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WATER POLLUTION (S SENGUPTA, SECTION EDITOR)

Nitrogen and Phosphorus Recovery from Wastewater

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Abstract Use of nitrogen- and phosphorus-based synthetic fertilizers shows an increasing trend, but this has led to large-scale influx of reactive nitrogen in the environment, with serious implications on human health and the environment. On the other hand, phosphorus, a non-renewable resource, faces a serious risk of depletion. Therefore, recovery and reuse of nitrogen and phosphorus is highly desirable. For nitrogen recovery, an ion exchange/adsorption-based process provides concentrated streams of reactive nitrogen. Bioelectrochemical systems efficiently and effectively recover nitrogen as NH_3 (g) or $(NH_4)_2SO_4$. Air stripping of ammonia from anaerobic digestate has been reported to recover 70–92 % of nitrogen. Membrane separation provides recovery in the order of 99–100 % with no secondary pollutant in the permeate. With regard to phosphorus (P) removal, physical filtration and membrane processes have the potential to reduce suspended P to trace amounts but provide minimal dissolved P removal. Chemical precipitation can remove 80–99 % P in wastewater streams and recover it in the form of fertilizer (struvite). Acid hydrolysis can convert recovered P into usable phosphoric acid and phosphate fertilizers. Physical-chemical adsorption and ion exchange media can reduce P to trace or non-detect concentrations, with minimal waste production and high reusability. Biological assimilation through constructed wetlands removes both N (83–87 %) and P (70–85 %) from wastewaters, with recovery in the form of fish/animal feeds and biofuel. The paper discusses methods and important results on recovery of nitrogen and phosphorus from wastewater.

Keywords Nutrient recovery · Nitrogen recovery · Phosphorus recovery · Sustainability

Introduction

Nutrients found in waste streams are mostly compounds of carbon, nitrogen, and phosphorus (CNP). All of them are important for sustenance of various life forms. Nitrogen and phosphorus are essential components of cell's DNA, amino-acids, and chlorophyll. In eukaryotic cells, phosphorus is the "energy currency" of the cells in the form of adenosine tri-phosphate, or ATP [1]. Nitrogen and phosphorus play critical roles in plant growth and food supply. While nitrogen abundantly exists in atmosphere (78 %) in a highly stable and non-reactive form N_2 gas, its content is limited in soils. Therefore, in order to make it usable and increase its availability in soils, nitrogen is fixed in reactive forms such as amino-acids, nitrate, and ammonia.

Most naturally occurring reactive nitrogen (6.5 Tg (teragram) N/year in US [2] and 100–300 Tg N/year globally [3]) comes from lightning (2 %) and biological fixation (98 %). However, natural fixing of nitrogen is insufficient to meet the food and energy demand of the rising world population [4]. Therefore, anthropogenic production of reactive nitrogen shows an increasing trend [5].

On the other hand, the problem with phosphorus in the environment is of exhaustion, since it is a non-renewable resource. The most common form of phosphorus on earth is locked in igneous and sedimentary deposits, with mining of these rocks being the most viable method of extraction. Using

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the current rates of extraction and consumption, these "readily exploitable" sources of phosphorus will be depleted within next 45–100 years, as shown in Fig. 1 [6]. Moreover, as these reserves become exhausted the quality will inevitably become more variable, leading to lower phosphorus concentrations and higher impurities [7].

The use of synthetic fertilizer shows an increasing trend of 15 Tg/year, with developing countries contributing more to the increase [3]. Smil et al. [8] estimate that the use of nitrogenous and phosphorus fertilizers has made a difference between malnutrition and adequate diet for nearly one-third of humanity. Evidently, use of nitrogenous and phosphorus-based fertilizers is critical to fight world hunger. However, only 4 Tg of reactive nitrogen (out of 170 Tg applied annually) actually accumulates in crop and the rest is lost through air and water pathways [8], impacting human health, bio-diversity, and air and water quality [3, 9]. Two percent of global reactive nitrogen introduced annually escapes as N_2O and contributes to global warming and affects the ozone layer [9] and 12 % escapes as NO_x and NH_3, affecting the atmosphere in numerous ways [10]. Additionally, resulting climate change and nitrogen interactions may also affect agricultural productivity by exposing crops to elevated O_3 levels [11], flooding and extreme precipitation, drought, and heat. Moreover, phosphorus discharge, even in concentrations, as low as 0.02 mg/l can induce eutrophication of rivers and lakes, making them bogs that are unfit for navigation, fresh water supply, recreation, or agriculture [12, 13]. Ever increasing large fertilizer production may not be able to fully meet the food demand unless nitrogen and phosphorus are managed judiciously.

Since a large fraction of the synthetic fertilizer production escapes into the atmosphere [8], recovery of lost nutrient holds promise in mitigating this problem. It works on the principle of 3R's: reduce, reuse, and recycle. Nutrient recovery, therefore, reduces the burden on reactive nitrogen and phosphorus production, which in turn would ensure less reactive nitrogen and phosphorus entry into the environment. This would lead to efficient use of nutrient and cause less adverse effect on the environment. Nutrient recovery would re-introduce recovered nitrogen and phosphorus as fertilizer and drop its price and thus the overall food cost. Apart from tangible economic benefits, it would also reduce the nitrogen and phosphorus loading in the atmosphere, leading to a cleaner and greener environment [14].
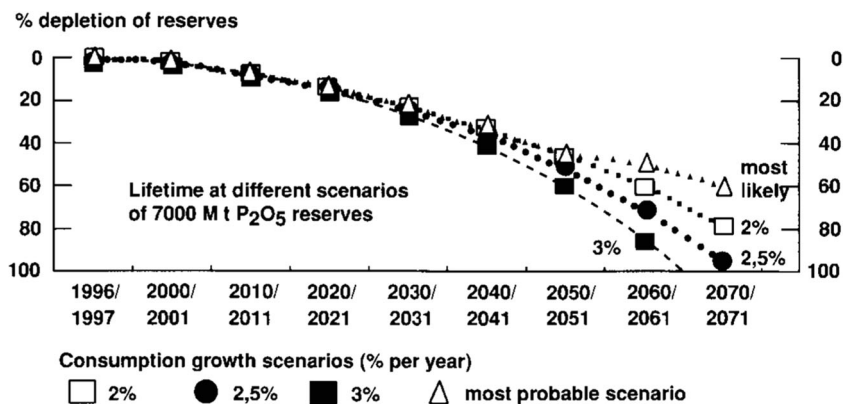
The objective of this review is to study and compile the methods used for nitrogen and phosphorus recovery from wastewater. The work outlines the theoretical mechanism and concepts and recent innovations and results of each method. The review covers methods based on physical, chemical, and biological principles.

Methods of Nitrogen Recovery

Ion Exchange and Adsorption-Based Methods

Reactive nitrogen exists as NH_4^+ at typical wastewater pH values [15]. It is also a significant contaminant in domestic grey water and urine [16]. Because it is a cation, ion exchange and adsorption-based processes are highly relevant because of their unique properties such as high selectivity for NH_4^+, high removal, fast uptake kinetics and regeneration [17–20], less space requirements and simplicity of application and operation [21], being environmental friendly [22] as it uses naturally occurring and easy-to-modify ion-exchanger/adsorbent such as zeolite [23•], and releases non-toxic exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}). The most popular ion exchanger/adsorbent for nitrogen recovery is zeolite. Natural zeolites have a tetrahedral framework where aluminum and silicon atoms are covalently bonded to common oxygen atoms forming interconnected cages and channels [22]. Substitution of each Si^{4+} with Al^{3+} causes a net negative charge on the framework. These substitutions are termed isomorphous as small sized atoms occupy sites previously occupied by larger atoms. The greater the substitution, the higher the negative charge on the zeolite. These negative charges within the pores are balanced by charged cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} on the zeolite surface. These cations are held by weaker electrostatic forces and are exchanged with NH_4^+ in the solution. There are more than 50 kinds of naturally occurring

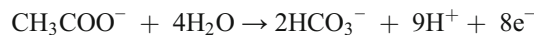Fig. 1 Estimated global phosphorus reserves (Source: Duley, 1998 [6])

zeolites [24] which occur at different places and have different characteristics [25, 26]. These differences in characteristics are attributed to variations in the regional geological formation [18]. Therefore, each zeolite has to be studied and modified individually to determine its optimum performance [26]. Performance of zeolites has been studied from the perspective of their homoionic forms, grain size, pH, influent NH_4^+ concentration, hydraulic retention time, ionic strength- competition with respect to other cations, and temperature [18, 19, 26]. Modification improves adsorption capacity and purity of zeolites. Treatment with acids, alkali and salts of alkaline metals, integrated calcinations, and microwave treatment are some of the popular modification techniques [23•, 26, 34•].

Once adsorbents/ion-exchangers are exhausted, nitrogen recovery and reuse opportunities are exploited. The loaded zeolites can be applied directly onto agricultural fields as slow-release fertilizers [26]. Most popular is the regeneration technique using NaCl solution [23•, 26] where NH_4^+ is desorbed and exchanged with Na^+ in solution. This provides a concentrated stream of NH_4^+ [18, 20]. Other regeneration techniques such as acid regeneration [20], heating regeneration (particularly useful for exothermic adsorption process) [23•], and biological regeneration [27] can also be used, depending on the recovery process employed subsequently [20]. The regeneration step results in concentrated stream of NH_4Cl in chemical regeneration [19, 25] or $NaNO_3$ in biological regeneration [27, 28]. The concentrated regenerant solution, after raising its pH above 9.3 (pKa of NH_4^+-NH_3 system), can be air stripped of its ammonia content, and the brine solution can be recovered. The NH_3 gas can be further sorbed into H_2SO_4 solution [29] or HNO_3 solution [30]. Liberti et al. [29] reported that the NH_3-sorbed H_2SO_4 solution could be used as a fertilizer. The nitrate-rich solution obtained after biological regeneration can also be used as a fertilizer [28]. Liberti et al. [31] proposed a combined anion and cation exchange scheme where both ammonium and phosphate ions were concentrated and then precipitated as magnesium ammonium phosphate also known as struvite, a known slow-release fertilizer. Karapinar [17] utilized ammonium-loaded zeolite as a seeding material for precipitating calcium phosphate and suggested the possibility of using the precipitate-ammonium-loaded zeolites as fertilizer. Lind et al. [32] used saturated clinoptilolite, wollastonite, and a natural zeolite and a small amount of MgO to recover nitrogen (65–80 % recovery) as struvite and as adsorbed crystalline NH_4^+ on the zeolites. Lin et al. [33] proposed a two-step scheme where NH_4^+ adsorption to a zeolite released Ca^{2+} ions to solution which formed the precipitate of calcium phosphate. Additionally, the used zeolite can be used as green fertilizer. Huang et al. [34•] used $MgCl_2$-modified zeolite to simultaneously precipitate ammonium and phosphate ions as struvite utilizing the Mg^{2+}-loaded zeolite as the magnesium source. Recently, some novel adsorbents, such as carbon nanotubes [35], hydrogels [36], and
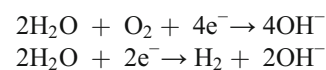
natural substances such as wheat straw and volcanic tuff, [37] have been reported for ammonium removal. Wang et al. [38] synthesized palygorskite nanocomposite which exhibited excellent adsorption capacity of 237.7 mg/g and was reused as a slow-release fertilizer. Zheng et al. [39] reported the use of chitosan-g-poly(acrylic acid)/attapulgite (CTS-g-PAA/APT) hydrogels prepared by in situ co-polymerization in aqueous solution. It showed an adsorption capacity of 21 mg/g. The NH_4^+-loaded hydrogel, with its unique water retention characteristics and multi-functionality, can be used as a fertilizer in agriculture. Wheat straw as adsorbents have received much focus recently [40, 41]. Wheat straw has a high ammonium uptake capacity of 148.7 mg/g [40]. Liu et al. [41] prepared super adsorbent resin (SAR) from wheat straw, optimized its performance, and suggested its use as a slow-release fertilizer. Jellali et al. [42] reported the use of another natural biodegradable waste Posidonia oceanica (P. oceanica) for ammonium recovery and suggested its possible use as bio-compost in agriculture. Wahab et al. [43] used sawdust to recover ammonium ions from the wastewater and suggested the use of ammonium-loaded sawdust as bio-compost and fertilizers.

Bioelectrochemical Systems (BES)

In BES, chemical energy contained in the organic matter is directly converted to electrical energy by certain microorganisms. Bio-oxidation of organic matter generates electrons and simultaneously produces other valuable compounds. At the anode, anaerobic bacteria oxidize the organic matter, often represented by the oxidation of acetate [44]:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$

Microorganisms transfer these generated electrons to anode, which is connected over an external circuit to cathode—the site of reduction reaction. Based on the cathodic reaction, BESs can be classified into two types: galvanic and electrolytic cells. Galvanic cells are microbial fuel cells (MFCs) which produce electricity by coupling the anodic oxidation to the reduction of an electron acceptor [45]. In electrolytic cells, typically called microbial electrolysis cell (MES), electricity is needed to carry out the reduction reaction at the cathode and anodic oxidation is coupled to reduction of protons to hydrogen gas [46, 47]. The cathodic reaction of an MFC is oxygen reduction reaction (ORR) and for MEC is hydrogen evolution reaction (HER). At near neutral or alkaline pH, the reaction can be written respectively as:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Anode and cathode chambers are separated by an ion exchange membrane to prevent mixing of the oxidation and reduction products [46, 48]. The ion exchange membrane

maintains electro-neutrality by allowing anions and/or cations to pass through.
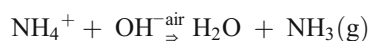
BES scheme is potentially a sustainable way of treating wastewater as it produces electricity and recovers ammonia and utilizes low-grade substrates such as wastewater itself as an electron source, thus reducing the use of carbon source. However, present energy recovery is too low [49]. Therefore, low energy recovery and requirements (due to reduced aeration) make it more suitable for contaminant removal and resource recovery.

In the case of ammonium recovery, the organic matter in wastewater is oxidized at the anode by bacteria, while ammonium ions are transported over a cation exchange membrane to the cathode chamber [50••], where the high pH allows for recovery as ammonia. BES systems do not need addition of a strong base as compared to other ammonia recovery technologies. Kuntke et al. [51••] successfully recovered ammonia from urine through volatilization due to high pH of the cathode chamber and aeration and subsequent absorption in an acid solution in an MFC. Desloover et al. [52] recovered ammonia from anaerobic digestate using an MEC, where ammonia transported across a membrane in the cathode was stripped by the produced hydrogen gas with much lower energy demand than the conventional stripping. Haddadi et al. [53] established that higher current density would greatly enhance the ammonia recovery in an MFC as 61 % of ammonia transport is electricity driven. Wu and Modin [54] using an MEC achieved simultaneous hydrogen production and ammonia recovery (96 % from synthetic wastewater and 79 % from real wastewater) by manipulating the catholyte pH to 12 obtained due to current generation.

BES schemes are new and need optimization of various parameters. Ammonia recovery greatly depends upon current density, catholyte pH, concentration of ammonium ions in the waste stream, type of membrane, and equilibrium among ions. These parameters are inter-related, e.g., current density determines catholyte pH which in turn is affected by type of membrane and ions in the solution [55]. Janicek et al. [56] conclude that pilot studies are essential to show the practical feasibility of BES. No full-scale applications of BES technologies have been reported so far. In 2013, Wetsus has set up a pilot plant at the water board of Fryslân, Leeuwarden, The Netherlands.

Air Stripping of Ammonia

Air stripping of ammonia has been in use for nitrogen removal [57]. It is a pH-dependent scheme where at pH around 9.3, ammonium nitrogen from solution converts to ammonia gas. Therefore, in the process, lime or caustic soda is usually applied to keep the pH around 10.8–11.5. This converts ammonium ions to ammonia in solution, and simultaneous air supply converts it to ammonia gas and strips ammonia according to the following reaction [58]:

$$NH_4^+ + OH^- \overset{air}{\Rightarrow} H_2O + NH_3(g)$$

For high stripping efficiency, the process is carried out in a packed tower, as it provides large mass transfer area. The process is affected by various factors such as ammonium concentration of feed, hydraulic loading, air flow rate, packing, etc., but most important are pH and temperature [59–61]. Guo et al. [59] reported increased ammonia recovery efficiency from 80 to 92 % on pH increase of 8–11. Gustin and Marinsck-Lograb [58] noted 27 % recovery efficiency at pH 8.5 but it rapidly rose to 92 % as the pH changed to 11. Several studies established a pH value of 11–12 for economically optimum recovery [60, 61]. Gustin and Marinsck-Lograb [58] reported a pH of 10.5 at temperature of 50 °C. Bonmati and Flotats [62] obtained 87 % recovery at a pH of 9.5 and a temperature of 80 °C; they also concluded that the air stripping is independent of pH at temperature greater than 80 °C. Katehis et al. [63] obtained a temperature value of 75 °C at which the process becomes pH insensitive. Ammonia stripping has been successfully used for large-scale treatment of municipal wastewater treatment plants [64]. However, in practice, packed towers are easily fouled [61]. Therefore, Quan et al. [60] came up with a newly designed gas liquid contactor, a water-sparged aerocyclone (WSA). The contactor displayed higher stripping efficiency and excellent mass transfer efficiency and consumed less air compared to stripping tanks and packed towers. Another concern in ammonia stripping is the chemical demand, which consists of (i) alkali for raising the pH and then (ii) acid for lowering the pH post stripping. CO_2 absorption using stripped ammonia can be used to adjust the pH. McLeod et al. [65••] came up with a novel scheme where ammonia-rich wastewater was used as an absorbent to selectively extract CO_2 from biogas, during its upgrading to biomethane in a packed bed mode. The study claimed recovery of ammonia as NH_4HCO_3, which is a commercially profitable fertilizer. Jiang et al. [66] recovered 90 % ammonia from anaerobically digested dairy manure as $(NH_4)_2SO_4$. The study suggested its use as concentrated nitrogen fertilizer. The scheme also produced electricity and biogas. Ledda et al. [67] used animal slurries to recover nitrogen as $(NH_4)_2SO_4$ from an integrated process scheme utilizing ultrafiltration, reverse osmosis, and cold ammonia stripping. The scheme recovered 71 % nitrogen with 1.8 m^3 concentrated $(NH_4)_2SO_4$ obtained for every 100 m^3 of treated digestate.

Membrane-Based Recovery Schemes

Membrane-based separation processes have been utilized in many wastewater operations [61, 68–70] with microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) being the predominant technologies. Nunes and

Peimmann [69] recovered ammonia gas in an acid solution using a gas-permeable membrane operated by vacuum pressure. Hasanoglu et al. [70] recovered ammonia as $(NH_4)_2SO_4$ on the permeate side of a macroporous hydrophobic membrane. Kurama et al. [71] recovered 96.9 % of ammonium ions from using RO. Gerardo et al. [72] using cross-flow MF recovered nitrogen and phosphorus from dairy farm sludge. Mondor et al. [73] produced a concentrated nitrogen fertilizer (containing 13 g/l of NH_3-N) from liquid swine manure using electro-dialysis and reverse osmosis; however, they noticed significant (21.2 %) ammonia volatilization in the process. Membrane-based processes offer distinct advantages as ammonia recovery is independent of gas or liquid flow rates, absence of secondary pollutants in ammonia permeate, and concentration of ammonia does not affect ammonia removal efficiency.

A summation of all nitrogen removal and recovery methods, as discussed above, is provided in Table 1:

Methods of Phosphorus Recovery

Physical Filtration and Membrane Processes

In areas where phosphorus concentrations are close to the regulated effluent levels, rapid sand filtration can offer a simple and practical solution for tertiary phosphorus reduction. Phosphorus in wastewater can exist as both solid organics and as dissolved phosphates. Solid organic phosphates are directly related to the concentration of 5-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), and volatile suspended solids (VSS) of the wastewater [74].

Performance evaluations performed by Barrett have shown that rapid sand filtration can remove, on average, 90 % of TSS in wastewater, leading to an effluent concentration of ~0.05 mg P/L in the form of organic phosphates [75]. While rapid sand filtration could provide a viable option for solid organic phosphate removal in wastewater, it will not help in the reduction of dissolved phosphorus, nor will it provide an easy source of recoverable phosphorus.

An alternative to rapid sand filtration is membrane filtration, which has been gaining ground in recent years due to improvements in performance and cost. Unlike rapid sand filtration, membrane filtration has the added benefit of collecting dissolved as well as solid phosphorus, drastically improving phosphorus removal. Some of the more common membrane filters currently in use are tertiary membrane filters, reverse osmosis (RO) systems, and membrane bioreactors (MBRs), which use a suspended growth medium to aid in removal. Facilities using these systems have seen effluent concentrations of ~0.04 mg P/L for tertiary membranes and MBRs, and as low as 0.008 mg P/L for RO systems [76]. Although these processes produce excellent results, they are often expensive and, like rapid sand filtration, do not provide an easily recoverable source of phosphorus.

Table 1 Summary of methods for nitrogen recovery

Method	Process	Recovery results	Remarks	Ref.
Ion exchange and adsorption	Na^+-activated natural zeolite	98 % recovery NH_4Cl	Max uptake at pH 7	[26]
	Concerted NH_4^+ uptake and PO_4^{3-} precipitation	Precipitate-NH_4^+-loaded natural zeolite	Uptake in 5 min	[17]
	Palygorskite nanocomposite	Uptake of 237.7 mg/g	Uptake in 15 min	[37]
	Resin prepared from wheat straw	Simultaneous uptake of NH_4^+ and PO_4^{3-} ions	Excellent water retention	[40]
Bioelectrochemical systems	Microbial fuel cell (MFC) and cation exchange membrane (CEM); recovery from urine	NH_3(g) recovery as $(NH_4)_2SO_4$	Low energy; no alkali needed	[50••]
	Recovery from anaerobic digester microbial electrolysis cells (MECs)	NH_3(g) stripped by produced H_2(g)	Low energy demand	[51••]
	Recovery from WW using MEC	H_2(g) produced and NH_3 recovery (96 %)	Low energy	[53]
Ammonia stripping	Ammonia-rich WW as absorbent to extract CO_2 from biogas	Recovered as NH_4HCO_3	High commercial viability; cleaner biogas fuel	[64]
	An integrated scheme involving ultrafiltration, reverse osmosis (RO) and cold stripping air stripping in packed bed tower	71 % recovery as $(NH_4)_2SO_4$ 92 % recovery	Recycled clean water (49 % of initial volume); high commercial viability process optimized for pH and temperature	[57, 62, 66]
Membrane separation	Macroporous hydrophobic membrane	Recovered as $(NH_4)_2SO_4$ on the permeate side	99.83 % recovery; requires ammonia volatilization	[69]
	RO on liquid swine manure	Recovered as conc. nitrogen fertilizer (13 g/l NH_3-N)	High NH_3 volatilization (21.2 %)	[72]

Chemical Precipitation

In some cases, the easiest and cheapest way to remove excess dissolved phosphorus from wastewater effluent is through chemical precipitation, often through the use of calcium, aluminum, or iron. The most common precipitates used by wastewater treatment facilities are lime ($Ca(OH)_2$), alum ($Al_2(SO_4)_3 \cdot 18H_2O$), and ferric chloride ($FeCl_3$) [77]. The use of these chemicals can also form trace amounts of soluble hydroxide and phosphate complexes, though the concentrations of these complexes are low enough that they should not interfere with precipitation.

Alkalinity, pH, and hardness are major factors to consider when using chemical precipitation to remove phosphorus from wastewater. Iron phosphate and its oxyhydroxide complexes approach minimum solubility at pH ranges of 4.0–6.0, while aluminum phosphate and its oxyhydroxide complexes reach minimum solubility at a pH range of 5.0–7.0. Because of this, adjusting pH is generally not a major issue; however both processes consume alkalinity, so adjustments may be required depending on the source of the wastewater influent. Calcium apatite ($Ca_{10}(PO_4)_6(OH)_2$) requires relatively high pH (>9.0) to reach minimum solubility, which requires softening of the wastewater through the formation of calcium carbonate ($CaCO_3$). The formation of $CaCO_3$, coupled with the intended precipitation of calcium apatite, dramatically adds to the sludge production of the treatment facility [74]. In spite of this increase in sludge, experimental usage of calcium precipitation with wastewater effluent [78], anaerobic digester liquor [79], and synthetic waste streams [80, 81•] show phosphorus removal between 80 and 99 %, assuming elevated pH values are used.

While precipitation will reduce dissolved phosphorus, reuse and recovery of the phosphate from the sludge is impractical, unless tertiary infrastructure is in place to perform chemical reduction [6]. Precipitation without recovery also has the negative effect of drastically increasing the amount of sludge formed during primary and secondary treatment, especially when using lime- or alum-based precipitation [82]. Even when the majority of phosphorus has been precipitated out of solution, residual calcium, aluminum, and iron salts will continue to precipitate with hydroxide; estimates show that sludge volume after chemical precipitation can increase by as much as 35 % [83].

One experimental attempt to recover calcium phosphate is the Geestmerambacht enhanced biological treatment process. Using a fluidized bed reactor, seed particles of silica are introduced to the effluent, collecting calcium phosphate and forming an easily extractable pellet. These pellets have relatively high phosphorus content (up to 11 % as phosphorus), low water content (5–10 %), and low heavy-metal impurities; although they are not as concentrated as phosphate rock, they do provide a clean source of phosphorus. Experimental data,

however, shows lower phosphorus loading than models would suggest, possibly due to interference from organic loading on the silica seeds [84].

In addition to calcium phosphate, many wastewater treatment plants have observed the natural formation of struvite, either in magnesium ($MgNH_4PO_4$) or potassium (KNH_4PO_4) form. This precipitate forms spontaneously at elevated pH levels (>8.0) when equal parts dissolved phosphate, ammonium, and either magnesium or potassium enter a highly turbulent system, such as in the underground transfer pipe networks of treatment facilities. Struvite is problematic for certain forms of phosphorus production due to its ability to release ammonia gas and produce high nitrogen emission levels. However, struvite can be used as a form of high-grade slow-release fertilizer, which makes it ideal for preventing excessive phosphorus concentrations in runoff [6]. Struvite formation has the added benefit of not only reducing dissolved levels of phosphorus and nitrogen but also in reducing hardness caused by magnesium. In many cases, particularly those where animal and agricultural waste is the main source of N and P, Mg must be supplemented into the system to promote crystallization. In recent years, struvite recovery has been implemented in the treatment of a variety of wastewater sources, including landfill leachate [85], anaerobic digester effluent [86], as well as swine [87, 88], poultry [89], and fertilizer wastewater [90•]. In all cases, after the introduction of Mg, struvite recovery was shown to be between 85 and 97 %.

High-Temperature Acid Hydrolysis

As phosphorus accounts for approximately 2–3 % of the organic solids in typical primary and secondary wastewater treatment sludge (higher if chemical precipitation is used), high-temperature acid hydrolysis and extraction of the phosphorus can be a viable option for some treatment facilities [91]. Research performed by Hultman has shown that normal wastewater treatment sludge that is dewatered, incinerated, and then digested in hydrochloric acid (HCl) can release phosphorus in the usable form of phosphoric acid (H_3PO_4) with up to 85 % yield [92]. H_3PO_4 is a key element to modified solvent extraction processes, which are essential to the development of feedstock. Acid hydrolysis does have the added drawback of co-dissolving concentrated amounts of iron, aluminum, calcium, and heavy metals alongside the phosphorus; recent work with pH adjustments [93], sulfide precipitation [94], and cation exchange [95•] have helped reduce these contaminant levels.

Sludge treatment can also be used to collect phosphorus in alternative forms. The CAMBI/KREPRO™ process uses high-temperature acid hydrolysis to reduce sludge into iron phosphate and a concentrated sludge residue, which can be used as a fertilizer and biofuel, respectively. This process has proven successful in Helsingborg, Sweden, where a full-scale

pilot system has proven to be capable of handling 500 kg TS/h with a 75 % recovery rate [92]. Additional work is also being done to react iron phosphate with iron sulfide to release soluble phosphates, which can then be used as a hybrid hydrolysis/precipitation process to form calcium phosphate or struvite. In some novel cases, the iron sulfide is being created on-site through sulfur-reducing microorganisms, allowing both the reduction of phosphorus and sulfur in the treated effluent [6].

Biological Assimilation

The use of constructed wetlands (CWs) for biological assimilation of excess nutrients is a fairly new concept, with Dr. Käthe Seidel conducting the first serious research into the design of efficient wetlands in 1953, and the first full-scale CW constructed in 1967 [96]. Since these first attempts, CWs have been used to treat a wide range of wastewaters, including effluent from domestic wastewaters, dairy farms, palm oil production, distilleries, natural rubber production, tanneries, textile manufacturing, electroplating, pulp and paper production, pesticide production, and heavy metal production [97].

Depending on location and the wastewater being treated, CWs can be categorized by their water level (free water surface or subsurface flow), the types of plants used (free-floating, floating-leaved, submerged, or emergent), and the flow direction (horizontal, vertical downflow, or vertical upflow). Nearly all CWs, however, use a combination of shallow water, low flow velocity, dense vegetation, and long, narrow channels to help create plug flow conditions to remove a wide variety of wastewater contaminants [98]. Suspended solids are removed through sedimentation, aggregation, and surface adhesion, while settleable organics are removed by deposition and filtration. Soluble organics are degraded aerobically and anaerobically by suspended microbial growth, and oxygen is added to the system through the air-water interface and the plant life present in the CWs [99]. Nitrogen is removed through nitrification/denitrification in aerobic and anaerobic zones; ammonia is oxidized in aerobic zones, and nitrate is converted to nitrogen gas and nitrous oxide in anoxic zones [100].

Phosphorus can be removed through microbial and vegetative assimilation, precipitation with di/trivalent cations in the soil/sediment, or adsorption onto clays and organic matter. Phosphorus can also be stored in peat accumulations. Subsurface CWs rarely precipitate or adsorb phosphorus due to the fact that the media used (crushed stone or pea gravel) is very low in iron, aluminum, and calcium, although high-sorption media such as steel slag and light weight clay aggregates do show promise for future CWs [101]. Microbial assimilation of phosphorus is often high, but it represents a short-term solution due to the high

turnover rate of microbes in CWs [102]. The temperature-dependent nature of many of these species restricts their use to tropical and subtropical regions, however [103]. This restriction prevents the use of biological assimilation in cold climates, although pilot plants such as the Houghton Lake Project in Ann Arbor, MI have been tested to develop stronger CW systems [104].

Because of these issues, biological assimilation through plant and algae uptake is one of the only reliable long-term method for phosphorus removal in most CWs [102]. The most common species of vegetation used for free-surface assimilation are *Eichhornia crassipes* (water hyacinth), *Pistia stratiotes* (water lettuce), and several species of *Lemnaceae* (duckweed); these aquatic plants can be harvested and sold as a source of nutrients in fish and animal feeds, while also removing as much as 83–87 % total nitrogen and 70–85 % total phosphorus removal from the wastewater streams [105]. In some places such as Ghana, fish and other aquacultural methods are being introduced to CWs that have high algae content; in addition to the harvested plant matter, the fish themselves thrive on the high-nutrient algae and can be sold for a profit [106••]. The conditions present in most CWs are also favorable for the controlled growth of algae that can be used to develop biofuels such as biodiesel, biomethane, and bioethanol [107•, 108•].

Physical-Chemical Adsorption and Ion Exchange

Physical-chemical adsorption offers many benefits over alternative phosphorus removal methods. Depending on the sorbent material, the attraction between sorbent and sorbate can be either physical or chemical; physical sorption generally uses van der Waals forces to attract the targeted solute, while chemical sorption removes the targeted solute through a chemical reaction [109].

Adsorption and ion exchange can be used either in the form of a fixed-bed column system through which wastewater is passed, or it can be dispersed throughout wastewater to be settled out in a downstream clarifier. Dispersal is best used when the sorbent material cannot be reused, if recovery of the solute is not necessary, or if increasing sludge volume is not a problem; powdered activated carbon is often used in this manner. When appropriate sorbents are used, fixed-bed column systems have several major advantages over other methods of phosphorus removal and recovery. Downstream from the column, the wastewater effluent contains non-detect or very low phosphorus concentrations until exhaustion of the sorbent is reached. Due to the physical nature of most commercial sorbents, there is also no additional sludge formed. The sorbent can also be regenerated and reused repeatedly, and phosphorus can be easily recovered from the regenerant in a usable form such as struvite [110]. Except for periodic cleaning, redirection of wastewater flow from exhaustion to

regeneration, and the subsequent removal of phosphorus from regenerant, sorption is an entirely passive process that requires little to no maintenance while running. A pilot-scale version of this process, called the REM NUT® process, was tested in Massafra, Italy. The hybrid ion exchange/precipitation process was able to remove ammonium, potassium, and orthophosphates through the use of a mixed bed of cation and anion exchange resins. Regeneration was performed using a 0.06 M NaCl solution, and the removed nutrients were then precipitated out as struvite through the addition of magnesium [111].

Many different materials have been suggested as phosphorus adsorbents. Unfortunately, each material is subjected to limitations based on its own specific composition, which makes it difficult to determine common removal and regeneration efficiencies. Ferric and aluminum hydroxides are common adsorbents, due to their ability to form ligands with oxy-anions such as phosphates [112–114]. Recent research has also included phosphorus

sorption onto fly ash [115], blast furnace slags [116], gas concrete [117], crushed oyster shell powder [118], alum sludge [119], active red mud [120], synthetic boehmites [121], and calcite [122].

Some common limitations to adsorption are the high cost of the regenerant solutions and the sorbents themselves, pretreatment of wastewater influent to function within the specific sorbent's capabilities, and the safe disposal of spent regenerant. Depending on the sorbent and regenerant used, these can be overcome through several means. Sorbents made from the waste products of other processes, like blast furnace slags and alum sludge, bring the cost of materials down. Precipitating phosphorus out of regenerant allows for the continued recycling and reuse of the solution. Using nonhazardous regenerant solutions, like seawater at a neutral pH, also reduces the need for hazardous waste disposal [30, 110].

A summation of all phosphorus removal and recovery methods, as discussed above, is provided in Table 2:

Table 2 Summary of methods of phosphorous recovery

Method	Process	Recovery results	Remarks	Ref.
Physical filtration and membrane processes	Rapid sand filtration	90 % TSS removal	Good suspended P removal, but minimal dissolved P removal	[74]
	Membrane filters	P reduction to trace amounts (0.008–0.04 mg/L effluent P concentrations)		[75]
	Membrane bioreactors			
	Reverse osmosis			
Chemical precipitation	Calcium, aluminum, and iron precipitation	Dissolved P removal of 80–99 %	Requires alkalinity and pH control, and leads to increased sludge production	[6, 73, 76–80, 81•, 82]
	Geestmerambacht enhanced biological treatment process	High P content (~11 %), low water content (5–10 %), low impurities	Low energy demand, no sludge formation	[83]
	Struvite	Reduces dissolved P to trace amounts, struvite recovery 85–97 %	Mg addition is required, spontaneous formation, can be used as high-grade fertilizer	[6, 84–89]
Chemical reduction and extraction	HCl digestion of WWTP sludge	Releases P as phosphoric acid with ~85 % recoverability	Produces key element for modified solvent extraction	[91]
	CAMBI/KREPRO™ process	reduction of WWTP sludge to iron phosphate with 75 % recovery	Produces iron phosphate fertilizer	[91]
	pH adjustments, sulfide precipitation, and cation exchange supplementation	Supplements other chemical reduction techniques	Reduces heavy metal contaminants and buildup of Fe, Al, and Ca ions	[6, 92–94]
Biological assimilation	Constructed wetlands	Combined nitrogen (83–87 %) and phosphorus (70–85 %) removal	Many alternative designs. Recovery as fish/animal feeds, biofuels, aquaculture	[95•, 96, 97, 99–105, 106••, 107•]
Physical-chemical adsorption and ion exchange	Fly ash	Wide variety of materials with wide range of results, non-detect and trace P concentrations possible	No additional sludge formation, regeneration allows for multiple uses and easy P recovery, passive systems, low maintenance	[114]
	Blast furnace slags			[115]
	Gas concrete			[116]
	Crushed oyster shells			[117]
	Alum sludge			[118]
	Active red mud			[119]
	Synthetic boehmites			[120]
	Calcite			[121]
	Ferric and aluminum hydroxides			[111–113]

Conclusion

Macronutrients nitrogen and phosphorus are essential for life on the earth. However, their removal from waste streams is also critical to mitigate the environmental problem of eutrophication of water-receiving bodies. A plethora of technologies exists that can achieve this goal; however, biological nitrification and de-nitrification and chemical precipitation are the most common processes used today to remove nitrogen and phosphorus, respectively. But both processes cannot achieve recovery of nitrogen or phosphorus. As readily extractable phosphorus deposits dwindle, and energy footprint plays an increasing role in nitrogenous fertilizer production, recovery of nitrogen and Phosphorus from waste stream is increasingly growing in importance. This practice is in alignment with a paradigm shift where the waste stream is not just to be looked upon as a cost item (to remove pollutants from it in order that environmental regulations are met) but as a carrier of extractable resources.

This paper presents an exhaustive review of processing technologies that can meet the goal of recovering Nitrogen and Phosphorus from a waste stream. Future research is needed to combine fundamental understanding with adaptation of technology for particular site/wastewater.

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