Review

Exploiting the Nutrient Potential of Anaerobically Digested Sewage Sludge: A Review

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Abstract: The world is currently witnessing a rapid increase in sewage sludge (SS) production, due to the increased demand for wastewater treatment. Therefore, SS management is crucial for the economic and environmental sustainability of wastewater treatment plants. The recovery of nutrients from SS has been identified as a fundamental step to enable the transition from a linear to a circular economy, turning SS into an economic and sustainable source of materials. SS is often treated via anaerobic digestion, to pursue energy recovery via biogas generation. Anaerobically digested sewage sludge (ADS) is a valuable source of organic matter and nutrients, and significant advances have been made in recent years in methods and technologies for nutrient recovery from ADS. The purpose of this study is to provide a comprehensive overview, describing the advantages and drawbacks of the available and emerging technologies for recovery of nitrogen (N), phosphorus (P), and potassium (K) from ADS. This work critically reviews the established and novel technologies, which are classified by their ability to recover a specific nutrient (ammonia stripping) or to allow the simultaneous recovery of multiple elements (struvite precipitation, ion exchange, membrane technologies, and thermal treatments). This study compares the described technologies in terms of nutrient recovery efficiency, capital, and operational costs, as well as their feasibility for full-scale application; revealing the current state of the art and future perspectives on this topic.

Keywords: anaerobic digestion; circular economy; nitrogen; phosphorus; potassium; resource recovery

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1. Introduction

In recent decades, great attention has been devoted to the recovery of nutrients from secondary resources, such as waste streams, and to their use for sustainable agriculture [1]. This interest arises from the fact that the world population is growing, resulting in an increasing demand for food. In this context, the nexus 'water–energy–food' is at the center of the challenges arising from the growth of the world population, climate change, and the depletion of natural resources. This is also reflected in the development of strategies to facilitate the transition to a circular economy, based on renewable resources. From this point of view, the increasing need for nutrient compounds for agronomic utilization makes it necessary to identify technologies able to recover nutrients, limiting the consumption of natural resources [2].

Nitrogen (N), potassium (K), and phosphorus (P) have a key role in biological ecosystems [3–7]. Nitrogen is essential for the biological cycle of plants, being the main element responsible for their growth. Potassium facilitates water absorption and protects plants from parasites. Phosphorus, however, is useful for plant metabolism, by promoting a fast maturation. The first two nutrients are widely available in nature. Nitrogen is the fourth most abundant element in cellular biomass and comprises the majority of the Earth's atmosphere [8]. Before the development of the Haber–Bosch process, i.e., the industrial fixation of nitrogen gas (N_2) into ammonia (NH_3) in 1909 [9], the generation of reactive nitrogen species (e.g., NH_3) was exclusively possible through the activity of microbes fixing the inert N_2 of the atmosphere. Potassium is mainly derived from K-rich minerals mined from underground deposits, formed millions of years ago from the evaporation of sea water [10]. Phosphorus is extracted from phosphate (PO_4^{3-}) rocks (phosphorites) rich in apatite (calcium phosphate minerals). The PO_4^{3-} obtained from the beneficiation (i.e., the separation of phosphatic minerals) of phosphate rocks is either solubilized to produce wet-process phosphoric acid, or smelted to produce elemental phosphorus [11]. Phosphorites are the main commercial source of phosphorus, but they also represent a critical resource, being limited and geographically concentrated, and they will inevitably be exhausted in the coming centuries [12].

On the other hand, the uncontrolled discharge of high levels of nutrients into water bodies causes a serious deterioration of environmental quality, due to eutrophication. This is even more detrimental when considering that these are valuable resources that could be recovered and brought back into the material chain, in accordance with the circular economy model (Figure 1) [1]. This model addresses the scarcity of raw materials, by promoting recovery of residual flows, thereby reducing their disposal and environmental impact. The new Circular Economy Action Plan—one of the main blocks of the European Green Deal, Europe's new agenda for sustainable growth—announces initiatives to foster sustainable consumption patterns and to ensure that resources are kept in the EU economy for as long as possible. In this framework, the EU Commission will consider reviewing directives on wastewater treatment and SS and will develop an integrated nutrient management plan, in order to ensure a more sustainable application of nutrients and to stimulate the market for recovered nutrients [13]. In view of this, handling SS is going to turn into a great opportunity, although some challenges still need to be tackled.
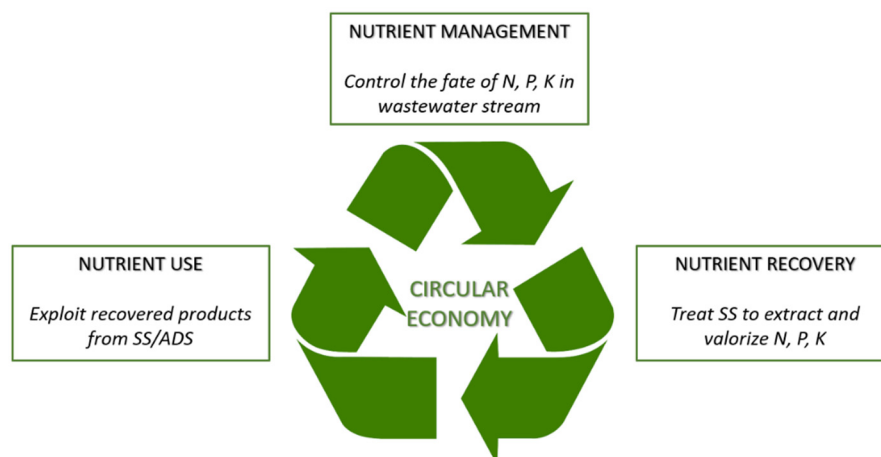
Figure 1. Sustainable management of nutrient-containing wastewater according to the circular economy model.

SS is an unavoidable by-product of wastewater treatment, holding organic matter, nutrients, and often pathogens and toxic substances, such as organic contaminants and heavy metals (HMs). The management of this by-product represents a challenge, due to the high investment and operational costs related to its treatment and disposal [14]. SS is usually exploited through anaerobic digestion (AD), because it can realize sludge stabilization by converting a part of its organic content into biogas, which is a renewable energy source. However, AD of SS is not always practicable in small-scale wastewater treatment plants (WWTPs) or in developing countries, due to the large footprint requirement and high capital costs. In this case, dewatered SS can be collected and treated in centralized plants performing high-solid anaerobic digestion (HSAD), which can be followed by agricultural utilization of the ADS, as a strategy to reuse the nutrients contained in the SS [14].

In the scientific literature, there are many studies that describe the current technologies applied to efficiently recover nutrients from different residual flows, including wastewater [15–17], human urine [18–20], industrial effluents [21,22], and SS [1,23–26]. Notwithstanding the great number of existing studies on the topic of nutrient recovery, only a few are available on nutrient recovery from ADS. Additionally, the latter are mainly focused on N and P recovery, whereas the fate and recovery of K from ADS has been poorly studied.

This review offers an overview on the current state of the art of nutrient recovery from ADS, with a focus on opportunities and challenges related to nutrient reuse coupled to HSAD of SS. Technologies for the recovery of nutrients from ADS are critically reviewed and compared, with a special attention to recent technological advances, in order to identify their state of application at industrial level, main advantages, and drawbacks, as well as to address future research directions.

2. Anaerobically Digested Sewage Sludge: A Nutrient Source

SS is the main residue of wastewater treatment and a major sink for the removed pollutants. It consists of a concentrated suspension of organic and inorganic solids and has a variable moisture content, depending on its origin. Conventional WWTPs generate primary and secondary SS, being different in organic and water content. Primary sludge derives from the primary sedimentation process and consists mainly of organic substances, with a content of solids in the range of 2–8%, typically 4% (96% humidity). Secondary sludge derives from secondary settling and contains mostly microbial biomass. It has a lower percentage of solids than primary sludge, with a typical value of 1% (99% humidity). Typically, SS treatment in the sludge streamline of a WWTP pursues volume reduction via thickening and dewatering, as well as a biological stabilization via digestion

processes. In small plants, due to the need for operational simplicity and limited SS flows, the digestion process is either not performed or can be performed under aerobic conditions, while in medium and large plants, AD is more commonly implemented, since the energy recovery from SS can be substantial.

AD generates a gaseous flow (the biogas) and a solid-liquid flow (the ADS). Biogas generated from AD of SS typically contains 55–65% methane (CH_4), 35–44% carbon dioxide (CO_2), and small concentrations of other gases, such as hydrogen, hydrogen sulfide, carbon monoxide, and ammonia [6,27]. As a result, biogas can be further processed to produce biomethane and/or thermal/electrical energy for plant operation, thereby eliminating or reducing the external supply of energy. However, anaerobic digesters generally require huge operating volumes and heating energy, due to the high water content of the treated sludge, which often leads to insufficient biogas production to sustain the energy demand of the process [14,28]. Consequently, conventional AD is not always carried out in small WWTPs and highly urbanized areas with limited space [14,29]. In recent years, centralized AD plants collecting unstabilized dewatered SS from different WWTPs have been developed, with the aim of reducing the operating and capital costs for sludge treatment. These plants treat SS with a high concentration of TS (>6%): as a result, power consumption for heating is significantly reduced and more biogas is produced per liter of treated sludge, leading to energy-neutral or even net-energy-positive AD plants [14].

ADS is a mixture of biomass, water, and both inert and undigested solids, with potential fertilizer properties. During AD, the biological degradation of the organic matter contained in the sludge increases the concentration of soluble nutrients species, i.e., total ammonia nitrogen (TAN) and ortho-phosphate, which can be rapidly assimilated by plants for their growth [30] if the sludge is used for agricultural applications. Moreover, AD can ensure sufficient hygienization of SS, especially if performed under thermophilic conditions (50–55 °C) [31]. Although, pathogen reduction can also be achieved at mesophilic temperature (30–35 °C) [32], the latter has been reported to be less effective in reducing pathogens than thermophilic AD, due to lower operational temperatures. One of the most sustainable systems for the disposal of ADS is direct injection on agricultural land [33]. Reusing ADS as fertilizer fits the circular economy approach and has several advantages, which include the return of the organic materials and nutrients into the biocycle. Moreover, the use of ADS as a fertilizer allows reducing the demand for chemical fertilizers and, in turn, the costs for farmers.

In this context, HSAD can be considered the most direct and cost-effective pathway for the reuse of nutrients contained in SS. Indeed, HSAD generates an ADS particularly rich in nutrients and, thus, advantageous for application in agriculture [33]. Moreover, HSAD is often carried out at thermophilic temperatures, resulting in excellent hygienization of ADS, due to the higher levels of pH and ammonia compared to mesophilic conditions [31]. On the other hand, HSAD of SS presents certain challenges related to the high viscosity of ADS and concentration of organic compounds containing nitrogen and sulfur, which may lead to the development of inhibitors (NH_3 and H_2S) that can slow down biological kinetics. To limit inhibition of the anaerobic process, specific treatments for ammonia and/or sulfide removal must be carried out, which can lead to the generation of agronomically valuable products, such as ammonium sulfate [33] and biogenic elemental sulfur [34]. Therefore, even though it is more challenging, thermophilic HSAD can lead to a sustainable recovery and reuse of nutrients from SS.

Nonetheless, the quality of ADS must be carefully evaluated prior to its use in agriculture, as it carries not only nutrients, but may also contain organic and inorganic pollutants [1]. According to Directive 86/278/EEC, the use of ADS in agriculture is subjected to specific restrictions regarding the pH, homogeneity, purity, and contents of nutrients, dry matter, organic dry matter, biological (pathogenic) materials, and chemical pollutants [35]. The generation of poor-quality ADS would require proactive interventions, aimed at improving the quality of the sewage entering the WWTPs, in order to enable the direct

utilization of digestate in agriculture. In the absence of remedial measures, nutrient recovery from ADS could be performed by adopting different techniques within the WWTP, in order to valorize a waste material, i.e., SS, and comply with the principles of a circular economy. It should be highlighted that nutrient recovery from ADS would be not economically profitable in the absence of incentives from national and European governments, due to the high process costs and low market value of recycled fertilizers. However, strategies for nutrient removal and recovery from ADS may be needed to avoid inhibition of the anaerobic process and/or to reduce emissions of N and P to the hydrosphere.

2.1. Nitrogen

Nitrogen in ADS mainly originates from the biological degradation of proteins in the feedstock. After anaerobic hydrolysis and fermentation, approximately 70% of organic nitrogen is mineralized to ammonium nitrogen ($N-NH_4^+$) and free ammonium nitrogen (FAN or $N-NH_3$), which constitute the TAN of the sludge. Di Capua et al. [14] reported average total Kjeldahl nitrogen (TKN) and FAN concentrations in ADS of 52–77 g/kg TS and 21–45 g/kg TS, respectively. TAN concentrations exceeding 1500 mg/L may result in a strong inhibition of AD, even leading to process instability [36]. Thermophilic AD systems are more exposed to process instability, as the levels of FAN increase with temperature [37]. Ammonia inhibition proceeds through different mechanisms, i.e., proton imbalance, potassium deficiency, change of intracellular pH, increase of energy requirement, and inhibition of enzymatic reactions [14]. Typically, FAN enters microbial cells by passive diffusion, resulting in abnormal cell ectoplasm, and sodium potassium exchange balance; then, FAN entering into the cell by passive diffusion can indirectly lead to a change of pH, which affects cell stability [37]. In this way, the adoption of strategies for nitrogen recovery can be also seen as a method (if nitrogen is recovered before or during AD) of reducing the inhibitory effects of reduced nitrogen species on the anaerobic process and optimizing the process yield.

2.2. Phosphorus

Phosphorus is a fundamental and irreplaceable element for living organisms and has an essential role in global food production, as it is widely used by the fertilizer industry and as an additive for animal feed [38]. In 2015, according to data from the International Fertilizer Association (IFA), the total world production of phosphate rock was about 197 million tons; considering a nominal content of P_2O_5 of about 30%, this corresponds to about 26 million tons of P, with the highest production in China, Morocco, and USA [38]. The future trend of phosphorus production and consumption is currently one of the most debated issues among researchers. Based on current trends, it is estimated that the peak phosphorus production will occur by 2035 [38]. In this scenario, the need is clear for investments in innovative technologies capable of recovering phosphorus from secondary material, such as SS, wastewater, and urban and agro-industrial wastes [39]. The percentage of P in the dry fraction of SS can reach up to 10% in weight [40]. Based on this, SS is considered among the most abundant sources of this element among organic wastes [41]. The amount of phosphorus in SS depends on the type of wastewater treatment, since the phosphorus contained in wastewater has to be sequestrated into a solid to be removed. Conventional phosphorus removal works by fixing the phosphorus into the sludge in one of two ways: chemically or biologically. Chemical processes are based on the use of coagulants that hydrolyze rapidly and form multicharged polynuclear complexes with enhanced adsorption characteristics; once suspended particles have flocculated into larger particles, they can be removed from the treated water by sedimentation [3]. Typically, precipitation of soluble phosphorus occurs with aluminum or iron salts, which convert it into insoluble P compounds [42]. Although easy to implement, chemical precipitation increases the cost of sewage treatment and the volume of sludge to be managed [43]. Bio-

logical processes exploit the ability of phosphorus accumulating organisms (PAO) to accumulate $P-PO_4^{3-}$ as polyphosphates in amounts exceeding their metabolic need [42]. The most widely used technology for biological treatment is conducting alternating aerobic and anaerobic processes, enabling the combined removal of carbon, nitrogen, and phosphorus. The first step is to carry out the anaerobic process, during which PAO hydrolyze polyphosphates and release phosphorus from cells in the form of ortho-phosphates, to gain energy for the uptake of organic carbon, which is absorbed as simple organic compounds (e.g., volatile fatty acids) and stored within the cell as polyhydroxyalkanoates (PHA). Next, the activated sludge goes into an aerated basin, where PAO begin to uptake ortho-phosphates to be retained within their cells as polyphosphate, resulting in a net $P-PO_4^{3-}$ uptake [44,45]. The phosphorus sequestrated into bacterial cells ends up in the sludge streamline of the WWTP and eventually enters AD. Here, P is partly retained in solids and partly released in the liquid phase, due to PAO activity under anaerobic conditions and VS degradation. As a result, both liquid and solid fraction of ADS can be considered valuable sources of phosphorus.

2.3. Potassium

Similarly to nitrogen and phosphorus, potassium is one of the essential microminerals for plant survival. Potassium is of great importance for soil health, plant growth, and animal nutrition. Its primary function in plants consists in maintaining osmotic pressure and cell size, thus influencing photosynthesis and energy production [10]. Most potassium is found in the earth's crust in the form of minerals, such as orthoclase (potassium feldspar, a common rock-forming mineral), sylvite (KCl), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$), and langbeinite ($MgSO_4 \cdot K_2SO_4$). In 1980, the main mining area used for potassium salt extraction was in Germany, while today most of the potassium minerals (especially sylvite and carnallite) come from Canada, the United States, and Chile. The world production of extracted potassium is about 50 million tons, and the reserves are estimated to be over 10 billion tons [46]. Potassium-based fertilizer prices have increased by as much as four times during the last decade and there are issues around supply of K-based fertilizers to developing nations, due to the limited global distribution of potash ores (the main source of K) [3]. Potassium concentrations in SS and ADS range between 0.3% and 0.7% of K per weight of dry solids [14,25,47]. As indicated, the potassium content in the ADS is low, which is why potassium is typically recovered through technologies also applied for phosphorus and nitrogen recovery, in particular through K-struvite precipitation, membrane technologies, and thermal treatments.

3. Technologies for the Recovery of Nutrients from ADS

This section aims to give an overview of the different possible methods for recovering nitrogen, phosphorus, and potassium from ADS. These technologies can either target a specific nutrient (e.g., ammonia stripping) or allow the simultaneous recovery of multiple elements (e.g., struvite precipitation for $P-PO_4^{3-}$ and $N-NH_4^+$ or potassium recovery). Typically, nutrient recovery technologies are applied directly to the ADS (or SS) stream or to a ADS liquid fraction (e.g., centrate).

3.1. Selective Nutrient Recovery: Ammonia Stripping

This process removes part of the TAN contained in the sludge by shifting the NH_4^+/NH_3 equilibrium towards FAN, which is removed from the system by a gas stream. Ammonia stripping is conventionally executed in heated packed column reactors on the liquid fraction achieved from sludge dewatering [14]; the air blown in the column from the bottom (stripping gas), traveling along the surface of the contact material, carries the ammonia. The stripped ammonia is transported to an absorption unit, where it is absorbed into sulfuric (or nitric) acid solutions, resulting in the production of ammonium sulfate (or nitrate), a marketable platform chemical for the production of base fertilizers

and other chemical products [47]. Recently, approaches based on NH_3 stripping from ADS and the liquid fraction of ADS have been established and extended from lab-scale to full-scale around the world [48].

Ammonia stripping is established based on the change of physical conditions of the sludge, enabling the transition of NH_4^+ to NH_3, which must be efficiently removed from the liquid phase [49]. Increasing temperature and pH shifts the NH_4^+/NH_3 equilibrium towards FAN. It was shown that increasing the pH (up to 10), temperature, and flow rate of the stripping gas can significantly improve the amount of stripped nitrogen [50]. Nevertheless, effective ammonia stripping during AD of SS can be obtained without using alkaline reagents for pH increase, as the concomitant stripping of CO_2 helps increase the pH of the system and shift the NH_4^+/NH_3 equilibrium towards FAN [51].

The ammonia stripping process is strongly conditioned by the type of matrix being treated; the passage in the stripping column is suitable for low viscous fluids, such as wastewater and the liquid fraction of municipal SS. For high-viscosity fluids, however, reactors with packed materials are not suitable, as they would result in rapid clogging. Therefore, TS content plays a key role in choosing the most suitable technology for ammonia stripping, as if affects the rheological characteristics of the medium [52]. To overcome this issue, it is necessary to develop new technologies specifically suited to ADS, especially if it comes from HSAD. Due to the higher TS concentration compared to conventional AD, the operation of packed columns for direct ammonia removal from ADS is impossible. Moreover, the high TS concentration in HSAD results in much higher TAN and FAN levels inside the digester, which may inhibit the biological process. Therefore, TAN removal cannot be performed as a post-treatment only on the liquid fraction of ADS but should be foreseen as a side-stream process of HSAD.

Side-stream ammonia stripping represents a strategy for reducing ammonia toxicity during AD. The HSAD of SS produces TAN levels as high as 4 g/L, due to the high concentrations of proteinaceous organic materials in the feedstock [53]. High ammonia concentrations may be responsible of inhibitory effects on AD, hindering and slowing down the digestion process. The ammonia toxicity is amplified when the process is conducted at thermophilic temperatures [14]. To solve the problem of ammonia inhibition, numerous techniques, including dilution, co-digestion, and side-stream ammonia stripping, could be applied. The latter approach seems to be the most promising. During AD, a portion of the digested sludge is continually removed and treated in a stripping unit, where the ammonia produced from the digestion process is transferred to a gas phase (commonly biogas or air) and then put into contact with a sulfuric acid solution, to produce ammonium sulfate. This process prevents the inhibition of the anaerobic process and simultaneously recovers ammonia as ammonium sulfate, which can be used as fertilizer. Costamagna et al. [54,55] proposed a thin film evaporator (TFE) as a suitable technology for the continuous side-stream stripping of ammonia from dewatered SS (12.5% TS) during thermophilic HSAD. As an alternative to conventional packed columns when treating dewatered SS, this technology does not require solid/liquid separation and avoids clogging issues [14]. With this technology, the ADS is continuously recirculated to the TFE column, which is thermally insulated and allows the contact between the ADS film (5–15 mm) and the uprising biogas flow, which is enriched in ammonia. The treated sludge is then recirculated to the digester and the ammonia-rich biogas collected from the TFE is fed to an absorption column to remove ammonia and producing ammonium sulfate. During the trial period, Costamagna et al. [55] could recover 4.1 g $N–NH_4^+$ per kg of sludge fed to the digester, i.e., 19.3 g $N–NH_4^+$ per kg TS fed to the digester, as ammonium sulfate. Side-stream ammonia stripping during HSAD couples process non-inhibition with the possibility of recycling nutrients from SS using a two-fold production of fertilizer, i.e., ammonium sulfate and high-solid ADS. Recently, Di Capua et al. [51] proposed the use of air as a stripping gas in the TFE during the HSAD of SS (TS 11.04% and VS 7.01%). In this process, ADS is continuously recirculated from the digester to the TFE, where ammonia is stripped by an air stream. The TFE performance was monitored for 140 days, by gradually increasing the

specific airflow rate from 1.5 to 4.6 m³ air/kg ADS. The authors demonstrated that ammonia removal from SS was primarily influenced by the airflow rate, as the removal efficiency increased from 17.1% to 33.3% when the flow rate was increased from 1.5 to 4.6 m³ air/kg ADS. In contrast, changes in temperature (from 63.6 °C to 73.6 °C) and CO_2 concentration (between 5% and 17%) did not influence the ammonia stripping significantly. Use of air as a stripping gas did not exert any inhibitory impact on methane production, even when 4.6 m³ air were fed per kg of ADS, which was attributed to low residence time of 2.5 min in the TFE and small fraction of ADS (only 1.7% of the total digestion volume) fed daily to the TFE. The process allowed avoiding inhibition of the HSAD process and, at the same time, producing nutrient-rich ADS and ammonium sulfate, to be applied as fertilizers.

Ammonia stripping from SS has been carried out before or after AD. In the former case, it serves as a pretreatment and has the advantage of improving the AD process, limiting the problems related to ammonia inhibition in AD [56,57]. In the latter case (Table 1), the ammonia nitrogen produced from the digestion process can be recovered as ammonium sulfate/nitrate, since the air leaving the stripping tower, enriched in the ammonia transferred to the gaseous phase, can be treated in a scrubber with sulfuric/nitric acid to obtain ammonium sulfate/nitrate.

Table 1. Removal and recovery of N-NH_4^+ from ADS streams through ammonia stripping.

Sludge Type	Type of Ammonia Stripping	TS (%)	Influent TAN (g/L)	T (°C)	N-NH_4^+ Removal (%)	Ref.
Digestates taken from an anaerobic digester	Down-stream	-	4.98	70	17–86	[58]
	In situ	-	6–6.3	35	58–90	
	Side-stream	-	3.98	70	34–84	
	Up-stream	-	6–6.25	70	44–88	
Anaerobic digestion effluent	Up-stream	2 [1]	1.544	15	72.1–95.3	[56]
ADS	Side-stream with TFE	10.7	3.65	65	21.2	[54]
High-solid anaerobic digestion of SS	Side-stream with TFE	11.04	3.714	63.6–73.6	17.1–33.3	[51]

[1] Total suspended solids.

3.2. Multiple Nutrient Recovery

3.2.1. Struvite Precipitation

Struvite is a crystalline mineral composed of equimolar concentrations of Mg^{2+}, NH_4^+, and PO_4^{3-}, with the chemical formula $MgNH_4PO_4 \cdot 6H_2O$. Struvite consists of PO_4^{3-} (tetrahedral), $Mg(6H_2O)^{2+}$ (octahedral), and NH_4^+ (tetrahedral) groups, which are held together by hydrogen bonds [59]. The formation of struvite is controlled by two mechanisms: nucleation (the initial formation of the crystal) and crystal growth. This last phase is characterized by a mass transfer through the diffusive layer surrounding the crystal and by the capture of the solute inside the crystal. In most of the published works on the principles of struvite formation, it has been highlighted that supersaturation ratio and pH have been found to be the most influential parameters on the crystallization mechanism [42]. The crystal formation process is also strongly influenced by other parameters, such as the presence of other ionic species (e.g., Ca^{2+}, Na^+, K^+) that can interfere with crystal formation, replacing N–NH_4^+ (e.g., K^+) or Mg^{2+} (e.g., Ca^{2+}) and leading to the formation of a mineral similar to struvite but different in composition. When K^+ replaces N–NH_4^+, potassium struvite precipitation ($KMgPO_4 \cdot 6H_2O$) can occur [60]. This precipitate is also known as K-struvite, an isomorphous analogue of struvite that can also be used as slow-release fertilizer [61]. The physical and chemical properties of K-struvite are similar to those of typical struvite crystals (e.g., the needle-like shape and transparent to whitish appearance [62]),

although the density of K-struvite (1.864 g/cm³) is slightly higher than that of struvite (1.711 g/cm³) [63]. A suitable pH range for K-struvite precipitation is between 9.0 and 11.0, which is moderately higher than the pH range for struvite formation (8.5–9.5) [64].

Struvite precipitation depends on several parameters, perhaps most notably pH and the molar ratio of NH_4^+, PO_4^{3-}, and Mg^{2+} in the liquid phase [65]. Several researchers investigated the pH of minimum solubility for struvite [66], reporting values ranging from 7.8 [67] to 10.3 [68]. Generally, struvite precipitation occurs when NH_4^+, Mg^{2+}, and PO_4^{3-} concentrations overcome the solubility product (K_{sp}) of struvite under alkaline conditions [69]. In the literature, different K_{sp} values are reported, ranging from $2.50 \cdot 10^{-13}$ to $7.50 \cdot 10^{-14}$ [66]. Struvite precipitation occurs spontaneously in many WWTPs, resulting in scale deposits that are a significant concern for plant operation. As a result, struvite formation is perceived as a nuisance, affecting the efficiency of treatment processes and causing maintenance problems. However, for intentional struvite precipitation, most of the potential struvite sources need an input of chemicals for a pH increase and/or for the adjustment of Mg, NH_4^+, and PO_4^{3-} concentrations, to reach an optimal molar ratio (Mg^{2+}:PO_4^{3-}:NH_4^+). This must be assessed case-by-case, as it strongly depends on the chemical-physical characteristics of wastewater [70]. Uysal et al. [71] observed that the optimal Mg:PO_4^{3-}:NH_4^+ molar ratio for struvite precipitation from SS was near to the equimolar ratio, being 1.5:1:1 at a pH of about 9.0. A supply of Mg^{2+} is generally required to make struvite precipitation effective, due to the lack of adequate Mg concentrations in the majority of potential struvite sources, including SS [72].

Table 2 shows data present in the literature regarding nutrient removal and recovery from ADS through struvite precipitation, in relation to the parameters described above. Munir et al. [73] showed an increase in phosphate recovery, due to an increase of pH, i.e., 7.1 mg/L at pH 8 compared to 10.5 mg/L at pH 9. This result was also confirmed by Marti et al. [74], where the PO_4^{3-} recovery was 152 mg/L at pH 7 compared to 164 mg/L at pH 8. Uysal et al. [71] and Zheng et al. [75] observed that as the ratio Mg:N:P changes, the nutrient removal/recovery efficiency varies as well, with the best results obtained for a molar ratio of 1.3:1:1.

Table 2. Recovery of N, P, and K from ADS streams through struvite precipitation.

Sludge Type	TS (g/L)	pH	Mg:N:P	P Recovery (%)	N Recovery (%)	K Recovery (%)	Ref.
ADS	-	8	1:1:1	<0 [1]	85.42	-	[70]
		8.5	1:1:1	<0 [1]	89.16	-	
		9	1:1:1	47.1	88.79	22.2	
		9	1.3:1:1	92.5	89.35	32.5	
		9	1.5:1:1	95.0	89.35	24.7	
ADS	37.26 ± 8.4	6.8–7.2	1:1.7:1.2	58	-	-	[73]
Acidified ADS	-	9.6	1–1.4:1:0.8–1.2	96–100	75–90	-	[74]
ADS supernatant	1.309	10	1–3:1–7.871:1–2	20.9–99.6	29	-	[75]
ADS centrate	-	7.67	1–2:1:0.8–1	95.9–99.8	76.7–99.5	-	[76]
Liquid fraction of ADS	16–29.6	6.2–8.7	1–1.5:6.7–7.9:1	76.0–83.9 (35.4–72.6 as struvite)	-	-	[77]
ADS	29.3	9.5	1–1.2:1:1–1.2	81–86.7	92.6–96	-	[78]

[1] Negative values are due to H_3PO_4 addition, to obtain the desired Mg:N:P ratio.

Struvite is considered a valid fertilizing product, because it contains nutrients such as nitrogen and phosphorus (essential for plant growth) [79], and its low solubility induces a slow release of nutrients in the soil, which allows optimal plant growth and avoids potentially harmful overdose phenomena [2]. As a result, the crystallization of struvite has gained interest for phosphorus recovery [42] and to remove NH_4^+ [80] from waste

streams, such as wastewaters and SS. Interestingly, struvite precipitation in HSAD digesters treating dewatered SS may have a double positive effect: (1) avoiding process inhibition, due to TAN removal, and (2) increasing the fertilizing potential of the produced ADS [14]. The occurrence and quantification of struvite precipitation during the HSAD of SS and the struvite content of the produced ADS should be investigated in future studies.

3.2.2. Ion Exchange and Adsorption

Ion exchange and adsorption are similar physical-chemical processes as they both utilize sorbents in a column bed to extract the target compounds from the feed solution. Adsorption is a mass transfer phenomenon, by which one or more constituents present in the liquid phase are fixed on a porous solid surface. Contrarily to ion-exchange, which is driven by ionic forces, adsorption occurs due to weak intermolecular forces, i.e., Van der Waals forces, and, thus, the process is considered reversible. In ion exchange, mobile ions of a solid matrix (adsorbent) are exchanged with ions having a similar electric charge present in the solution (adsorbate). Electrostatic forces allow the bonding between the ions of the adsorbate and the charges present on the surface of the adsorbent. Ion exchange and adsorption may occur simultaneously in one media, such as zeolites, clays, and resins, whether or not chemically or thermally modified [48]. After a certain period, the sorbent reaches its capacity and must be regenerated. Regeneration can be achieved with various techniques, including washing with nitric acid (HNO_3) or sodium chloride (NaCl) [81]. Ion exchange through natural minerals (e.g., zeolites or bentonites) has gained importance because of its low cost and ease of use. Furthermore, ion exchange enables the recovery of $N–NH_4^+$ and its reuse for fertilizing purposes [82,83]. For example, the ammonium-zeolite complex can applied directly to soil as it is decomposed slowly by soil bacteria and released to the soil as a nutrient [84]. The high ion exchange capacity, large reserves, shortage of competing minerals, and relatively low market price make zeolite an attractive mineral for application at large scale [85]. Despite this, there are no applications at full-scale, but only at lab-scale, due to the rapid obstruction of the adsorbent bed (which makes zeolite treatment potentially feasible only for the liquid fraction of ADS), as well as the necessary maintenance of the capacity of the bed after multiple recovery/regeneration cycles, which can increase the operating costs. Zeolite minerals differ in silicon (Si) and aluminum (Al) contents. Zeolite minerals differ in silicon (Si) and aluminum (Al) contents; among natural zeolites, clinoptilolite (Si:Al ratio equal to 5.7) is usually used for ion exchange, due to its high sorption and ion-exchange capacity and selectivity [86]. Zeolites exert their ammonia removal action through two different mechanisms: 1) ion exchange for $N-NH_4^+$, and 2) adsorption of $N-NH_3$ [87]. Temperature and pH strongly influence the removal efficiency of ammonia: the higher the temperature, the higher the removal efficiency achieved; regarding pH, the removal efficiency is approximately constant between values of 4 and 8, and rapidly decreases outside this range [80]. Zeolites are used for both $N–NH_4^+$ and $P-PO_4^{3-}$ removal [88]; $P-PO_4^{3-}$ can be adsorbed by zeolite, although the removal efficiency has been reported to be much lower than that of $N–NH_4^+$ [89]. This is due to the fact that zeolite, or rather, clinoptilolite has a higher selectivity for monovalent ions such as $N–NH_4^+$ and K^+ [85,90–92]. The best results in terms of removal/recovery of $N–NH_4^+$ were obtained with the use of mesolite [93] and polymeric resins [92], of 95% and 98%, respectively. Kocatürk-Schumacher et al. [94], using clinoptilolite, demonstrated that $N–NH_4^+$ and K^+ can be removed from the liquid fraction of digestate with high removal efficiencies, i.e., 86% and 78%, respectively. These authors also showed that preconditioning of clinoptilolite with sodium ions had no significant effect on the removal of NH_4^+ and K^+ and that increasing the initial loading ratio significantly increased the nutrient concentrations of clinoptilolite but decreased the nutrient removal efficiencies from the liquid fraction of the digestate. This result was also confirmed by Gong et al. [95], who observed that an increased initial load leads to a higher concentration of nutrients in the polymer resins, but results in a low removal efficiency (37%). The costs of ion exchange and adsorption depend on several factors, including the availability of the sorption

material used, the applied recovery/regeneration method, and the regeneration frequency of the adsorption medium. To date, no cost–benefit analyses for nutrient recovery from ADS using zeolites or other sorbents have been reported in the literature [81].

3.2.3. Membrane Technologies

Membrane filtration is generally applied to the liquid fraction of the ADS, which is forced through a membrane by means of pressure [96]. With a driven pressure applied, porous membranes can retain larger particles, while allowing smaller ones to pass through [48]. Membrane systems can be operated either with a constant permeate flux (flow rate per unit of membrane area, L/m^2 h) and variable transmembrane pressure (TMP) or with a constant TMP and variable permeate flux [97]. Membrane technology has evolved considerably in recent years and it can be applied in almost all industrial sectors [98], including nutrient recovery from waste streams such as SS and ADS (Table 3). Gerardo et al. [99] used membrane filtration coupled with acid treatment and dialysis techniques and showed that 271.11 mg/L $N-NH_3$ and 25.60 mg/L $P-PO_4^{3-}$ could be recovered from filtered ADS supernatant with initial concentrations of 686.2 mg/L $N-NH_3$ and 41.51 mg/L $P-PO_4^{3-}$. Membrane filtration effectively separates the ADS stream into a fraction rich in solids (retentate or concentrate) and an aqueous solution that passes through the membrane (permeate). Based on the operating TMP, membranes can be categorized as low-pressure membranes (LPMs) and high-pressure membranes (HPMs). LPMs include microfiltration (MF) and loose ultrafiltration (UF) membranes, typically operated at TMPs below 200 kPa. Meanwhile, HPMs such as tight UF, nanofiltration (NF), and reverse osmosis (RO) membranes are operated at TMPs above 200 kPa [97]. MF and UF are mainly applied for the removal of suspended solids, microorganisms, and macro-molecules, while NF and RO are used for the removal of smaller organics and ions, including NH_4^+, PO_4^{3-}, and K^+ [100,101]. The main drawbacks of membrane processes is fouling, which leads to a rapid decline of the permeate flux over time; to maintain their separation performance, membranes must be cleaned and replaced periodically [97]. Recently, of the different membrane technologies, there are three processes: forward osmosis (FO), membrane distillation (MD), and electrodialysis (ED), showing promising results for nutrient recovery. Their selectivity is conducive to the formation of valuable nutrients, and their energy requirements and related costs are competitive with common pressure-driven membrane processes.

Nanofiltration and Reverse Osmosis

NF and RO have been widely applied, from laboratory to full scale, for potable water reclamation from wastewater and the removal of contaminants such as HMs and emerging organics [102–104]. In terms of nutrient removal and recovery from SS streams, NF and RO have been applied with the objective of recovering P by concentration in the retentate stream and precipitation with Ca ions. This process requires the use of acid-resistant and durable membranes, as cleaning with strong acids is periodically required to remove the Ca-P crystals attached to the membranes. Nitric acid is regarded as the best option, as it generates a solution rich in N and P, which can be locally applied as a fertilizer. Nir et al. [105] proposed a two stage NF/RO system for the simultaneous removal and recovery of P from WWTP secondary effluents, which could also be applied to the liquid fraction of ADS. In the first stage, a NF/RO treatment allows obtaining a permeate with high recovery ratio (i.e., ratio of permeate to influent flow). The obtained concentrate is sent to a second NF stage, where P and Ca ions exceed the supersaturation levels. Proper P precipitation is achieved in a crystallizer by adjusting the pH to reduce the formation of $CaCO_3$ crystals, which may reduce the weight fraction of P in the precipitate. At a 95% recovery ratio, P recovery in the retentate could reach >90%. The costs of the proposed scheme, including membrane replacement and acid addition for pH adjustments, were estimated to be around 0.05 USD per m^3 of influent wastewater, being competitive with the conventional P removal and recovery method based on chemical P precipitation through addition of Al/Fe salts.

Forward Osmosis

FO is carried out by placing a semipermeable membrane between two solutions with different solute concentrations: a concentrated draw solution, and a more diluted feed solution. Instead of hydraulic pressure, FO employs an osmotic pressure difference [106]. For this reason, unlike other membrane processes with a hydraulic pressure requirement, such as NF (3–20 bar) and RO (5–120 bar), FO has the advantage of low energy consumption. Moreover, FO has demonstrated a lower fouling propensity and higher fouling reversibility compared to pressure-driven RO [107–109].

The application of FO is promising, due to its distinctive advantages but, up to now, FO has only been assessed in laboratory-scale studies, and pilot and full-scale validations should be conducted. Nguyen et al. [109] evaluated the feasibility of applying FO on municipal wastewater sludge, showing recovery efficiencies of around 96% of $N–NH_4^+$ and 98% of $P–PO_4^{3-}$. Soler-Cabezas et al. [110] studied the recovery of nutrients in ADS centrate by FO using two industrial effluents as draw solutions; the results showed that NH_4^+ and K^+ could be concentrated with a factor (ratio between final and initial concentrations in ADS centrate) of 1.2 and 1.08, respectively. Conversely, phosphorous cannot be concentrated because of its spontaneous precipitation as calcium phosphate during FO.

Membrane Distillation

Membrane distillation (MD) utilizes low-grade heat to drive separation [111]. In this process, the feed stream is separated from the distillate by a hydrophobic and microporous membrane, which cannot be penetrated by the liquid. The transport mechanism through the membrane occurs only in the vapor phase, and it is driven by a difference in the partial vapor pressure; consequently, MD can offer complete rejection of all non-volatile constituents in the feed solution [106,112]. From this point of view, MD can be used for the recovery of valuable components, concentrating them either in the feed or in the permeate. For example, non-volatile inorganic nutrient ions, such as K^+ and PO_4^{3-}, can be concentrated in the feed stream to make the following nutrient precipitation easier [84], while NH_3, being more volatile, can be transported through the hydrophobic membrane pores along with the vapor. Xie et al. [106] reported that over 96% of the ammonia could be recovered from the ADS centrate in the form of an aqueous solution, which could then be reused as fertilizer. To further enhance the capture of ammonia vapor in contact with MD, a low concentration of sulfuric acid (H_2SO_4 0.1 M) was used on the permeate side; in this way, ammonia recovery was improved up to 99%, with ammonium sulfate produced as a fertilizer. Kim et al. [113] applied a MD process, on laboratory scale, to treat the supernatant of ADS produced from the treatment of livestock wastewater. The authors, performing a short-term distillation for 90 min with a feed solution (pH 8.5) at 60 °C and permeate stream at 20 °C, achieved a more than 99% rejection of phosphorus and 90.3% rejection of TN. Xie et al. [114] demonstrated the extraction of phosphorus from ADS centrate by a hybrid FO−MD system with a $MgCl_2$ draw solution. In this FO−MD hybrid process, FO concentrates $P–PO_4^{3-}$ and $N–NH_4^+$ for the following nutrient recovery in the form of struvite, while MD is used to recover the draw solution. The reverse Mg^{2+} permeation (reverse Mg^{2+} flux of 12 mmol/m^2 h) was also important, which substantially increased the feed Mg^{2+} concentration in the system, thereby supplementing Mg^{2+} for struvite formation. Struvite formation was not quantified but was indicated by the continuous decrease of solution pH and by the ionic product that was $10^{-5.77}$ M^3, above the struvite conditional solubility product. To prove this, the precipitates obtained in the hybrid process were verified to be struvite crystals by examining the crystal morphology, element composition, and crystal structure.

Electrodialysis

Electrodialysis (ED) is a membrane process in which semi-permeable membranes are applied to separate ions under the influence of an electric potential that allows cations and anions to migrate towards the cathode and the anode, respectively. ED can selectively fraction nutrients from wastewater streams into high-quality nutrient products [106]. Ion separation is achieved by ion-exchange membranes, which comprise cation-selective, anion-selective, and bipolar membranes (which comprise a cation-selective and an anion-selective membrane). When bipolar membranes are used in an ED process, dissociation of solvent molecules, such as water, into H^+ and OH^- can be realized and this can diversify the final products and enhance the purity for nutrient recovery [106]. Combining H^+ and anions in certain chambers leads to the production of acids, while the combination of cations and OH^- leads to the production of the corresponding base. Wang et al. [115] employed the ED process with a bipolar membrane to convert the $P-PO_4^{3-}$ contained in sludge supernatant to purified phosphoric acid at a concentration of 0.075 mol/L. Wang et al. [116] conducted an experimental study on the recovery of ammonia and PO_4^{3-} by ED integrated with struvite precipitation; ED was mainly employed to obtain a concentrated nutrient salt solution that was fed into the precipitation reactor in order to precipitate N and P salts as struvite. By further treating the concentrate solution with ammonia stripping, the authors could obtain a removal ratio of about 95.8–100% for NH_3 and 86.1–94.4% for PO_4^{3-}. In the literature, no studies report on the recovery of potassium from ADS with ED. Nevertheless, there are some useful applications of K recovery from other organic waste substrates. Barros et al. [117], aiming at the generation of a potassium concentrated stream, were able to recover 72% of potassium from vinasse, which is characterized by a high concentration of K^+ (0.04–11 g/L).

Table 3. Removal/recovery of N and P from SS and ADS streams through membrane technologies.

Sludge Type	TS (g/L)	pH	Membrane System	Influent N–NH_4^+ (mg/L)	Influent P–PO_4^{3-} (mg/L)	N Removal (%)	P Removal (%)	Ref.
Wet-oxidized ADS and SS	5–20	1.5–2	UF-NF	-	87–152	-	68 [1]	[100]
Nutrient-enriched SS	-	7.2	FO	100–200	100–200	96–98	98–99	[109]
ADS centrate	-	7–8	FO-RO	1011	78	83–95	100	[118]
ADS centrate	1800	7.72	FO-MD-struvite precipitation	418	73	90	97	[113]

[1] assuming a permeate recovery of 90% and a rejection of 50%.

3.2.4. Thermal Treatments

Thermal treatments include incineration, pyrolysis, gasification, and hydrothermal carbonization (HTC), depending on temperature, pressure, and oxygen conditions. Conversion of municipal SS by different thermal processes yields solid residuals (ashes and chars) with significant differences in their composition, values, and qualities [119,120]. Thermal treatments are not applied only to raw SS, but can also be carried out on ADS, providing an energetically favorable treatment cycle, which includes sending the SS to AD to produce biogas and then sending the ADS to thermal treatment [121]. Since the products of thermal processes retain most of the P, N, and K originally contained in the treated sludge, it is possible to use them directly as soil improvers or to further treat them via chemical and thermochemical routes to release the nutrients [3].

Incineration

Due to a significant reduction of the SS volume, thermal degradation of toxic components, and high energy efficiency, incineration is one of the most applied thermal technologies for SS treatment [122]. During the incineration process, combustible material is oxidized and energy is released as thermal energy in the flue gas, while the organic pollutants, endocrine disruptors, and pathogens contained in SS are destroyed, and volatile HMs, such as quicksilver, are transferred to the flue gas. Nutrients, especially P, are not transferred to the flue gas, as they are kept in the incinerator ash [123]. The content of P in SS is estimated to range from 1% to 5%, while the P content in SS ash can reach 20% [41]. As a result, more phosphorus can be recovered per kg of ashes than of SS. Unfortunately, incineration appears economically viable only in large WWTPs, mainly because of the large capital costs associated with the compliance with ecological criteria. An opportunity could be to exploit existing incineration plants in the vicinity of the WWTPs. Moreover, during the combustion process, phosphorus is transferred into low-solubility mineral phases with low availability for plants. It is therefore necessary to transfer the P-PO_4^{3-} by means of a suitable thermochemical reaction to a plant-available form [123]. Adam et al. [124] suggested a two-step thermal treatment based on (1) mono-incineration of municipal SS, and (2) thermochemical treatment of the resulting ashes. The authors were able to completely remove the critical organic pollutants from mono-incineration, obtaining, as a product, ashes with a P_2O_5 content of 21.4%, comparable with conventional P-fertilizers. However, the phosphorus in the raw ashes has a poor bioavailability and high HMs concentrations. Therefore, in a second thermochemical step, HMs are removed and P is transferred into mineral phases available for plants. Smol et al. [125] thermochemically treated SS ashes coming from mono-incineration, together with sodium additives and a reducing agent (dried SS), to remove HMs and transform the insoluble P present in the SS ashes into $CaNaPO_4$, which is available to plants. The authors also made a comparison between the P solubility in the raw ashes and in the thermochemically treated ashes, using neutral ammonium citrate as a bioavailability indicator, and found that the P solubility was significantly increased from 19.7–45.7% to 76.5–100%. Nevertheless, P recovery processes mainly aim at separating HMs from the valuable P and at converting P to a form readily available to plants for reuse as fertilizer or into a raw material for the P-industry.

Two categories of P recovery technologies are available from SS ashes: wet chemical approaches, and thermal approaches. Thermal approaches separate P and HMs at temperatures of 1000–2000 °C and transform P into a plant-available form [123,124,126], while wet chemical approaches include acid and alkaline dissolution techniques. Chemical extraction is the most used method for its high efficiency and low cost, but it also leaches metal/metalloids present in SS ashes. To recover P from the leachate, it can be precipitated by adjusting the pH to 4, but it is necessary to add cations to transform the metal-P precipitates into plant-available fertilizer [126]. However, due to P losses during the purification process, the conventional method for P extraction results in a low recovery efficiency [127]. To solve this problem, it is necessary to find suitable leaching agents to separate P from metals/metalloids. Organic acids induce chelating effects that greatly increase the leaching of metals/metalloids from ash and soil [126]. Inorganic acids leach alkali metal oxides and release all phases containing P, of which sulfuric acid and nitric acid proved to have a high P releasing capacity [128,129]. In order to ameliorate these drawbacks, Petzet et al. [127] developed a combined acid–base extraction procedure: the investigated process requires an acidic pre-treatment in which the P fraction of the raw SS ashes that is bound as calcium phosphate is converted into aluminum phosphate. This newly formed aluminum phosphate can be dissolved via alkaline treatment and easily separated from the leachate via precipitation of calcium phosphate. The described sequential treatment process yields P-recovery rates as high as 70–77%. Currently, the recovery of phosphorus from fly ashes is more expensive than the production of P from phosphorus ores; the former is, therefore, not economically feasible [41,123]. At the same

time, a price increase is expected for phosphorus from natural deposits in the future, which may make the costs for phosphorus recovery from SS more competitive [41,130]. N and K cannot be effectively recovered through incineration, as N is lost as nitrogen gas during combustion, while K is generally water-soluble and not incorporated into the SS ash [131].

Pyrolysis and Gasification

Pyrolysis is the thermal process by which organic material decomposes under oxygen-free atmosphere at ambient pressure and temperatures between 400 and 800 °C [132]. Differently from incineration, which occurs in the presence of oxygen and above 800 °C, pyrolysis operates in the absence of oxygen and at lower temperatures [3]. Moreover, compared to the incineration process, which is highly exothermic, pyrolysis is endothermic, of the order of 100 kJ/kg dry solids [133]. This process generates gas and vapors, and liquid (bio-oil and tar) and solid (biochar) products [134] in a ratio which depends on the process parameters [122]. Due to the anoxic conditions, most of the carbon substances (e.g., cellulose, starch, lignin, and glucose) can be hydrolyzed and converted to biochar, with non-vapor elements coexisting [48]. Pyrolysis can be applied to convert raw, digested and waste-activated SS into syngas and biochar as by-products. It has been estimated that AD of SS followed by pyrolysis yields higher rates of energy recovery than stand-alone AD or pyrolysis [135]. Cao and Pawlowski [135] assessed the energy conversion efficiency of two parallel sludge-to-energy pathways: one pathway was based on AD followed by pyrolysis; the other pathway was based on pyrolysis alone. To characterize the energetic performance of the two pathways two indicators were used: the apparent energy efficiency (AEE), i.e., the ratio of the energy content in the target products to the energy content of the sludge feedstock, and the gross energy efficiency (GEE), which also considers the energy in process by-products (e.g., biochar). The results proved that the combination of AD and pyrolysis achieves higher energy efficiency (AEE 71.4%–GEE 92.5%) compared to the pathway employing pyrolysis alone (AEE 60.4%–GEE 89.8%).

Although similar to pyrolysis, gasification usually transforms organic materials to combustible gas or syngas, using between 20% and 40% of the oxygen required for total combustion [136]. Gasification can limit the problems commonly faced in the incineration process, such as the need for a supplemental fuel; emissions of SO_x, NO_x, HMs, and fly; ash as well as the potential production of chlorinated dibenzodioxins and dibenzofurans. The gasification syngas, which is a mixture of CO, H_2, and other gases, has a heating value typically in the range of 4–12 MJ/Nm³. Syngas is limited to local consumption, because its compression, storage, and transport are not economically attractive [136]. To date, pyrolysis and gasification are still poorly applied worldwide for full-scale valorization of SS. The main limitation to the spreading of these processes is the low quality of the obtained products, which require significant treatment before being used for energy and/or material recovery. For instance, tar is a complex mixture of condensable hydrocarbons, phenolic compounds, and HMs, and may cause various operational problems within the plant, e.g., blockage of filters, fuel lines, valves, and fuel injectors of engines. Moreover, tar compounds are a serious concern if released into the environment, being toxic and potentially carcinogenic [137]. The syngas obtained from SS may contain high levels of corrosive gases, i.e., H_2S and HCl, and has a lower calorific value compared to biogas (up to 40 MJ/Nm³) [138]. Utilization of char in agriculture may be limited by the high concentration of HMs, being mostly retained in the solid residue and concentrated because of the mass reduction resulting from thermal degradation [139].

In terms of nutrient recovery, both pyrolysis and gasification of SS could be coupled for efficient P removal and recovery. Indeed, the solid residues from pyrolysis and gasification are a sanitized source of minerals and some organic elements, including valuable fertilizing components, such as P_2O_5, K_2O, MgO, and Fe_2O_3, which makes them a potential substitute for natural phosphorus ore [140]. Pyrolysis can be designed and operated to retain most of the P and K and some of the N in the solid or liquid by-products.

Bridle and Pritchard [141] showed that pyrolysis of dried SS pellets performed at 450 °C at a pressure of 1.5 kPa retained 99% of P and K and 55% of N in the char. Results from this study showed that the phosphorus in the char was in its soluble form, available for plants, while nitrogen was in an insoluble form and, thus, less available for plant use. Based on these results, it appears that there is the potential to use pyrolysis as an effective means of recovering and reusing both the energy and phosphorus present in SS [89]. Vali et al. [142] showed that over 90% of the phosphorus contained in SS was retained in the char after pyrolysis at temperatures up to 850 °C, while higher temperature led to the formation of gaseous P compounds. At the same time, the concentration of HMs in the char decreased significantly (except Cu and Zn), as most of them were volatilized in the gas phase or solubilized into the aqueous phase. As reported in Table 4, K was also retained in the char at all tested temperatures. The obtained char could be used as soil improver or for further refinery in the fertilizer industry. Atienza-Martínez et al. [143] recovered nearly all phosphorus contained in the gasification ash of SS by extraction with sulfuric and oxalic acid at stoichiometric concentrations. Likewise, Gorazda et al. [140] demonstrated that acidic extraction (with nitric and/or phosphoric acid) was able to recover P with extraction efficiencies of 73–82%, transferring it from solid residue of ADS gasification into a plant-available form in leachates, which can be used for fertilizer production. Other studies confirm the presence of K in the gasification ashes of SS [144]: 0.55wt% [145], 4.63wt% [146], and 1.11wt% [147]. Nevertheless, these studies did not focus on the recovery of this element. The recovery of N through gasification is not possible, as it is diluted in the form of N_2 in

Hydrothermal Carbonization

HTC is a hydro-thermal process that takes place in liquid water at temperatures of 180–250°C, pressure of 60–100 bar, and in the absence of oxygen. HTC requires lower temperatures than pyrolysis and gasification, but very high pressure [122]. During the HTC reaction, water, carbon dioxide, and other compounds are generated from the biomass, producing, in less than 10 h, a carbonaceous solid, the biocarbon (or hydrochar—HC), with characteristics similar to lignite, and an aqueous residue rich in the nutrients previously contained in the raw material (process water). The use of water as a solvent is a key factor for HTC, due to its good heat transfer and solvent properties [148]. In recent years, HTC has emerged as a promising technology for sustainable SS minimization and valorization of the solid products [149]. It can significantly reduce SS volume, decompose organic pollutants by hydrolysis and carbonization reactions, and generate valuable byproducts, including the hydrochar and process water [150]. In particular, HTC process water from SS is characterized by a higher nitrogen content than that resulting from the HTC of other biomasses [149]. HTC releases energy through carbonization and increases or maintains the reaction temperature in the HTC reactor, not requiring much additional energy input after the initial heating phase if the reactor energy losses are minimized. Escala et al. [151] calculated the energy balance based on assumptions regarding potential recoverable energy and showed that no additional external energy input is needed to support the reaction process for SS. These results were also confirmed by Aragón-Briceño et al. [152]; the authors demonstrated that the integration of the HTC process to the AD of SS showed a positive energy balance, with a maximum net energy production of 312.9 kWh per ton of treated sludge if the hydrochar is considered as a fuel source; increasing the net energy production 10 times compared to when only biogas is used as energy source.

HTC process water is commonly regarded as a wastewater and needs to be appropriately treated. However, it has a high soluble concentration of both organics and nutrients (particularly ammonia and potassium), allowing a potential application in liquid organic fertilizer production [153]. During HTC, nitrogen and phosphorus migrate from the raw SS to the process water in the form of NH_4^+ and PO_4^{3-}, which can be precipitated as struvite. Munir et al. [72] reported that struvite precipitation used as a

post-treatment on liquid residue, after SS hydrothermal treatment, was a cost-effective option for P-PO_4^{3-} recovery. P-PO_4^{3-} was recovered by adding $MgCl_2$ solution (1000 ppm) at pH 9 to facilitate precipitation of struvite. In this way, the struvite production was 9.5 kg/m^3 and P-PO_4^{3-} recovery of 80% was obtained. According to Aragón-Briceño et al. [154], the best scenarios for struvite production showed that 0.06 kg of struvite could be produced per ton of SS when coupling HTC to AD for SS treatment.

Table 4. Recovery of N, P, and K from ADS and SS streams through thermal treatments.

Sludge Type	System	T (°C)	Pressure (kPa)	Extraction Method	N, P and K Recovery	Ref.
Municipal SS	Incineration/ gasification	1000	-	-	(%P)IN ASHES = 11–25 (%K)IN ASHES = 0.6–2.8	[124]
SS	Pyrolysis	450	1.5	Sequential extraction	(%N)IN CHAR = 55 (%P)IN CHAR = 100	[141]
Char from pyrolysis of SS	Combustion/ Gasification	600–900	-	Leaching with oxalic acid	(%P)IN LEACHATE ≥ 90	[143]
Dry ADS	Gasification	800–1000	-	Leaching with nitric and/or phosphoric acid	(%P)IN SOLID RESIDUE = 8.76 (%P)IN LEACHATE = 73.5–81.5 (%K)IN SOLID RESIDUE = 0.703	[140]
SS	HTC	200	2100	-	(mg/L in liquid fraction) N: 2392–2419 P: 804–813 K: 1516–1519	[155]

4. Comparative Assessment of the Strategies for Exploiting the Nutrient Potential of ADS

Based on the above compiled information, a critical comparative overview of the described technologies and strategies for exploiting the nutrient content of ADS is given in this section.

Struvite precipitation/crystallization and ammonia stripping are the most applied technologies for nutrient removal and recovery from ADS at full scale and are typically performed on the liquid fraction of ADS, obtained from the solid–liquid separation commonly carried out within the WWTP by screw press separators, screening drum presses, or decanter centrifuges. Solid–liquid separation reduces the transportation cost of the digestate [156] and avoids clogging in the struvite crystallizer (usually a fluidized-bed or a mechanically stirred reactor) [157] and stripping column (being fed with the liquid fraction only) [158].

Table 5 lists the costs of the different technologies that can be applied for nutrient recovery from ADS. Struvite crystallization is the most expensive approach for nutrient recovery, although it results in the production of the most valuable recovery product (struvite) from ADS processing. Both struvite precipitation and ammonia stripping from the liquid fraction of ADS are not viable strategies when the removal of ammonia must be carried out to avoid inhibition of the process, such as during HSAD of SS, due to the high sludge viscosity. The application of a new technology, i.e., TFE, enables directly stripping ammonia from the digesting sludge [52,55,56], resulting in a powerful means for simultaneous process non-inhibition and two-fold production of fertilizers (high-solid ADS and ammonium sulfate) at full scale. Moreover, struvite precipitation during HSAD further increases the agronomic value of the produced ADS, promoting its application and public acceptance as a fertilizer, and can be also regarded as an alternative method of avoiding ammonia inhibition during HSAD of SS, as it can limit the build-up of ammonia in the digester.

Mg is commonly the limiting element for struvite precipitation. To promote the application of struvite precipitation at real scale, a cheaper source of Mg should be utilized. This could be obtained by combining struvite precipitation with other technologies, e.g., coupling struvite precipitation to ion exchange with zeolite. Natural zeolite can be modified by incorporating magnesium salts, and the Mg^{2+} released from the adsorption process can promote struvite crystallization [159]. In the hybrid process, zeolite rich in N and P removed from ADS could be used as a nutrient source for fertilizer production, partly recovering the costs for the purchase of zeolites. This would promote the use of zeolite for nutrient recovery, as, to date, no application has been reported at full-scale and no cost–benefit analyses exist in the literature for nutrient recovery from ADS using zeolites. Future research could be directed towards an assessment of the market value of recovered N- and P-rich zeolite, to be used as a slow-release fertilizer.

Membrane technologies can efficiently concentrate nutrients. However, the operating costs of the process at full scale, which are closely linked to power consumption, cleaning frequency, and membrane replacement, need further investigation. Future studies will have to find solutions to improving membrane filtration performance, in terms of chemical and energy requirements, which can be achieved by limiting the fouling problem and utilizing renewable energy sources. It is worth highlighting that a comprehensive analysis of the costs of membrane filtration should consider the possible final reuse of the permeate and concentrate, which in turn are region specific. However, membrane processes are not as versatile for nutrient recovery as other options discussed in this study; for instance, high-solid substrates are not likely to be conveniently addressed by this technology because they would worsen fouling issues and increase the process complexity.

Table 5. Cost estimation of different strategies for nutrient recovery from ADS.

Technology	Process Cost	Marketing Value of Recovered End-Products	Ref.
Side-stream ammonia stripping coupled to HSAD	1.17–1.83 €/kg N	0.77 €/kg N [1]	This study [160]
Ammonia stripping	2–7 €/kg N	0.77 €/kg N	[160,161]
Struvite precipitation	9–49 €/kg N 4–22 €/kg P	0.79–5.50 €/kg N 0.36–2.49 €/kg P	[81,162]
Membrane filtration	4–5 €/kg P [2]	0.11–0.42 €/kg N [3] 2.0–2.1 €/kg P [3] 0.11–0.30 €/kg K [3]	[81,105]
Thermal treatment	2–6 €/kg P [4]	0.85–4.25 €/kg P	[163–165]

[1] potential revenue associated with the sale of ammonium sulfate; [2] NF; [3] with reference to RO concentrate; [4] cost of wet-chemical leaching of SSA.

From a wider perspective, it should be also noted that most technologies for nutrient recovery have been investigated on both SS and ADS. The advantage of using ADS within these processes lays in the possibility of taking the greatest advantage of the SS by exploiting not only its nutrient content, but also its biochemical potential for biogas generation. HSAD of SS seems the most efficient strategy for exploiting the nutrient potential of SS, as it results in the production of ADS with a significant agronomic value in terms of humified organic matter and nutrient concentrations, which can be directly injected into the soil (if compliant with the established regulations), and ammonium sulfate/nitrate as an additional fertilizer. Thermal treatments allow obtaining ash/char, from which a high recovery rate of nutrients can be reached. Nevertheless, thermal treatments are highly energy-consuming and require expensive emission control and

further downstream gas treatment for pollutant mitigation. Due to these drawbacks, which increase the complexity of the process and capital costs and reduce the energy conversion efficiency, this technology seems the least promising. However, to improve the energy balance of the cycle, thermal treatments could be integrated with AD, in order to generate biogas as well as energy and nutrient-rich products. From this point of view, the choice of coupling thermal treatments to AD could represent a convenient alternative to direct SS treatment, although in some cases it represents an obvious choice, for example when the produced ADS cannot be directly used in agriculture, due to low quality (e.g., high concentrations of HMs and/or other contaminants) or not being compatible with the local regulation for agricultural use.

5. Conclusions

This review outlines the potential for nutrient recovery from SS and its anaerobically digested form in a sustainable context. Various technologies were classified for their ability to recover a specific nutrient (e.g., nitrogen with ammonia stripping) or to allow the simultaneous recovery of multiple nutrients (struvite precipitation, ion exchange, membrane technologies, and thermal treatments followed by nutrient extraction techniques) and critically discussed to shed light on the state of the art, recent advances, opportunities, challenges, and feasibility for full-scale application.

It is evident that both SS and ADS can be considered as a resource to be exploited from a circular economy perspective. The use of ADS appears as the more convenient option, as it allows both the recovery of energy via biogas generation and nutrients via different strategies, resulting in a positive energy balance and wider applicability for nutrient recycling. From this perspective, HSAD can be considered as a promising and convenient option for simple, direct, and full exploitation of the nutrient potential of ADS, due to the possibility of producing a digestate that, compared to the conventional one, has a higher agronomic value. Nevertheless, HSAD needs further technological improvements, in terms of the energy recovery from SS, as well as a wider acceptance of ADS utilization in agriculture, which needs to be enhanced both at social and legislative levels. Further research is also needed in the field of struvite precipitation from ADS, since this can be regarded as a strategy to recover valuable nutrients, while reducing the formation of undesired deposits within the digesters. In this context, lab scale trials to unveil the formation and precipitation mechanisms should be combined with full-scale investigations to address the definition of sustainable technical solutions, fully implementing circular economy principles in SS management.

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