ash2Phos	Wet-chemical	SSA	Pilot	Ca-phosphates	90	[62]
RecoPhos	Wet-chemical	SSA	Full	TSP	> 90	[63]
ExtraPhos	Wet-chemical	SS	Pilot	Ca-phosphates	> 50	[6] [64]
TetraPhos	Wet-chemical	SSA	Pilot	H_3PO_4/ struvite	> 80	[65] [66]
AshDec	Thermal	SSA	Pilot	Ca-phosphates	> 98	[61] [65]
Phos4Life	Wet-chemical	SSA	Pilot	H_3PO_4/ struvite	> 95	[67]
NuReSys	Wet-chemical	SS	Full	Struvite	> 85	[68]
Pulse	Wet-chemical	SSA/ SS	Pilot	Ca-phosphates	> 70	[69]
Kubota	Thermal	SSA	Full	Ca-phosphates	> 90	[6]

7 Effects of impurities in phosphoric acid production

Many phosphate rocks have different origin and hence incorporate several impurities. They not only affect the acid quality but can also react with the acid and damage the process equipment, cause fouling problems, lead to loss in production time, etc. Impurities in the production of phosphoric acid can be divided into process impurities, phosphate rock impurities and trace elements present in the rock [49, 70] .

7.1 Process impurities

These arise from sulfuric acid and process water used in the production of phosphoric acid. Sulfuric acid is added in excess mainly for separating calcium from the rock, therefore some sulfates are always present in the reactor. Excessive sulfates do not usually affect the final product. When sea water is used as process water, the main impurity consists of sodium chloride. As PR also contains NaCl, excessive Na leads to precipitation of sodium silicofluoride which in turn hampers filtration. Process water containing chlorides should be checked for their corrosion behaviour [49].

7.2 Phosphate rock impurities

Iron and aluminium are frequently viewed to belong to the same impurity category. They lower the water solubilities of phosphate fertilizers by forming insoluble phosphates. The commercial limit to be considered is equal to the ratio: $(Fe_2O_3 + Al_2O_3) / P_2O_5 = 0.08\text{-}0.1$ [71].

Presence of Al_2O_3 improves the filtration rate as Al promotes growth and formation of uniform gypsum crystals. When the ratio of Al to F is high, viscosity and density of acid increases that leads to longer filtration rates. Al also reduces the number of F^- ions by forming the complex AlF^{-6} and acts as a corrosion inhibitor [49, 71].

Aluminium can precipitate from 30-40 % P_2O_5 acid solutions as Ralstonite ($AlF_6MgNa.6H_2O$) or together with iron as an X-compound ($(Fe, Al)_3KH_{14}(PO_4)_8.4H_2O$) beyond 50 % P_2O_5. If the Fe^{3+} is reduced to Fe^{2+}, the formation of iron X-compound can be restrained, but the reduced form is highly unstable in open air storage. Extensive P_2O_5 losses are caused when the strategy to precipitate X-compound is considered to remove aluminium and iron impurities. To eliminate aluminium from phosphoric acid, solvent purification process is followed as there is no other economical option [49].

Magnesium influences the viscosity and forms insoluble compounds in many finished products such as $MgNH_4PO_4$ when phosphoric acid is ammoniated. When combined with fluorine, it enhances crystallization, but over certain limit (2-3 %), it increases the viscosity of the acid which generates a rapid deterioration of the filtration rate. For complex precipitation of a compound containing MgO, Al_2O_3, F and P_2O_5, well-defined ratios of MgO, Al_2O_3, F have to be realized by adding fluoride ions. Allied Chemical Corporation has patented this procedure and it was possible to separate the precipitate by filtration at about 50^oC. Elimination of magnesium by using solid ion exchangers has also been investigated [49, 71].

The calcium content in the product acid is a function of the sulfate level left in the acid. As the acid cools, the solubilities lower and gypsum precipitates which can be separated by filtration [49].

Potassium expressed as K_2O in the phosphate rock can combine with sodium (when both K_2O and Na are in high quantities) and form a sodium potassium fluorosilicate ($NaKSiF_6$) precipitate that can scale the filter/flash cooler pipes. During the concentration of phosphoric acid to 50% P_2O_5 via evaporation, $(Fe, Al)_3KH_{14}(PO_4)_8.4H_2O$, also known as an X-compound precipitates. It is also considered as a problem of unwanted sludge. This X-compound contains only 4% potassium and shows that even small amounts of potassium can cause sludge formation. The formation of the X-compound can be minimized by precipitating potassium as K_2SiF_6 by recycling H_2SiF_6 from the concentration evaporator into 30% P_2O_5 acid [49].

Strontium partially precipitates as strontium sulfate within the wet process acidulation system. The presence of even small (0.1%) amounts of strontium affects the heat exchanger rates because of strontium sulfate deposited in the heat exchanger pipes [49].

Chlorides pose corrosion problems during phosphoric acid production. They are generally soluble in acid but their elimination from weak acids is uneconomical and difficult. It is preferred to remove chlorides from the rock than from acid if the corrosion problem becomes too great [49].

Fluorine can form complex salts and decrease the filterability of gypsum. It also causes problems in corrosion, mud, slurry formation and atmospheric pollution. Most of the fluorine is precipitated in the reaction tank with high amounts of sodium (1% or more) [71].

7.3 Trace impurities

Arsenic concentration is 3-15 ppm in phosphate rock. Removal of arsenic is not required when it is present in small quantities and used for production of TSP, DAP or commercial 50-54% P_2O_5 acid. However, it is necessary to decrease the arsenic content when producing phosphates for food and feed industry. This is achieved by H_2S treatment where arsenic sulfide precipitates and is separated by filtration [49].

Cadmium can be toxic in specific end products such as in fertilizers/animal food. Its content varies to a great extent in phosphate rock. The limit of cadmium consumption recommended by the World Health Organization is 57-70 µg per day per capita. Cadmium is removed via ion exchange by adding bromide or iodide ions. The Cd-halogenide complex formed is removed by anion exchange with basic ion exchange resins [49, 72].

Mercury is a toxic element and remains in gypsum as an insoluble mercury sulfide (HgS_2). Lead is found insoluble with the calcium sulfate solid phase while copper and zinc do not pose a problem. The recovery of uranium from wet process phosphoric acid has been investigated by using liquid phosphine oxide synergist [49, 73] .

Phosphogypsum produced also contains some impurities that can affect the environment negatively. This can be avoided by converting gypsum into a saleable product to be used as plaster, cement retarder, soil conditioner and in the paper industry [49].

8 Conclusion

Recovery and recycling of phosphorus has become one of the most important priorities for many regional and national economies because of their P-import dependency. The main challenges faced by industries are the disposal of wastes within proper limits set by the EU into the environment which serve as a huge potential source for phosphorus recovery. Although processes with high Technology Readiness Level (TRL) to recover P from wastewater have been already developed, their recovery rates are low. For processes that use mono-incinerated ashes obtained via fluidized bed, P-recovery rates are found to be higher. Several integrated technologies that accept ashes from mono-incineration are being researched for the recovery efficiency, operational conditions and energy demands. Production of phosphoric acid by following the hemihydrate-dihydrate route (wet-process) using low-grade PR along with P-rich ash is one of the routes being investigated to recover P.

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ESR1 ANNEX 1 - Abbreviations and Acronyms

AMO	Ammonia monooxygenase
AFR	Air flow rate
AOB	Ammonia oxidizing bacteria
AT4	Cumulative oxygen consumption in four days after lag phase
BA	Bulking agents
CANDO	Coupled aerobic-anoxic nitrous decomposition operation
CBAR	Critical bulking agent requirement
COD	Chemical oxygen demand
DGAO	Denitrifying glycogen accumulating organisms
DO	Dissolved oxygen
DPAOS	Denitrifying phosphate accumulating organisms
DPW	Dairy processing waste
DPWTS	Dairy processing waste treatment generated sludge
DRI24H	Dynamic respiration index as an average of the 24 hours of maximum activity
DS	Dry solids
D/W	Dry weight
EBPR	Enhanced biological phosphorus removal
EP	Eutrophication potential
ESR	Early stage researcher
FAS	Free air space
FNA	Free nitrous acid
GAM	Glycogen accumulating metabolism
GAO	Glycogen accumulating organisms
GHG	Greenhouse gases
GWP	Global warming potential
HAO	Hydroxylamine oxidoreductase
HRT	Hydraulic retention time
IASBR	Intermittently aerated sequencing batch reactors
LCV	Lower calorific value
MC	Moisture content
MSW	Municipal solid waste
N	Nitrogen
OHO	Ordinary heterotrophic organisms
P	Phosphorus
PAM	Polyphosphate accumulating metabolism
PAO	Phosphate accumulating organisms
PHA	Polyhydroxyalkanoates
PNEDPR	Partial nitrification endogenous denitrification and phosphorus removal
Poly-P	Poly phosphate
SBR	Sequential batch reactor
SNDPR	Simultaneous nitrification denitrification and phosphorus removal
SNPD	Simultaneous partial nitrification endogenous denitrification
SRT	Solid retention time
STRUBIAS	STRUvite, BIochar, or incineration AShes
SS	Sewage sludge

VC	Volatile compounds
VOC	Volatile organic compounds
VSC	Volatile sulfur compounds
VFA	Volatile fatty acids
VS	Volatile solids
W/W	Wet weight
WWTP	Wastewater treatment plant

ESR1 ANNEX 2 - Performance indicators for biodrying process in reviewed papers

						Control Parameters					FINDINGS				
Reference	**Tittle**	**Substrate**	**Initial MC (%)**	**Initial Dry Solids (%)**	**Initial VS (%)**	**Bulking Agent (BA)**	**Bulking Agent % w/w or ratio**	**AFR**	**Turning regime**	**C/N Ratio**	**I (Biodrying Index)**	**Final Dry Solids (%)**	**MC Removal (%)**	**LCV (MJ/Kg)**	**VS Reduction (%)**
Navaee-Ardeh et al., 2010	Key variables analysis of a novel continuous biodrying process for drying mixed sludge	Pulp and paper dewatered sludge	50,7	40.3	-	Biodried sludge	30	28 to 75 m^3/h	-	24-29	1.5 - 3.3	51	-	-	-
Colomer-Mendoza et al., 2013	Effect of airflow on biodrying of gardening wastes in reactors	Garden waste	67.35 - 77.73	-	-	Pruning waste and wood shavings particle size between 2 and 3 cm. initial moisture of 4.33%)	15	0.88 to 6.42 L/ (min·kg d/w)		6.75 - 8.88	-	-	51 - 87	4.5 - 13.7	-
Bilgin & Tulun, 2015	Biodrying for municipal solid waste: Volume and weight reduction	Municipal solid waste	48.49 – 50.00	-	-	-	-	50 L/h	-	-	-	-	37 - 49	19.58	-
Zhao et al., 2010	Effect of air-flow rate and turning frequency on biodrying of dewatered sludge	WWTP dewatered sludge	67.9	-	81.1	Straw and saw dust	15:01:02	0.045 - 0.0909 m^3 h^{-1} kg^{-1}. w/w	Per 2 - 4 days	10.2	-	21	57 - 68	14.7	31 - 36.7
Tambone et al., 2011	Effects of biodrying process on municipal solid waste properties	Municipal solid waste	32.72	-	77	-	-	10 - 20 Mg TS^{-1} h^{-1}	-	-	-	62	65.5	16.77	28
Shao et al., 2010	Biodrying and size sorting of municipal solid waste with high water content for improving energy recovery	Municipal solid waste	73	-	83	-	-	0.056 m^3 per kg wet waste per hour	Per 2 days	-	-	-	66.1	19.8	15.6

						Control Parameters					FINDINGS				
Reference	**Tittle**	**Substrate**	**Initial MC (%)**	**Initial Dry Solids (%)**	**Initial VS (%)**	**Bulking Agent (BA)**	**BA % w/w or ratio**	**AFR**	**Turning regime**	**C/N Ratio**	**I (Biodrying Index)**	**Final Dry Solids (%)**	**MC Removal (%)**	**LCV (MJ/Kg)**	**VS Reduction (%)**
Zhao et al., 2012	Sludge Biodrying Process at Low Ambient Temperature: Effect of Bulking Agent Particle Size and Controlled Temperature.	Dewatered SS	54.3 - 72.0	-	72.0 - 80.1	Rice straw (2 -5 and 20 - 30 mm diameter)	15	-	Per 7 days	-	-	-	25 - 31	15.3	9.7 - 17.0
Cai et al., 2015	The Effects of Different Mechanical Turning Regimes on Heat Changes and Evaporation During SS Biodrying	WWTP dewatered sludge	83.5	-	68.3	Biodried sludge and Sawdust	6:03:01	-	Per 3 days	-	-	-	43	-	12.6
González, et al., 2019	Filling in SS biodrying gaps: Greenhouse gases, volatile organic compounds and odor emissions	Dewatered SS	54.6	-	-	Diatomaceous earth and Pruning waste	1:0.15:0.48	0.12. 0.36. 0.60. 0.84 and 1.20 L·min^{-1}·kg^{-1} of initial total VS of mixture	Days 1. 2. 3. 6. 7. 8. 9. 10. 11	13.6	-	-	34.24	7.1	-
Evangelou et al., 2016	Monitoring the performances of a real scale municipal solid waste composting and a biodrying facility using respiration activity indices	Municipal solid waste	50	-	63-77	-	-	5.7 to 28.3 m^3 air/m^3 MSW/h		30 - 37	4.1	>45	20	10	6.5
Zhang et al., 2008	Biodrying of municipal solid waste with high water content by aeration procedures regulation and inoculation	Municipal solid waste	72	-	-	-	-	0.45 (m^3/(kg·m^2·h))	Per 2 days	-	-	-	20	-	10 -- 30

Reference	Tittle	Substrate	Initial MC (%)	Initial Dry Solids (%)	Initial VS (%)	Control Parameters					FINDINGS				
						Bulking Agent (BA)	BA % w/w or ratio	AFR	Turning regime	C/N Ratio	I (Biodrying Index)	Final Dry Solids (%)	MC Removal (%)	LCV (MJ/Kg)	VS Reduction (%)
Shao et al., 2012	Biodrying of municipal solid waste under different ventilation modes: drying efficiency and aqueous pollution	Municipal solid waste	74	-	71	-	-	0.014 m^3/kg initial waste/h	Day 8	-	4.82 - 5.93	-	67.2 - 68.4	-	48
Rada et al., 2007	Lower heating value dynamics during municipal solid waste biodrying	Municipal solid waste	-	-	-	-	-	14.5 nm^3 kg^{-1} MSW	-	-	-	-	30	23 - 26	33
Yang et al., 2014	Importance of Initial MC and Bulking Agent for Biodrying SS	Dewatered SS	23 - 81%	45	71.6	BAs: rubber, sawdust, air-dried sludge and biodried sludge	-	-	-	-	>3	-	8.1 - 45.7	-	0.84 - 7.96
Huiliñir & Villegas, 2015	Simultaneous effect of initial MC and AFR on biodrying of SS	Dewatered secondary sludge	59. 68. 78	-	-	Wood shavings of 2.5 mm diameter	10 -- 50	1. 2 and 3 L/min kg VS		7.82 - 206.15	0.54 - 1.66	52 - 77	7.6 - 26.36	-	4.0 - 10.0
Huiliñir & Villegas, 2014	Biodrying of pulp and paper secondary sludge: Kinetics of volatile solids biodegradation	Pulp and paper dewatered sludge	64 – 66	35	25 - 29	Rice husks	40	0.51. 1.61. 3.25 and 5.26 L/min kg VS	Per 2 days	40	-	35 - 55	15 - 55	3.7 - 6.4	0 - 17.0
Cai et al., 2013	Influence of forced air volume on water evaporation during SS biodrying	WWTP dewatered sludge	66	-	-	Biodried sludge + saw dust	3:02:01	19 - 41 m^3 ton^{-1} matrix d^{-1}	Per 3 days	-	-	-	73	-	-

(Full table considered for construction of Table 4, Table **5** and

Reference	Tittle	Substrate	Initial MC (%)	Turning regime	Controlled parameters	PERFORMANCE YIELDS	MAIN FINDINGS

				Initial VS (%)				**MC Removal ratio (%)**	**VS degradation ratio (%)**	**I (Biodrying Index)**	**LCV (MJ/Kg)**	
Zhao et al., 2012	Sludge Biodrying Process at Low Ambient Temperature: Effect of Bulking Agent Particle Size and Controlled Temperature.	Dewatered SS	54.3 - 72.0	72.0 - 80.1	Per 7 days	BA (Rice straw (2 -5 and 20 - 30 mm diameter))		25 - 31	9.7 - 17.0	-	15.3	As a common BA, straw, which has a small particle size of 2–5 mm, was beneficial for organic matter degradation, while it had a negative effect on water removal. The use of different types of straw (with larger particle size of 20–30 mm) as the BA gave poor performance, in which the organic matter degradation rate was 9.75% and the water removal rate was 25.9%.
Yang et al., 2014	Importance of Initial MC and Bulking Agent for Biodrying SS	Dewatered SS	Controlled	71.6	Day 6	BA: rubber, sawdust, air-dried sludge and biodried sludge	MC 23 - 81%	8.1 – 45.7	0.84 – 7.96	>3	-	50–70 w/w % was found to be the optimal initial MC range for effective sludge biodrying. Among the BA tested, air-dried and biodried sludge showed higher temperature increase, greater weight reduction, and greater water removal than shredded rubber and sawdust.

Table 6)

ESR6 ANNEX – Additional Information

Table 25: Potential quantities of wastes produced in selected countries (ESR6 Ref:[21])

Country	Manure/ Effluents	Potential Quantity Produced (X 10^3) (mg or kL/year)	Country	Manure/ Effluents	Potential Quantity Produced (X 10^3) (mg or kL/year)
Australia	Dairy Effluent	520,238	India	Dairy Effluent	3,847,538
	Municipal wastewater	10,270		Municipal wastewater	139,600
	Piggery effluent	29,194		Piggery effluent	121,363
	Cattle manure	23,409		Cattle manure	173,124
	Biosolids	407		Biosolids	22,086
United States	Dairy Effluent	1,691,454	China	Dairy Effluent	182,881
	Municipal wastewater	767,500		Municipal wastewater	0
	Piggery effluent	847,762		Piggery effluent	4175
	Cattle manure	76,109		Cattle manure	8229
	Biosolids	5645		Biosolids	24,691
United Kingdom	Dairy Effluent	181,277	Japan	Dairy Effluent	77,198
	Municipal wastewater	40,900		Municipal wastewater	140,000
		56,734			124,786

<table>
<tr><td></td><td>Piggery effluent
Cattle manure
Biosolids</td><td>8157
1120</td><td></td><td>Piggery effluent
Cattle manure
Biosolids</td><td>3474
2319</td></tr>
<tr><td colspan="6">Based on the average values of wastes generated and their P content.
Dairy effluent: 50L/animal/day; municipal wastewater: 109m3/year/country, 14 mg/L; Piggery effluent: 35 L/animal/day,1145 mg/L; Cattle manure: 821.18 kg/animal/year, 0.2%; biosolids: 18.3 kg/person/year, 2.23%</td></tr>
</table>