Phosphorus is essential to the growth of living organisms, and, therefore, its presence is considered vital for all forms of life. Research shows that phosphate rock reserves are reducing. Phosphate rock is used as raw material for the production of phosphate-based fertilizers, and its lack of supply could have adverse effects on the global food supply. New resources that can be a potential replacement for phosphate rock in the production of fertilizers and other phosphorus-containing substances are investigated.

This paper provides an overview of technology implementations, methods, and processes, as well as the latest achievements in the field of phosphorus recovery from waste streams. Different methods of phosphorus regeneration from sewage sludge and solid waste, and forms of phosphate regeneration are described. In addition, an overview of the following methods is given: nanonucleation, adsorption and ion exchange, solar evaporation, biological assimilation of P, and membrane technologies.

**Keywords:** phosphorus, recovery, waste streams, phosphorus fertilizers

### Introduction

Phosphorus is an essential element, and its deficiency can lead to a range of harmful effects on living organisms. It is a building block of DNA and RNA, and, being a constituent of phospholipids, also has a significant role in building cell membranes. It is also important for energy transfer through living cells, whereas significant amounts of phosphorus – mainly in the form of calcium hydroxyapatite, are present in the bodies of living things, primarily in bones and teeth\(^1,2\). All living organisms satisfy their phosphorus requirements through the food chain, primarily through the biological intake of phosphorus from the soil. However, the availability of phosphorus in the soil is low\(^3\). Namely, phosphorus can never be found free in nature due to its high reactivity; instead, minerals containing phosphorus (predominantly phosphates) are scattered around the world, mostly in sedimentary rocks.

Phosphate rock is the primary source of phosphorus and phosphates. Phosphate rock formations evolved over geologic time, as dissolved phosphorus in the ocean, gradually precipitated under certain conditions. Although phosphates are available as mineral deposits, phosphate rock is rarely used directly as a fertilizer due to low phosphorus availability and high transportation costs. Therefore, it serves as a basic raw material in the manufacture of artificial fertilizers.

The rate of exploitation of phosphate deposits exceeds by far the rate at which they are formed, making phosphorus a non-renewable resource. Phosphorus fertilizers are the leading input of inorganic phosphorus for agricultural soil, and approximately 70–80 % of phosphorus in cultivated soils is inorganic\(^4\). However, the increasing use of phosphate fertilizers in agriculture has led to the depletion of phosphate ores, and there has been more and more concern about a possible phosphate crisis in recent years.

Phosphate rocks are non-renewable resources. In 2014, the European Commission classified this raw material as critical from the aspect of estimated stocks. However, according to literature data on estimated phosphorus reserves from 2010\(^5,6\), the phosphorus crisis has been postponed for more than 300 years. Yet the distribution of world phosphorus reserves remains problematic. More than 70 % of world reserves are found in one country (Morocco). The imbalance between consumption and sources makes phosphorus a “geostrategic time bomb”\(^7\). On the other hand, about 85–90 % of phosphate in superphosphate is soluble in water\(^8\), so the rainwater
that enters an uncontrolled body of water leads to eutrophication, which causes negative consequences for aquatic ecosystems.

Therefore, there is a growing imperative to develop technologies that would regenerate phosphorus from other materials and, consequently, reduce the intake of phosphorus in aquatic ecosystems. The focus in science nowadays is to replace phosphate ores with secondary phosphates from waste streams according to the principles of circular economy. Unlike linear economy and the “take-make-dispose” approach, circular economy is based on the “reduce-reuse-recycle” model, which can be the key to solving the crisis caused by phosphate ore depletion. In addition, this model can be the solution for some environmental issues caused by excessive phosphate intake, such as the eutrophication of water.

This paper provides an overview of the literature on phosphorus regeneration from waste streams. The focus of the analysis are original research studies, which provide sufficient details about the applied technological procedures and methods for phosphorus regeneration. A review of the most important results is given further herein.

**Phosphorus cycle**

The phosphorus cycle is one of the slowest biogeochemical cycles on Earth. Its movement from rocks, across the land to the ocean is very slow (500 million years). Unlike many other biogeochemical cycles, the atmosphere does not significantly affect the movement of phosphorus. The global phosphorus cycle includes new phosphorus inputs into ecosystems, from weathering of rocks and minerals containing phosphorus and its transfer to soil and watercourses, deposition in the oceans, to the formation of new rocks due to pressure and temperature, and eventual uplift to terrestrial environment. Over time, some of the phosphorus is lost in watercourses and eventually in the sea, where it is re-incorporated into sedimentary rocks over long periods. The rate of phosphorus release due to rock decay depends on the type of mineral, topography, climate, and biota. Elution of primary minerals is an irreversible process. Once out of the rock structure, phosphorus can be physically or chemically adsorbed on soil particles or sediments that move by erosion or other processes that cause soil movement. Adsorption reactions are usually reversible. Phosphorus is taken from water and soil by microbes and plants, and then by animals. Phosphorus is returned to the soil by excretion from animals during their life and decomposition of plants and animals after death, where it can be taken over again by living beings. This part of the process, where the phosphate takes over the fauna and flora and then returns to the soil, can be repeated several times.

Today, the phosphorus cycle is dominated by human activities, especially agriculture. The obvious human impact on the phosphorus cycle comes from the exploitation of phosphate ore and its distribution throughout the planet in the form of fertilizers, animal feed, and detergents. Under human impact, approximately 3 times more phosphorus is released per cycle than in the period before the anthropogenic activities. Deforestation and associated land loss have also led to faster phosphorus loss from soil, due to increased erosion, and its transfer to surface waters. There is also a global movement of phosphorus through trade in agricultural products, livestock, and animal products. The movement of phosphorus locally from terrestrial to aquatic ecosystems also takes place through the discharge of untreated wastewater and leaks from septic tanks. The increased amount of phosphate in the soil from fertilizers and animal feces also leads to increased phosphate uptake into watercourses. Increased phosphate content in aquatic systems leads to the development of blue-green algae, which depletes water of oxygen and decimates aquatic ecosystems.

Thus, human activities affect many parts of the phosphorus cycle and result in the redistribution of phosphorus. It is obvious that the geological formation of phosphate rocks is negligible compared to their exploitation.

Due to the slow biogeochemical cycle of phosphorus, there is a problem with its recovery on land, which is manifested in declining reserves of accessible phosphate rocks, and more phosphorus in surface waters. These problems present the need for efficient phosphorus recovery and recycling schemes, which essentially replace the geological regeneration of phosphate rocks on a time scale relevant to the human-disturbed phosphorus cycle.

**Phosphorus crisis**

Humans directly exploit phosphorus from rocks to produce fertilizers and other phosphorus compounds. In 2021, approximately 22 million tons of phosphorus were excavated, of which about 95 % was added to agricultural systems in the form of fertilizers or animal feed. As the global population is expected to grow, demand for phosphorus will increase due to the rising need for food production. There is still a huge amount of unused phosphate resources due to the lack of feasible and economically viable methods for their extraction. In
general, two main approaches address the issue of phosphorus deficiency. The first one claims that the consumption rate will eventually regulate the rate of depletion of reserves, which will lead to a rather static state of reserves. Predictive approaches based on this assumption are the “ratio of reserves to consumption, i.e., production” (R/C ratio) for estimating the “lifetime” of available reserves. Prior to 2010, the R/C ratio for global phosphorus was estimated at just over a century, while the R/C ratio today is more than 300 years[11,13]. Another prediction approach consists of applying the Hubbert curve[14]. This is based on the assumption that the production of raw phosphate will follow the Gaussian distribution, and that the peak is half of the used up reserves[14].

Whichever assumption is correct, it should be distinct that some of the major phosphorus producers have an R/C ratio of only a few decades. In particular, China and the United States of America have had an R/C ratio of fewer than 30 years[15]. Walan et al. predict that exports in the future will largely depend on Morocco[16]. Cooper et al. predicted that 70% of global production is currently produced from reserves that will be consumed within 100 years, and Morocco with 73% of global reserves, will have to increase production by 700% by 2075[17].

All the presented data indicate that there is still no crisis in phosphorus resources. Yet the lack of P, whether it occurs decades or centuries from now, would be catastrophic for humanity. This risk suggests that society should now begin to modify current practices regarding P resource management, especially given that many of these practices result in environmental problems. On the other hand, an unstable political situation can jeopardize the certain supply of this particularly important raw material, so it is necessary to work constantly on the development of technologies that will enable efficient recovery – phosphorus regeneration.

**Recovery of phosphorus from waste streams**

The rise in awareness of the limitations of natural resources and the need for better management has increased in recent decades, and efforts have been made to develop a circular economy. The circular economy has become a new reality for which to strive. The use of circular economy in phosphorus management would be very useful, but examples of sustainable phosphorus chemistry are mostly limited to linear processes or small independent cycles, and do not close phosphorus cycles globally. The idea of collecting and using waste is becoming increasingly popular in the phosphorus industry. Various waste streams contain phosphorus[18], and if properly managed, they can be a significant source of this valuable element. Extracting phosphorus from waste can reduce the pressure on natural resources and the exploitation of phosphorus produced by traditional mining.

Over 50% of human phosphorus consumption in a country’s economy is lost through wastewater, so wastewater is a major resource for its recovery. Wastewater is mainly treated in wastewater treatment plants (WWTPs), where phosphate can be recovered from several sources: watercourses (untreated wastewater, urine, effluent after treatment), sewage sludge, or sewage sludge ash (SSA). Recovery of phosphorus from phosphorus-rich side streams has a recovery potential of maximum 50% of incoming phosphorus (using crystallization technologies), while extracting phosphorus from sewage sludge or sewage sludge ash can regenerate 90–95% of incoming phosphorus (total phosphorus removed from the WWTP is incorporated into sludge and ash)[19]. In addition, there are alternative sources of phosphate, including manure, slaughterhouse waste, and steel slag. Table 1 shows the technologies for the recovery of phosphorus from different waste streams.

The general characteristics of the process for the recovery of phosphorus from promising (prospective) waste streams and the forms in which phosphorus can be recovered are given further herein.

**Removal of phosphorus from wastewater**

When it comes to the removal of phosphorus from wastewater, only a few processes are successfully applied for its removal. Most of these processes are additions to other pretreatment processes, and improve overall phosphorus removal. There are three categories of processes for the removal of phosphorus: physical, chemical, and biological. These processes can be part of the primary, secondary, or tertiary treatment, depending on the configuration of the wastewater treatment plant (WWTP) [83-85].

Only a minor part of total phosphorus is removed by mechanical procedures. Significant removal of most of the phosphorus from wastewater can be achieved in two fundamentally different ways: physicochemical and biological processes, although both of these essentially include the formation of particles that can be separated from the water. Chemical precipitation, biological removal, and enhanced biological removal of phosphorus are more recent processes that reliably reduce the phosphorus load in wastewater. In addition to these two basic methods (physicochemical and biological), specific technologies are used, depending on the level of phosphorus removal to be achieved.
| Commercial name of the process/technology | Country | Comment / Use | Reactor type | Process efficiency (%) | Phosphorus removal technology | Laboratory / Pilot / Industrial use | Ref. |
|----------------------------------------|---------|---------------|--------------|------------------------|----------------------------|------------------------------------|------|
| AD-HAP                                 | Japan   | Recovery of phosphorus from wastewater in the form of calcium hydroxyapatite. Calcium chloride or lime is used as precipitating agent. | Continuous stirred-tank reactor | 72 | Chemical precipitation | – | 10–22 |
| AirPrex                                | Germany, Netherlands, USA, China | Recovery of phosphorus from wastewater or anaerobic digestion sludge in the form of struvite, with the addition of magnesium chloride, at pH about 8. | Airlift reactor with CO₂ stripping | 90–95 | Crystallization, precipitation, and separation | Commercially available technology | 22–25 |
| ANPHOS                                 | Netherlands, Italy, Spain | Recovery of phosphorus from wastewater or digestate in the form of struvite, with the addition of magnesium hydroxide, at pH about 8. | Airlift reactor with CO₂ stripping | 80–90 | Crystallization, precipitation, and separation | Commercially available technology | 26,27 |
| AshDec                                 | Germany | Recovery of phosphorus from sewage sludge ash in the form of calcined phosphate. | Fluidized-bed reactor | 95–98 | Thermochemical process at 850–900 °C | Pilot plant | 22,28,29 |
| Ash2^®Phos                             | Germany, Sweden | Recovery of phosphorus from sewage sludge ash in the form of mono/di-ammonium phosphate or mono/di-calcium phosphate. The process is based on wet chemical treatment. | Stirred-tank reactor | 90–95 | Wet chemical process | Pilot, Industrial | 22,30 |
| Crystalactor                           | China   | Phosphorus recovery from wastewater in the form of struvite. | Fluidized-bed reactor/crystallization reactor | 70–90 | Crystallization | Commercially available technology | 31,32 |
| EloPhos                                | Germany | Phosphorus recovery from sewage sludge in the form of struvite. | Crystallization reactor | 95 | Crystallization | Pilot plant | 33 |
| EUPHORE                                | Germany | Multistage process of thermochemical treatment of sewage sludge and other biomass (manure, digestate, possibly compost). Ash is obtained as a product, which could be used for P recovery. | Rotary pipe reactor | 95 | Thermochemical process (1st stage at 650–750 °C, 2nd stage at 900–1,100 °C) | Pilot, A mobile test plant is being implemented at the Mainz-Mombach sewage treatment plant to provide the basis for large-scale implementation | 34 |
| EXTRAPHOS®                             | Germany | Recovery of phosphorus from sewage sludge by dissolving phosphates and their precipitation in the form of dicalcium phosphate. Lime is used as precipitation agent. | Airlift reactor with CO₂ stripping | ~50 | Precipitation | – | 35,36 |
| Seabome/ Gifhorn                       | Germany | Recovery of nitrogen and phosphorus from sewage sludge and other organic waste in the mixture of struvite and calcium phosphate. | Stirred reactor, centrifuges, filters | 40–60 | Leaching, crystallization, precipitation | Laboratory, Pilot | 19,37,38 |
| Commercial name of the process/technology | Country | Comment / Use                                                                                                                                                                                                                                                                                                                                 | Reactor type                                                                 | Process efficiency (%) | Phosphorus removal technology | Laboratory / Pilot / Industrial use | Ref. |
|-----------------------------------------|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|-----------------------------|-----------------------------|----------------------------------|-----|
| Glatt® PHOS4green                       | Germany | Phosphorus recovery from sewage sludge and sewage sludge ash through a two-stage process (extraction with acid and additives followed by a process of continuous spray granulation in a fluidized-bed).                                                                                                                   | Batch reactor and granulator (continuous fluidized-bed spray granulation) | –                           | Leaching and fluidized-bed spray granulation | Industrial                        | 39,40 |
| J-OIL                                   | Japan, Taiwan | Phosphorus recovery from wastewater by acid degumming process in the form of hydroxyapatite. Calcium hydroxide is used as precipitation agent.                                                                                                                                                                                                  | – –                      | Precipitation               | –                           | 20                               |     |
| JSA                                     | Japan   | Recovery of phosphorus from wastewater in the form of calcium hydroxyapatite. Phosphorus precipitation performs with calcium hydroxide.                                                                                                                                                                                                                                                   | – 75                     | Precipitation               | –                           | 20                               |     |
| KURITA                                  | Japan, Taiwan | Recovery of phosphorus in the form of struvite or calcium phosphate from wastewater. If the phosphate rock is used as seed, calcium phosphate is formed.                                                                                                                                                                                                                           | Fixed-bed reactor for crystallization – | Precipitation               | –                           | 20,41                            |     |
| Kyowa Hakko                            | Japan   | Phosphorus recovery in the form of calcium hydroxyapatite. Calcium hydroxide is used as precipitation agent.                                                                                                                                                                                                                                                                                                                   | – >90                   | Precipitation               | –                           | 20                               |     |
| METAWATER                               | Japan   | Recovery of phosphorus from wastewater in the form of calcium hydroxyapatite directly from the sewage sludge ash, which is dissolved. Phosphates are precipitated with calcium hydroxide.                                                                                                                                                                                                                               | – –                      | Precipitation               | –                           | 42                               |     |
| NASKEO                                  | France  | Recovery of phosphorus in the form of struvite from wastewater. Magnesium oxide is used to precipitate phosphate.                                                                                                                                                                                                                                                                                                                  | Fluidized-bed reactor for crystallization 85–90                | Crystallization, Precipitation – | –                           | 27,43,44                        |     |
| Nippon PA                               | Japan   | Phosphorus recovery from sewage sludge ash in the form of phosphoric acid, by reaction of ash, as a partial replacement for phosphate rock, with sulfuric acid.                                                                                                                                                                                                                                                     | Extraction reactor –    | Extraction – Wet process of phosphoric acid production – | –                           | 20                               |     |
| NuReSys®                                | Belgium, Netherlands, Germany | Phosphorus recovery in the form of granular struvite from wastewater, digested sludge, dehydrated digestion sludge or residual liquid after sludge dewatering. Magnesium chloride is used as crystallization agent.                                                                                                                                                                                      | Stripping/ crystallization, stirred reactor 80–96              | Crystallization | Commercially available industrial technology | 45,46                            |     |
| Commercial name of the process/technology | Country | Comment / Use                                                                 | Reactor type                                                                 | Process efficiency (%) | Phosphorus removal technology | Laboratory / Pilot / Industrial use | Ref. |
|------------------------------------------|---------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------|-------------------------------|-----------------------------------|------|
| NutriTec® (Sustec, DMT)                  | Netherlands | Recovery of nitrogen and phosphorus from concentrated wastewater, or separately collected urine. Phosphate is separated by precipitation of struvite, followed by membrane separation of ammonia in the form of monoammonium sulfate. Magnesium chloride is added as precipitation agent. | Air lift crystallization reactor, membrane reactor | –                      | Crystallization Membrane separation | Industrial                       | 47   |
| OFMSW & BNR                              | Italy, Spain | Recovery of phosphorus from wastewater by a three-stage system that combines anaerobic digestion of the organic fraction of municipal solid waste, biological removal of nutrients and crystallization of phosphate as struvite. | Digester, stirred reactor, crystallization reactor | 70                    | Crystallization               | Laboratory, Pilot, Industrial     | 48–50|
| PEARL Fx (Multiform™)                    | USA     | Recovery of phosphorus in the form of struvite from urban wastewater treatment plants and agro-industrial wastewater. Magnesium chloride is used as crystallization agent. | Fluidized-bed reactor without recirculation | 80                    | Crystallization               | Industrial                       | 51,52|
| PEARL® (OSTARA)                          | USA, Canada, Netherlands, Poland, Norway, Israel, Spain, Ireland | Recovery of phosphorus in the form of highly pure crystalline struvite granules from wastewater by controlled chemical precipitation. Magnesium chloride is added as a precipitation agent. | Recirculated fluidized-bed reactor | 85–95       | Crystallization               | Commercially available technology | 53–55|
| PHORWater                                | Spain   | Phosphorus recovery in the form of struvite, from sludge before anaerobic digestion. Magnesium chloride is added as precipitation agent. | A continuously stirred reactor composed of a reaction zone and a sedimentation zone | >90                  | Crystallization               | Pilot                             | 56   |
| Phosnix®                                 | Japan   | Recovery of phosphorus in the form of struvite from wastewater after anaerobic digestion of sludge. Magnesium hydroxide is added as agent for phosphorus nucleation. | Reactor with aeration and fluidized-bed of struvite | 80–90       | Crystallization               | Commercially available technology | 57–59|
| PHOSPAQ™                                 | Netherlands, China, Poland, Great Britain, USA, Germany | Recovery of phosphorus in the form of struvite from industrial wastewater and sewage sludge liquids. Magnesium oxide is added as precipitating agent. | Reactor with CO₂ aeration | 70–95       | Crystallization Precipitation | Commercially available technology | 52,60,61|
| Commercial name of the process/technology | Country | Comment / Use                                                                                                                                                                                                 | Reactor type                                      | Process efficiency (%) | Phosphorus removal technology | Laboratory / Pilot / Industrial use | Ref. |
|-----------------------------------------|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|------------------------|-------------------------------|----------------------------------|------|
| PhosphoGREEN (SUEZ)                    | Denmark, France | Recovery of phosphorus in the form of struvite from wastewater after biological treatment/anaerobic digestion of sludge. Magnesium chloride is used as precipitation agent. | Reactor with aeration, fluidized-bed and recirculation | 90                     | Precipitation                 | Commercially available technology | 62,63 |
| PhosphoReduc LLC                       | USA     | Recovery of P by passive filtration systems, consisting of one or more filter units filled with iron and/or calcium-based filtration material.                                                              | Filter modules with filling (modular media filters) | 70–100                 | Filtration                    | Commercially available technology | 64,65 |
| Phostrip Process                       | USA, Germany, Austria | Phosphorus recovery in the form of calcium phosphate from recirculated activated sludge from non-EBPR plants. Phosphorus-enriched wastewater goes to a fluidized-bed reactor where precipitation is performed using lime. | Fluidized-bed reactor – Crystallization Precipitation | –                     | –                             | Laboratory, Pilot                | 66,67 |
| RIM-NUT Process                        | Italy   | Recovery of phosphorus and nitrogen from wastewater (from ion exchange regeneration) in the form of struvite. Magnesium chloride is used as precipitation agent.                                                   | Selective ion exchanger, precipitator – Ion exchange, precipitation | –                     | –                             | Industrial                       | 68,69 |
| Rintoru®                               | Japan   | Recovery of phosphorus from wastewater in the form of calcium phosphate. A mobile unit that uses amorphous calcium silicate that has a high affinity for phosphorus.                                           | –                                                | 70–80                  | Selective adsorption          | Pilot                           | 20   |
| STRUVIA™                               | Denmark | Recovery of phosphorus from wastewater (containing high concentrations of phosphorus, e.g., from dehydration of anaerobic sludge) in the form of struvite, directly from the wastewater stream. The precipitation of struvite is started by increasing the pH and adding magnesium sulfate. | Continuous stirred reactor (Turbomik™), Integrated lamella clarifier | >85                    | Crystallization                | Commercially available technology | 70   |
| Stuttgart Process                      | Germany | Recovery of P from wastewater in the form of struvite. First, it is necessary to perform acid leaching of phosphate from anaerobically stabilized sludge, then separation of heavy metals by complexing with citric acid, and finally precipitation of struvite with magnesium oxide. | Stirred reactor – Leaching, separation, precipitation | 45–65                  | –                             | Pilot                           | 71,72 |
| Swing                                  | Japan   | Phosphorus recovery in the form of struvite, directly from digested sludge. Magnesium hydroxide is used as precipitating agent.                                                                                     | Stirred reactor – Precipitation                   | 30–40                  | –                             | –                                | 20   |
| Commercial name of the process/technology | Country      | Comment / Use                                                                 | Reactor type                                                                 | Process efficiency (%) | Phosphorus removal technology | Laboratory / Pilot / Industrial use | Ref. |
|----------------------------------------|--------------|-------------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------|-------------------------------|-----------------------------------|------|
| Terra Blue Inc.                         | USA          | Phosphorus recovery from swine farming wastewater, through a multi-stage system which uses polymers and flocculants that promote particle coagulation, followed by separation of the liquid and solid phases. Ammonia nitrogen is removed from the liquid phase using bacteria adapted to high-load wastewater, and phosphorus is removed in the form of calcium phosphate. Lime is used as precipitating agent. | Stirred reactor, clarifier                                                | 88.5–92                | Precipitation                  | Industrial                                        | 73–75 |
| TetraPhos®                             | Germany      | Recovery of phosphate as phosphoric acid, with acid leaching of sewage sludge ash. (Brand RePacid®).                                                                                       | Stirred-tank reactor                                                     | >80                    | Leaching                       | Industrial                                        | 76,77 |
| Mobile plant                           | Japan        | Extraction of phosphorus from the liquid phase after anaerobic digestion of sewage sludge, using a bifunctional agent (amorphous calcium-silico hydrate) for adsorption-aggregation. | Stirred-tank reactor and bag filter separator                             | ~80                    | Adsorption, aggregation, precipitation | Potentially commercial application at small plants | 78   |
| Kubota process                         | Japan        | Recovery of phosphorus from sewage sludge in the form of slag. More than 90 % of phosphorus in slag is phosphorus soluble in citric acid.                                               | Kubota Surface Melting Furnace (KSMF)                                     | ~80                    | Termochemical process at 1300 °C | Laboratory, Pilot, Industrial                 | 79   |
| Ecophos process (ESPC3)                | Belgium, Netherlands, Syria, Bulgaria, Peru | Modular process for valorization of P from different alternative sources. The process is extremely flexible and capable of using several types of raw materials for the production of different products. The process has economic and environmental benefits. | Modular units that can be combined to generate target products             | ≥90                    | Acid digestion, separation, chemical precipitation, ion exchange | Laboratory, pilot and industrial applications (Commercial applications with phosphate ore and pilot applications with ash). | 80,81 |
| RecoPhos process                       | Germany, Netherlands | Regeneration of phosphorus from sewage sludge ash, meat and bone meal ash and struvite ash. No waste is generated, only products with a positive market value. | –                                                                          | –                      | Thermal process at 1600 °C     | Extensive pilot tests and few plant-level tests. | 82   |
| Tenova process                         | Germany, Netherlands | Production of phosphoric acid by treatment of sewage sludge ash with HCl by-product, which is purified in several extraction phases.                                              | –                                                                          | –                      | Extraction                      | Laboratory tests and only a few pilot plants.     | 82   |
Whether phosphorus is removed by chemicals or biologically, its removal is based on converting soluble forms, most of which are in the form of orthophosphate \((\text{PO}_4^{3-})\), into solids. Solid phosphorus becomes part of total suspended solids \((\text{TSS})\) and is further removed as sludge.

In chemical and biological processes, a significant amount of sludge is formed, so special attention must be paid to the issues of sludge handling and treatment of \(P\) in the side streams of sludge. Due to the high water content and poor sludge quality, the reuse of phosphates from the sludge in the past was not an economically viable option. However, as the total amount of phosphorus removed from wastewater ends up in the sludge, more attention has recently been paid to developing technologies for phosphorus regeneration and reuse, which is increasingly important for the long-term availability of this limited resource.

As chemical and biological processes are the two main techniques for removing phosphorus from domestic and industrial wastewater, many variations and combinations of these processes are used in practice.

**Chemical precipitation**

Chemical precipitation is one of the frequently used technologies for the removal of dissolved phosphorus from wastewater. By adding chemicals, dissolved phosphorus is converted into solids, which are removed from wastewater along with sludge. This procedure is based on the precipitation of insoluble metal phosphates after the addition of metal salts (usually iron, aluminum, magnesium, and calcium), and can be applied at different stages of the wastewater treatment process. Primary sedimentation includes the addition of chemicals before sedimentation, and the precipitate ends up in the primary sludge. In the case of secondary precipitation, iron or aluminum salts are added directly to the aeration tank in the activated sludge process, with phosphorus ending up in the secondary sludge. The third option is to add flocculant after sludge treatment, which produces relatively pure tertiary sludge. This phosphorus extraction technology has contributed significantly to the development of \(P\) recovery techniques\(^{68}\).

**Enhanced biological phosphorus removal**

All aerobic wastewater treatment systems have a natural ability to remove phosphorus. Phosphorus removal in conventional biological treatment is not good enough to meet effluent standards. Usually, phosphorus removal efficiency in classical biological wastewater treatment ranges from 10 to 25%.

That is the reason for using an advanced biological procedure named the Enhanced Biological Phosphorus Removal (EBPR). EBPR is a sustainable, environmentally friendly wastewater treatment technology that is implemented by changing anaerobic and aerobic conditions to enable the accumulation of phosphorus by phosphate-accumulating organisms (PAOs)\(^{90}\). These microorganisms can store more phosphorus than other bacteria naturally present in activated sludge, and their growth intensifies through alternating anaerobic and aerobic zones.

Phosphate-accumulating organisms accumulate phosphates by storing polyphosphates as energy reserves in intracellular granules. PAOs then use the energy previously stored as polyphosphate to grow biomass and release \(P\) during the anaerobic phase. The described procedure has been used for 40 years in wastewater treatment plants with activated sludge. This phosphorus extraction technology has contributed significantly to the development of \(P\) recovery techniques\(^{92}\).

EBPR is a much more advantageous technology for phosphorus regeneration than chemical phosphorus removal. Phosphorus is absorbed in activated sludge, and it is somewhat easier to regenerate it compared to chemical sludge. Due to the lack of chemicals used in this process, EBPR systems have lower sludge production, lower chemical costs, and lower metal content in the sludge. This process is particularly important for agriculture because phosphorus is not bound to metals, which makes it more accessible to plants. However, the EBPR process is highly dependent on wastewater characteristics, and is less stable and flexible compared to chemical precipitation\(^{93}\). The process usually involves more complex control mechanisms and reactors with larger volumes. Under favorable conditions, sludge can contain about 90% of incoming phosphorus\(^{94}\).

In a wastewater treatment system, the wastewater first enters an anaerobic medium containing readily biodegradable carbon \((\text{C})\), and is mixed with the flowback, followed by an anaerobic zone. The process is initiated when phosphate-accumulating organisms are mixed with conventional microorganisms. PAOs specialize in the storage and metabolism of phosphorus, while conventional bacteria can easily convert biodegradable material from the anaerobic zone to volatile fatty acids \((\text{VFAs})\) needed to complete the process. Under anaerobic condi-
tions, PAOs, in the presence of fermentation products, assimilate VFAs and store them as polyhydroxyalkanoates or PHAs, using stored polyphosphate as an energy source and releasing a soluble phosphate anion, magnesium, calcium, and potassium. The bacterial cells can then be separated and recycled, and the released soluble phosphate is removed by precipitation. In the aerobic phase, soluble P is absorbed to form cellular polyphosphate. The content of intracellular carbon polymers (e.g., polyhydroxyalkanoate) decreases, and oxidation takes place. Once oxygen is supplied to the system, PAOs adopt soluble phosphorus and accumulate it as polyphosphate using stored carbon as an energy source. Phosphate formed in the EBPR process is removed using activated waste sludge, in which the content of phosphate reaches up to 5%\(^{95}\). In these processes, activated sludge can circulate through the anaerobic and aerobic phases.

The reliability of the EBPR process varies among wastewater treatment plants (WWTPs). Many factors affect the EBPR process performance, including wastewater characteristics, process configurations, operating conditions, and environmental conditions (e.g., pH, temperature). The most commonly used EBPR processes include anaerobic-anoxic-oxidation (A2O), Bardenpho, the University of Cape Town (UCT) process, Johannesburg and the Virginia Initiative Plant (VIP). Both VIP and UCT configurations minimize nitrate recycling in the anaerobic zone. Studies have shown that phosphorus removal efficiency can be adversely affected by nitrate entry into the anaerobic zone, especially for low BOD loads\(^{19}\).

The EBPR process is particularly suitable for municipal treatment systems in which the effective P concentrations are relatively low (≤25 mg L\(^{-1}\)) compared to agricultural or industrial waste streams. The degree of phosphorus recovery relative to the WWTP influent largely depends on the type of P removal during wastewater treatment. The more P removed by biological processes (to be specific EBPR), the higher the rate of re-dissolution during anaerobic treatment of sludge, resulting in increased recycling (recovery). Therefore, a WWTP which predominantly uses the EBPR process is advantageous, having in mind that the recovery rate has a direct impact on economic efficiency\(^{96}\). According to Melia et al\(^{97}\), the efficiency of phosphorus removal from municipal wastewater with EBPR technology can reach more than 85%, while Muisa et al\(^{98}\) claim that 100% phosphorus removal can be achieved with this technology.

### Phosphorus recovery from wastewater

The main difference between phosphorus removal from wastewater and phosphorus recovery is that the former process aims to obtain phosphorus-free wastewater from wastewater treatment plants, while the latter focuses on phosphorus-containing by-products that can be reused.

Phosphorus recovery technologies are usually applied to industrial and urban wastewater. Only few methods are available for manure due to the lack of a suitable market for processed manure and the availability of cheap alternatives (e.g., disposal)\(^{99}\).

In the first case, the recovery of phosphorus can be conducted in different phases of wastewater treatment, from liquid to sludge phase, as well as from ash after mono-incineration\(^{10}\).

In the recovery of phosphorus from wastewater, a distinction can be made between phosphorus recovery from the liquid phase (wastewater and sludge treatment water), recovery from the sludge phase (raw and digested sludge), and recovery from the ash phase (after sewage sludge incineration).

Phosphorus can occur in the following forms\(^{100}\):
- dissolved phosphate anion (PO\(_4^{3-}\)) – the most common form, the dissolved form of phosphorus in water, easily recoverable;
- biologically bound phosphorus – P bound in biomass, must be released for recovery;
- chemically bound phosphorus – P bound in metal phosphates, biologically non-available or hardly available, and only slightly soluble.

Different technologies for phosphorus recovery from WWTPs have been developed, which use different phosphorus “sources” (wastewater, sewage sludge, digestion supernatant, ash), and have different efficiencies. The efficiency of the process largely depends on the “source” of phosphorus. The recovery capacity from the liquid phase can reach a maximum of 40–50%, while considerably higher efficiency can be achieved with the sludge phase (sewage sludge and sewage sludge ash), reaching up 60 to 90% compared to P present in wastewater. Ash from sewage sludge incineration is the most promising source of P when it comes to recovery technologies\(^{19,55}\).

Three main categories of phosphorus recovery technologies from municipal wastewater have been identified\(^{19,19,101}\):
- crystallization and precipitation,
- wet chemical processes, and
- thermochemical processes.

Crystallization with precipitation is the standard method for recovering phosphorus from the liquid phase, whether it is wastewater or liquid fraction after sludge digestion. In the precipitation of phosphorus with Fe/Al salts, the formed sludge is further treated by wet chemical and thermochemical...
Sewage sludge, liquid phase (effluent and digestion supernatant) wastewater or anaerobically digested sludge in the erlands, USA, and China, P is recovered from A. Salkunić et al., Review of Technologies for the Recovery of Phosphorus..., Chem. Biochem. Eng. Q., 36 (2) 91–116 (2022)

About 90 % of the P that comes to the WWTP can be concentrated in the digested sewage sludge, so the digested sludge is one of the most concentrated forms of phosphorus. However, pollutants such as heavy metals, pharmaceuticals, and pathogens are concentrated in the sludge, so the use of sewage sludge in agriculture is limited or banned. An alternative can be incineration, which produces ash rich in phosphorus. The ash from sewage sludge incineration contains about 90 % phosphorus. When sludge is burned, organic pathogens and pharmaceuticals are destroyed, but heavy metals and metalloids are concentrated, so the ash cannot be used directly in agriculture. The main disadvantage of sewage sludge incineration is the need for large infrastructural investments in incineration plants.

An overview of the main technologies for phosphorus recovery depending on the source is shown in Table 2.

In addition to these dominant processes, membrane separation, nanocrystallization, adsorption, ion exchange, biological assimilation, etc., can be used for phosphorus recovery from wastewater. These technologies are currently used on a much smaller scale, but given the large number of studies being conducted, an increase in their share in phosphorus recovery can be expected.

**Crystallization**

Crystallization and precipitation are the dominant processes for the recovery of phosphorus from the liquid phase (effluent and digestion supernatant), and mainly require the application of EBPR treatment. Without prior concentration of phosphorus by EBPR, only about 10–40 % of P can be recovered from the aqueous phase, depending on whether it is already bound to other metals or biomass. For economic viability, the liquid phase should have a phosphate concentration of at least 50–60 mg L\(^{-1}\), and constitutive ions must be present in sufficiently high concentrations\(^{10}\).

In the AirPrex process, used in Germany, Netherlands, USA, and China, P is recovered from wastewater or anaerobically digested sludge in the form of struvite using magnesium chloride as a precipitating agent at pH around 8. The process efficiency is 90–95 % and it is performed in a reactor with CO\(_2\) stripping. In the EloPhos process used in Germany, P from waste sludge is recovered in the form of struvite. A crystallization reactor is used, and the efficiency of the process is 95 %.

From the liquid phase, phosphorus is mostly regenerated in the form of struvite, calcium phosphate, and vivianite crystals, which precipitate from the solution. The main characteristics of these minerals and the conditions for their formation are discussed further on.

**Recovery of phosphorus in the form of struvite**

Currently, only struvite crystallization technologies are commercialized at the industrial level. Crystallization processes have other benefits, such as reducing sludge handling problems and increasing sludge dewatering.

Magnesium ammonium phosphate hexahydrate (MgNH\(_4\)PO\(_4\) \(\cdot\) 6H\(_2\)O), or struvite, is a white mineral that can form naturally under certain conditions in sewage systems and wastewater treatment plants.

In WWTPs, struvite is often considered a problem because of its tendency to deposit uncontrollably in undesirable places (pumps, aerators, and pipes) as a result of reduced pressure and consequent release of dissolved CO\(_2\). Removal of struvite deposits in these circumstances is quite expensive\(^{89,102}\). Struvite can also be formed under controlled conditions in crystallization reactors, where it is removed in the form of small, pure granules.

As seen from Table 1, phosphorus is primarily regenerated in the form of struvite. This is because struvite is widely used in agriculture as a very effective, slow-release phosphate fertilizer that contains enough nutrients and essential substances necessary for the growth of crops. Out of 41 analyzed processes, phosphorus was recovered in the form of struvite in 20 processes. Namely, struvite is a valuable product that contains nutrients essential for plant growth and can be applied directly to the soil as a safe and effective fertilizer. In addition to phosphorus, struvite also contains nitrogen, usually in the proportions of 12 % P and 5 % N. If it does not

| Source of phosphorus | Applied technology/process for P recovery from wastewater |
|----------------------|---------------------------------------------------------------|
|                      | Crystallization | Wet chemical process | Termochemical process |
| Liquid phase (effluent and digestion supernatant) | × | | |
| Sewage sludge | ×\(^*\) | × | × |
| Ash from mono-incineration of sewage sludge | × | × |

\(^*\) Crystallization and precipitation of P from the liquid phase after wet chemical treatment of sewage sludge.
meet the prescribed criteria for direct use in agriculture, the mineral fertilizer industry can use it as a valuable raw material. The drawback of phosphorus recovery through the precipitation of struvite is the possibility of its use only in wastewater treatment plants with EBPR systems, otherwise, it is not economically viable to perform recovery. Nevertheless, the precipitation of struvite is the most recommend-
ed method. The efficiency of phosphorus recovery using this technique can reach 97% if the concentrations of nitrogen and magnesium in the sludge are sufficient. The best P:Mg ratio is 1:1.05, but it is generally maintained at 1:1.3. The P:N molar ratio must be at least 1:103,104.

The struvite crystallization process is based on the following stoichiometric equations:

\[
\begin{align*}
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{2-} + 6\text{H}_2\text{O} & \rightarrow \text{MgNH}_2\text{PO}_4\cdot6\text{H}_2\text{O} \\
\text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + 6\text{H}_2\text{O} & \rightarrow \text{MgNH}_2\text{PO}_4\cdot6\text{H}_2\text{O} + \text{H}^+ \\
\text{Mg}^{2+} + \text{NH}_4^+ + \text{H}_2\text{PO}_4^- + 6\text{H}_2\text{O} & \rightarrow \text{MgNH}_2\text{PO}_4\cdot6\text{H}_2\text{O} + 2\text{H}^+
\end{align*}
\]

Recovery of phosphorus in the form of calcium phosphate

Removal of P using Ca compounds may initially precipitate several calcium phosphate minerals, such as brucite, octacalcium phosphate, hydroxyapatite, whitlockite, monetite, or amorphous calcium phosphate. However, the most common of these minerals is hydroxyapatite [Ca$_5$(PO$_4$)$_3$OH]$^{108}$. Hydroxyapatite has a composition similar to natural phosphate rocks. It is formed by the crystallization of phosphate, calcium, and hydroxyl ions at high pH values ($>$9)$^{97}$.

The following equation shows the chemical reaction of hydroxyapatite formation:

\[
10\text{Ca}^{2+} + 6 \text{PO}_4^{3-} + 2\text{OH}^- \rightarrow 2\text{Ca}_3(\text{PO}_4)_2\cdot\text{OH}^{-}(4)
\]

The presence of sufficient P to achieve thermodynamic supersaturation is a precondition for calcium phosphate precipitation$^{109}$. Precipitation begins with the nucleation of CaP, which is the first step in the crystallization process. Induced nucleation can be initiated by the addition of artificial nucleic materials such as sand, calcite, or tobermorite crystals$^{110}$.

The factors that affect P precipitation are pH, P concentration, and the presence of other ions such as carbonate. Calcium carbonate formation reduces the concentration of free Ca, which inhibits P precipitation as a result$^{111,112}$.

At pH 8, carbonate significantly slows down the rate of phosphate precipitation, and the corresponding precipitation efficiency also reduces. At pH 9, the effect of carbonate on phosphate precipitation is very small. That indicates that carbonate may reduce the deposition rate and efficiency of calcium phosphate, but the pH value of the solution is still the key factor influencing the precipitation process.

In general, the efficiency of removing phosphorus by this method is up to 75–80%$^{113}$. The
main advantage of the recovered product is that it contains fewer pollutants compared to natural phosphate rock.\(^\text{113}\)

Calcium phosphate is most often recovered from liquid fractions of manure, although it is increasingly used in the recovery of phosphorus from human urine. Even though the residual organic compounds contribute to the buffer capacity of liquid manure, carbonate and \(\text{NH}_4^+\) are the most important chemical components. Both contribute to the alkaline pH buffer capacity.\(^\text{114}\) Alkaline pH is necessary to form a P precipitate with calcium and magnesium compounds. When calcium or magnesium hydroxide is added to liquid manure, the hydroxide reacts with the existing bicarbonate to form carbonate, with ammonium (\(\text{NH}_4^+\)) to form ammonia (\(\text{NH}_3\)), and with phosphate to form phosphate-precipitating compounds.\(^\text{115}\)

For example, in the case of calcium hydroxide, the following equations define the reactions:

\[
\text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O} \tag{5}
\]

\[
5\text{Ca}^{2+} + 4\text{OH}^- + 3\text{HPO}_4^{2-} \rightarrow \text{Ca}_5\text{OH}{}(\text{PO}_4)_3 \downarrow + 3\text{H}_2\text{O} \tag{6}
\]

The chemical reaction in Eq. (5) is completed at pH 9.5, while the chemical reaction in Eq. (6) begins at pH > 7.0, but it is very slow at pH 9.0.

As the pH value of wastewater increases over 9.0, excess \(\text{Ca}^{2+}\) ions react with phosphate to precipitate in the form of calcium phosphate (Eq. (6)). Eq. (5) does not express the fact that wastewater containing a high concentration of \(\text{NH}_4^+\) requires large amounts of lime to increase the pH to the required values. The \(\text{NH}_4^+\) reaction tends to neutralize hydroxyl ions according to Eq. (7).

\[
\text{Ca(OH)}_2 + 2\text{NH}_4^+ \rightarrow 2\text{NH}_3 \uparrow + \text{Ca}^{2+} + 2\text{H}_2\text{O} \tag{7}
\]

Accordingly, the precipitation of P in wastewater from animal farms, using an alkaline compound such as lime, is very difficult due to the inherently high buffer capacity of liquid manure (\(\text{NH}_4\cdot\text{N} 200 \text{ mg L}^{-1}\) and alkalinity 1200 mg L\(^{-1}\)). This buffering effect prevents rapid pH changes. However, this problem is solved by a pre-nitrification step that reduces the concentration of \(\text{NH}_4^+\) (Eq. (8)) and the alkalinity of the bicarbonate (Eq. (9)).\(^\text{116}\)

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \tag{8}
\]

\[
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_3^{2-} \uparrow + \text{H}_2\text{O} \tag{9}
\]

The buffer effect of \(\text{NH}_4^+\) (Eq. (7)) is reduced by biological nitrification of \(\text{NH}_4^+\) (Eq. (8)). At the same time, the buffering effect of bicarbonate (Eq. (5)) is highly reduced with the acid formed during nitrification (Eq. (8)). These two simultaneous reactions provide less buffered fluid under optimal pH conditions for efficient \(\text{P}\) removal with the addition of small amounts of lime (Eq. (6)). This procedure does not require the use of a fluidized bed crystallizer or reactor. In practice, soluble \(\text{P}\) can be removed from pre-nitrified liquid porcine manure in a precipitator by adding hydrated lime to obtain a fine precipitate at pH 10.5. Afterward, the fine precipitate is aggregated by the addition of a polymer and separated by filter bags, yielding 99% of the total \(\text{P}\) relative to the unfiltered material.\(^\text{113}\)

This calcium phosphate removal procedure has been applied to remove \(\text{P}\) in animal waste treatment systems with lagoons and lagoon-free systems.\(^\text{115,116}\) In systems with anaerobic lagoons (or other anaerobic digesters), the anaerobically digested supernatant, rich in \(\text{NH}_4\cdot\text{N}\) and alkalinity, is first subjected to nitrification. Phosphorus is then removed by adding hydrated lime. The efficiency of this technology has been tested in semi-industrial conditions, where 95–98% of \(\text{P}\) was precipitated from anaerobic lagoons.\(^\text{116}\) In lagoon-free systems, raw liquid fertilizer is firstly treated with an improved polymer separation process to remove most of the carbon material from the wastewater. The separated water is then treated with a nitrification process, and soluble \(\text{P}\) is removed. A denitrification tank is built into the treatment system to ensure total \(\text{N}\) removal with \(\text{P}\) removal. This configuration has been tested full-scale, with a soluble \(\text{P}\) removal efficiency of 94%\(^\text{100}\). Recovered \(\text{P}\) was more than 99% soluble in citrates, which is very important for the fertilizer industry where it could be used as a raw material.

Recovery of phosphorus in the form of vivianite

Vivianite (\(\text{Fe}_4(\text{PO}_4)_3 \cdot 8\text{H}_2\text{O}\)) is found in the sludge of wastewater treatment plants, especially in digested sludge, and makes up most of the FeP-bound fraction. The efficiency of phosphorus recovery through vivianite precipitation can reach 62.1%\(^\text{118}\). The two main components of vivianite are Fe and P. In particular, Fe ions in natural water can be formed by dissolving iron minerals, while in wastewater, Fe ions are often formed by adding salts used as flocculants.\(^\text{109}\) In addition, Fe usually already exists in water in the form of \(\text{Fe}^{2+}\), \(\text{Fe(OH)}_2\), and hydrated ferric oxide (HFO). In environments rich in organic matter (OM) and reducing agents, \(\text{Fe}^{3+}\) will be easily reduced to \(\text{Fe}^{2+}\) by dissimilatory metal-reducing bacteria (DMRB), while organic phosphorus is converted to phosphate by anaerobic microorganisms.\(^\text{120,121}\) As these two processes continue, the concentrations of \(\text{Fe}^{2+}\) and \(\text{PO}_4^{3-}\) increase. When the target value of the solubility product (Ksp) is reached, vivianite is formed. Eqs. (10)–(12) describe the process of vivianite formation:}
Vivianite formation is a chemical process that can be influenced primarily by microorganisms, pH, and sulfate concentration (S), as well as by various other factors, such as Fe/P molar ratio, temperature, reaction time, and alkalinity. Microorganisms can affect the formation of vivianite both directly and indirectly. Direct effects caused by microorganisms include the following transformations: from Fe(II) to soluble Fe(III) through reduction and electron transfer by DMBR bacteria; from organic phosphorus to inorganic PO$_4^{3-}$ by anaerobic methane oxidation (AOM); and from SO$_4^{2-}$ to S$_2^-$ through reduction by sulfate-reducing bacteria (SRB). Indirect effects are associated with the modification of the reducing conditions, consuming electron acceptors such as O$_2^-$, NO$_3^-$, and Fe$^{2+}$, and the formation of CO$_2^-$, which lowers the pH.

The influence of the pH value is reflected in the changes in ionic strength and solubility products. In particular, for the formation of vivianite, Fe$^{2+}$ ions require an environment with a lower oxidation-reduction potential and a lower pH value (<9). The lower the pH value, the wider the range of acceptable values of oxidation-reduction potentials. Experimental research shows that, at pH 6.0, Fe is mainly in the solid phase in the form of vivianite (54.7 %), but with a further decrease in the pH value of Fe, it mostly dissolves in the supernatant. For example, in a pH 3.0 environment, soluble iron is the dominant type of Fe (77.9 %), and vivianite in that pH range is almost non-existent. Sulfate concentration also has a critical effect on vivianite formation. Sulfate can bind to Fe to form mackinawite (FeS), which competes with P and reduces vivianite production and purity.

The stoichiometric molar ratio of Fe/P in the vivianite chemical formula is 1:5:1. Experimental data have shown the following: (1) the concentration of Fe$^{2+}$ in the solution should slightly exceed the stoichiometric value since OH$^-$ tends to combine with Fe$^{2+}$ to form Fe(OH)$_2$; (2) a small amount of Fe(II) can be oxidized to Fe(III), both of which can lead to competition in vivianite formation.

Research has also shown that alkalinity, which is common in sewage and supernatant of anaerobic sludge, has the potential to compete with PO$_4^{3-}$ for Fe$^{2+}$, namely, to precipitate siderite (FeCO$_3$). Vivianite has considerable potential for application in agriculture, as well as in chemical and electrical industries, primarily owing to its high content of P and the relatively simple technology of its separation from wastewater using a magnetic field.

**Wet chemical processes**

Wet chemical processes are used to dissolve phosphorus from sewage sludge or sewage sludge ash. This procedure is based on the leaching of phosphorus from previously precipitated phosphate, using acids and bases, which implies the release of P into the solution from the sludge treated with mineral acids and its subsequent precipitation. Different acids (sulfuric, hydrochloric, phosphoric, and carbonic) can be used in this process. The P recovery potential for these processes mostly depends on process conditions such as pH of leaching and P species in sludge, and ranges from 50 to 80 %.

Acid leaching is the most common technique used for the treatment of sewage sludge ash. However, acid leaching simultaneously dissolves heavy metals present in the sludge and potentially large amounts of iron and/or aluminum, depending on which salt is used to precipitate the metal phosphate from the liquid phase. Since heavy metals are well soluble, when using wet chemical processes, the removal of heavy metals from the solution must be taken with attention. The re-dissolved phosphorus can be isolated by various methods, but the most popular are crystallization and precipitation in the form of struvite or apatite. To protect the quality of the precipitated struvite, citric acid is added as a complexing agent before the addition of MgO and NaOH, with the resulting salts of metal citrates remaining in the solution during the precipitation of struvite.

Direct acid digestion of ash with mineral acids is also possible. In some processes, phosphate is extracted from ash using phosphoric acid, and then treated with sulfuric acid to obtain phosphoric acid, which acts as the final source of acid (Table 1 – Nippon PA process in Japan performed in an extraction reactor, where part of the phosphate is replaced by ash and extraction with sulfuric acid is performed). Conversion to phosphoric acid can be achieved by acid treatment with CO$_2$ instead of mineral acids. Blowing CO$_2$ into an aqueous ash suspension forms carbonic acid. Carbonic acid can react with phosphate in the ash to form phosphoric acid. Others use ash digestion followed by phosphate deposition with lime to produce dicalcium phosphate (Table 1 – EXTRAPHOS process in Germany, where P is recovered from waste sludge by dissolving phosphates and their precipitation into dicalcium phosphate, where lime is used as a precipitating agent. The process is carried out in a reactor with CO$_2$ stripping, and the process efficiency is approximately 50 %). Formed calcium chloride can be deposited in the sea. Metals remain with an insoluble residue or they are removed by ion exchange. Alkaline leaching is a less used alternative
to wet acid chemical treatment. It is based on the treatment of sewage sludge ash with hydroxide solutions and has a lower efficiency of phosphorus recovery (up to 40 %) compared to acid leaching, and higher costs due to high consumption of chemicals. Although the efficiency of phosphorus recovery is low, alkaline leaching in Japan is used in the industry due to the good removal of heavy metals. Caustic soda waste can be used to reduce operating costs. After leaching, the ash is washed and treated with a dilute H₂SO₄ solution to remove heavy metals. The obtained solids can be used as additives to cement, asphalt, or soil.

Thermochemical processes

Thermochemical processes are based on the application of heat in the treatment of sewage sludge or ash from sewage sludge incineration, and include processes that take place at different temperatures and with different oxygen contents. In general, thermochemical procedures for the treatment of sewage sludge can be classified as hydrothermal treatment, pyrolysis, and gasification, and take place without the addition of chemicals. In the thermochemical treatment of sewage sludge ash, chemicals can be used.

In this process, large amounts of phosphorus can be recovered. When applying these procedures for the treatment of sewage sludge, lower temperatures are used compared to the treatment of sewage sludge ash. Higher temperature and higher oxygen content have a favorable effect on the removal of pathogens and organic matter from sewage sludge. However, metals and metalloids generally lag behind after these treatments and make sewage sludge inadequate for agricultural use, so the obtained materials require further treatment

Thermochemical treatment of sewage sludge ash is based on the reaction of ash with chemicals at higher temperatures. The main goal of this method is to remove heavy metals and increase the bioavailability of phosphorus in the ash, making the ash suitable for the production of fertilizers. A typical example is an AshDec process. In this process, the ash is loaded into a rotary kiln together with sodium, magnesium, or potassium salts and a reducing agent, such as dry sewage sludge, and heated to 900–950 °C for 15–20 minutes. The system ensures the removal of heavy metals by evaporation in a reducing atmosphere, resulting in bioavailable phosphorus compounds. To increase the removal of heavy metals in the case of high concentrations, chlorides such as MgCl₂ or CaCl₂ can be added, which can lead to the formation of chlorinated phosphate compounds with low bioavailability, and Ca- and Mg-phosphates that dissolve efficiently only in acidic soils.

The disadvantage of this technology is high energy consumption, which can be mitigated to some extent by proper process control. The advantage is the fact that the thermochemical process can also be used for other phosphorus-rich ash.

Thermal treatments are suitable for less contaminated materials such as manure, bones, and food waste. None of these (hydrothermal) processes have yet been widely used.

Direct use of the sewage sludge

The simplest way to recover phosphorus from sludge is to use activated sludge directly as fertilizer. However, the transport and management of highly hydrated sludge (usually above 50 % H₂O) can generate 25 to 65 % of the total operating costs of a treatment plant.

At the same time, sewage sludge can contain significant amounts of potentially hazardous organic pollutants (such as aromatic hydrocarbons) and heavy metals. The toxicity of heavy metals and metal oxides nanoparticles on the formation and properties of the biologically (EBPR) removed phosphorus depends on their type and concentration. The phosphorus release and uptake by phosphorus-accumulating organisms (PAOs) can be affected by inhibition of the key enzymatic activity. The possible effects of the toxicity of heavy metals and metal oxide nanoparticles are disruption of the cell membrane, DNA damage, protein denaturation, enzyme disruption, etc. Additionally, the generation of the reactive oxygen species can contribute to the toxicity of both heavy metals and metal oxide nanoparticles. Legislation restricting the use of sewage sludge as fertilizer is becoming more stringent, especially that defining the maximum allowable concentrations of heavy metals in the sludge entering the soil. For this reason, sludge treatment and indirect phosphorus recovery technologies are becoming increasingly popular. However, it is important to understand that sewage sludge is often used directly as fertilizer, especially in “third world” countries, mainly due to a lack of access to and resources for sewage sludge incineration or chemical treatment technologies to recover phosphorus.

Sewage sludge ash is applied in some plants as an amendment of the phosphate rock, up to 2.5 %, in the production of fertilizers, and technologies for removing metals from phosphoric acid solutions are not applied for economic reasons. The advantage lies in the fact that the ash does not pass through the absolutely liquid phase, preventing excessive solubilization of the metal. As such, SSAs derived from WWTPs that use chemical precipitation with iron and/or aluminum are less suitable for mixing than WWTPs that use biological removal.
Phosphorus recovery from sewage sludge ash (SSA)

Incineration is the direct combustion of organic raw materials in the presence of air. Incineration is used as the most common type of sewage sludge treatment. Sewage sludge incineration produces ash rich in P. As such, it can be used as a fertilizer, an additive to mineral fertilizers, or as an additive to construction materials. In many countries, an increasing percentage of sewage sludge is thermally treated, due to presence of organic and inorganic pollutants that can contaminate soil and groundwater during landfilling. In addition, according to the literature, the recovery of phosphorus using the ash from burning sewage sludge is recommended because the ash has a much higher content of phosphorus, mainly due to a significant reduction in the volume of burned materials (70–90 %)131.

Even ash with an average amount of phosphorus, about 8 % (up to 15 %), corresponds to the content found in medium-rich phosphate deposits132. Moreover, 5 to 10 times more phosphorus can be recovered from ash compared to sewage sludge and leachate. Unfortunately, because of the high capital costs of building a sludge incineration plant, such technologies are economically viable only in large wastewater treatment plants. These solutions, however, have already been used in practice, and one such example is the Netherlands132,133.

The direct use of sewage sludge ash as a fertilizer or as an additive to construction materials is questionable due to the content of heavy metals, such as Cu, Cr, Ni, Pb, and Zn, which may exceed the limit values134.

Takahashi et al.135 reported dissolving 89–93 % P from burnt sewage sludge at pH below 2.0 using 0.5 M sulfuric acid solution (10:1 L/S liquid/solid ratio). Another study134 showed that 66–99 % of the total P was dissolved from sewage sludge ash at a pH lower than 1.8 with a 2.5 M sulfuric acid solution (2:1 L/S).

Apart from sewage sludge, animal waste can also be subjected to thermal treatment. One of the methods for animal waste disposal is pyrolysis, which produces a combination of gas, liquid fuel, and coal known as biochar. Wet pyrolysis and supercritical gasification can be used as an alternative. These technologies enable the direct use of wet raw materials, such as raw animal manure and sewage sludge. However, they are rarely used136.

Adsorption and ion exchange

The P adsorption technique is widely investigated to remove P from wastewater in treatment plants using different adsorbents. Cheap materials, such as industrial by-products and natural materials, can be used for this purpose137(Table 390,138).

Phosphorus adsorption depends on various factors, such as the type of adsorbent used, its surface area, pH, and contact time.

Ion exchange enables a more precise separation of solutes from waste streams. Ion exchange is a reversible process and helps P regeneration in the form of a precipitate by subsequent addition of dissolved substances (Ca, Fe, and Al)99,138. The advantage of ion exchange compared to adsorption is that the ion exchange mass can be renewed and reused. The following materials can be used for ion exchange: quaternary chitosan beads, polymer ligands, anion exchanger made of wheat straw, polypropylene nonwoven fiber, and polymer resin impregnated with iron oxide99.

Membrane technologies

Phosphorus recovery using membrane technologies is a relatively new process, and it is still under development. Membrane media have great potential in increasing the concentration of constituent ions in the solution for further precipitation, for example struvite compounds and calcium phosphate100.

Reverse osmosis (RO), forward osmosis (FO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and a combination of these processes can be used for simultaneous wastewater treatment and nutrient recovery. In general, membrane technologies make it possible to obtain concentrated flows that can be subjected to a deposition process to recover P, Mg2+ and Ca2+ sources, and pH adjustments are required to achieve the initial conditions for the precipitation process, while the performance of these systems can be affected by several parameters. Influent quality, hydraulic load, salinity, and membrane fouling (organic, inorganic, or biological contamination) are the most important parameters104.

Osmotic membrane bioreactors (OMBRs) are a new approach to P recovery using membrane technology139,140. Osmotic membrane bioreactor (OMBR) is a new high-efficiency wastewater treatment technology that integrates the forward osmosis (FO) process into the membrane bioreactor (MBR) or combines biological treatment with membrane separation. Since 2008, when this concept was put forward for the first time, it has gained increasing popularity in wastewater treatment and reuse141–143.

The process is an integration of osmosis-driven membranes and a biological treatment that has recently been used to recover phosphorus, mainly in the form of amorphous calcium phosphate (ACP, Ca₁₀(PO₄)₆·nH₂O). OMBR uses a non-porous osmotically driven membrane instead of conventional porous MF or UF membranes that move under hy-
 Hydraulic pressure. The use of osmotically driven membranes, such as FO membranes, has many advantages, some of which are less membrane fouling and lower costs. Qiu and Ting have shown that >95% P can be recovered through this system. Despite its high efficiency and high P recovery rates, membrane systems have been developed exclusively on a laboratory scale. The feasibility of continuous operation of these membranes remains a challenge, as membrane performance will decrease significantly with the accumulation of deposits (fouling), which requires frequent cleaning and involves a gradual loss of performance. The operating costs of the entire process (cleaning, maintenance, and deposition chemicals) are still high, which currently makes the application of membrane technologies difficult.

### Biological assimilation

Adsorption and assimilation of phosphates by algae is another promising method for the recovery of P from wastewater. Photosynthetic algae use CO₂ and nutrients (NH₄⁺, NO₃⁻ and PO₄³⁻) for their growth, while producing oxygen at the same time. Afterward, they are used by heterotrophic bacteria for their metabolism, thus forming NH₄⁺, NO₃⁻ and PO₄³⁻ ions.

Although algae have been used in aerobic lagoons for wastewater treatment in the removal of organic carbon and pathogenic pollutants, the removal of phosphorus using algae has only been done sparingly. The main reason is that aerobic ponds are not optimized for biomass production. Algae assimilation has a great potential for P assimilation.

### Table 3 – Selected adsorbents, adsorption conditions, and efficiency

| Adsorbents                  | Specific surface area (m² g⁻¹) | pH of the solution | Initial concentration (mg L⁻¹) | Sorption efficiency (mg g⁻¹) |
|-----------------------------|--------------------------------|-------------------|--------------------------------|-----------------------------|
| Apatite                     | 530                            | –                 | 30                             | 0.41                        |
| Fluorapatite                | 480                            | –                 | 30                             | 0.37                        |
| Hydroxyapatite              | 720                            | –                 | 30                             | 0.31                        |
| Bentonite                   | 84.98                          | 8–10              | 50                             | 0.28                        |
| Bauxite                     | –                              | 3.2–5.5           | 10                             | 6.73                        |
| Calcium-rich sepiolite      | 231                            | 3–6               | 800                            | 9.04 (pH=7)                 |
| Kaolinite                   | 3.66                           | 2                 | 50                             | 0.32                        |
| Calcite                     | 0.98                           | 2–8               | 50                             | 1.82                        |
| Limestone                   | 7.4                            | 7.8               | 40                             | 0.68                        |
| Diatomaceous earth          | 24.77                          | 2–5               | 40                             | 10.2 (pH=4) 1.7 (pH=8.5)    |
| Zeolite (clinoptiolite)     | 13.83                          | 6                 | 50                             | 0.37                        |
| Iron-zirconium binary oxide | 339                            | 5.5               | 200                            | 33.4                        |
| Red mud                     | 22.71                          | 5.5               | 50                             | 0.23                        |
| Mesoporous ZrO₂             | 232                            | 6.7–6.9           | –                              | 29.7                        |
| Ferric oxide                | 47.9                           | 3.3               | 20                             | 8.6                         |
| Fly ash                     | 0.53                           | 11.5              | 80                             | 71.87                       |
| Activated alumina           | 230–300                        | 5.5               | –                              | 13.8                        |
| Bituminous coal ash         | 96.9                           | 9.5               | 5–40                           | 4–81 mg kg⁻¹                |
| Lignite ash                 | 27.7                           | 11.6              | 950–1500                       | 19–29 mg kg⁻¹               |

106. Qiu and Ting have shown that >95% P can be recovered through this system. Despite its high efficiency and high P recovery rates, membrane systems have been developed exclusively on a laboratory scale. The feasibility of continuous operation of these membranes remains a challenge, as membrane performance will decrease significantly with the accumulation of deposits (fouling), which requires frequent cleaning and involves a gradual loss of performance. The operating costs of the entire process (cleaning, maintenance, and deposition chemicals) are still high, which currently makes the application of membrane technologies difficult.

139. Biological assimilation

Adsorption and assimilation of phosphates by algae is another promising method for the recovery of P from wastewater. Photosynthetic algae use CO₂ and nutrients (NH₄⁺, NO₃⁻ and PO₄³⁻) for their growth, while producing oxygen at the same time. Afterward, they are used by heterotrophic bacteria for their metabolism, thus forming NH₄⁺, NO₃⁻ and PO₄³⁻ ions. Although algae have been used in aerobic lagoons for wastewater treatment in the removal of organic carbon and pathogenic pollutants, the removal of phosphorus using algae has only been done sparingly. The main reason is that aerobic ponds are not optimized for biomass production. Algae assimilation has a great potential for P assimilation.
iration under optimized conditions, as dry algal biomass can contain up to 3.3 % P. El Hamouri reported the removal of 63 % P in an algae pond. Light intensity, influent phosphorus concentration, pH, aeration, mixing speed, and temperature are important factors for efficient phosphorus recovery by algal biomass. Microalgae are often used in these wastewater treatment systems. Algae can be collected at the end of treatment by filtration, precipitation, or centrifugation. Although there are successful examples of collecting algae on a pilot scale, the application of such systems on a large scale is still a challenge.

The advantage of phosphorus recovery by algal assimilation lies in the value of the produced biomass. The collected biomass of algae can be used in various industries, including the production of slow-release fertilizers, production of animal feed, pharmaceuticals, food processing, etc. Owing to its high lipid content, the collected biomass can also be used as a raw material for liquid biofuels.

**Recovery of phosphorus from manure**

Direct wet extraction is an alternative method for recovering P from raw solid waste without thermal treatment. The treatment process is called quick wash, and it is developed for the extraction and recovery of P from poultry waste and manure. The products of this process are P-depleted washed residue and a concentrated phosphate material that can be used as fertilizer.

The quick wash process consists of three consecutive steps:

- P extraction,
- P recovery, and
- P recovery enhancement.

In the first step, the main fraction (60–90 %) of the initial total P in raw animal waste is selectively extracted by hydrolysis reactions using mineral or organic acids. A mixture of animal waste and extraction solution is stirred in the pH range from 3.0 to 5.0. Further, the washed residue is precipitated to prevent unnecessary oxidation and digestion of C and N. In this step, a liquid extract containing suspended solids and extracted soluble P is obtained. In the second step, P precipitates from the liquid extract by adding lime (for the pH increase to 9.0–11.0) to form a P product containing Ca. In the final step, an organic flocculant is added to enhance precipitation and P concentration in the precipitate. The P-rich sludge is drained and used further as fertilizer, while the liquid phase is recycled back to the fast wash system.

The advantage of this procedure over thermal pretreatment is the low content of heavy metals in the phosphate product and the conservation of C and N in the acid-washed residue. The washed solid residue has a higher N:P ratio than the initial raw waste, which makes the washed residue better balanced, thus improving the efficiency of its beneficial effect on crops with two nutrients and avoiding excessive use of P.

Wnetrzak et al. found that the production of biochar from pig manure by pyrolysis is a viable option for recycling P, and the recovery of phosphorus from biochar with mineral acids is possible. In the process of pyrolysis, 92 % to 97 % of phosphorus present in fresh pig manure ends up in the biochar fraction. From biochar, 60–75 % P can be extracted as orthophosphate, and 90 % as total P, using 0.2 M sulfuric acid solution (50:1 L/S).

The thermochemical conversion technologies such as incineration or pyrolysis require relatively dry raw materials.

**Phosphorus recovery from animal waste**

Meat and bone meal (MBM) is an important by-product of slaughterhouses. It contains about 8 % N, 5 % P, 1 % K and 10 % Ca. The raw materials used for the production of MBM may differ somewhat, but the principle of its production is the same – animal remains (bones, heads, intestines and skin, etc.) are firstly crushed, sterilized, separated from fat, and finally after grinding, fine flour is produced.

Previously, MBM was used for animal feed and directly as an organic fertilizer, but due to the possibility of transmitting the causative agent of bovine spongiform encephalopathy (BSE) in ruminants, the EU strictly banned the use of animal residues as raw materials in the food and feed industry. However, as of 1 February 2006, the use of MBM as a fertilizer for field crops in the EU is permitted by Commission Regulation (EC) no. 181/2006, but its full use as an organic fertilizer in vegetable production is limited, due to the fear of poisoning through the food chain, because there is a possibility that traces of contaminated meat and bone meal may remain on the product (if the animals were infected with “mad cow” disease).

One of the possible uses of slaughter by-products (also meat and bone meal) is pyrolysis. The ash after combustion of MBM contains approximately 15 – 16.5 % P and 29.5 – 33 % Ca, depending on the combustion conditions. The main components of ash after burning MBM are: hydroxyapatite, $\beta$-Ca$_3$(PO$_4$)$_2$, as well as small amounts of sodium, potassium, and magnesium. This product is practically free from heavy metals, unlike natural apatite and phosphorite. The chemical properties of ash indicate that it can be used successfully in the chemical industry for the production of phosphoric acid and its derivatives.
Leng et al.¹⁵⁹ have shown that MBMA (meat and bone meal ash) can also be used to remove P from synthetic wastewater. Removal of P can be performed in a wide range of initial pHs within one hour, with achieving a removal capacity of ~115 mg g⁻¹. The main mechanisms of P elimination can be explained by HAP precipitation due to the MBMA nucleation effect. After the wastewater treatment process, the P content in the ash increased from 13.48 % to 16.18 % (or 37.06 % P₂O₅).

**Phosphorus recovery from urine**

Most P recovery methods are chemically, energy, and operationally demanding. Their use has yet to gain significant momentum. Alternatively, solar radiation can be used as an energy source to evaporate and dry liquid waste such as urine or wastewater. The resulting solid residues can be used as N and P fertilizers¹⁶⁰.

Human urine and feces are a significant potential source of phosphorus. According to the World Health Organization, urine is a fluid rich in N and P, with the ability to provide half of the seed’s requirement for P¹⁴. The results show that, in 2009, the availability of phosphorus from urine was approximately 1.68 million metric tons (with a similar mass available from feces), and the estimated amount that can be expected by 2050 is 2.16 million metric tons (with a similar mass available from feces). The potential availability of P from urine and feces produced in urban areas is estimated around 0.88 million metric tons per year, with a tendency to increase with population growth to over 1.5 million metric tons by 2050. The availability of P from urine and feces could cover 22 % of the overall global demand for P¹⁶¹. A special sewage network for the recovery of phosphorus of human origin is especially interesting in developing regions such as Africa and Asia, which have a large population and do not have a regulated sewage system.

The separation of urine at the source is potential for the recovery of phosphorus, taking into account the high concentration of P and the small volume. However, the treatment of urine is a challenge due to its unpleasant odor and hygiene problems. Since these problems can be solved by acidification to keep urine pH below 4, a new strategy for obtaining P from acidified urine using adapted hydrated nanoparticles of zirconium-coated magnetite (Fe₃O₄@ZrO₂) has been proposed¹⁶². This strategy includes selective phosphate adsorption with Fe₃O₄@ZrO₂, adsorption of adsorbed phosphate, and precipitation of desorbed phosphate as a calcium phosphate fertilizer. The results showed that, at pH 4, phosphorus was selectively adsorbed in synthetic urine and could be depleted using Fe₃O₄@ZrO₂. Almost all (> 97.5 %) of the P was isolated using ≥1 M NaOH solution, and ~100 % of the isolated P was successfully transformed into calcium phosphate by adding CaCl₂ at pH>12. Liquid/solid (Fe₃O₄@ZrO₂ particles) can be separated for reuse using an external magnetic field.

Wei et al., worked on the recovery of struvite and ammonium sulfate from the urine of pregnant women in the pilot plant for treatment, by deposition and removal of air/acids¹⁶³. The system achieved 94 % efficiency of struvite precipitation, but only 55 % of the crystals were removed and extracted. The low recovery of phosphorus was due to the leaching of small crystals that escaped from the sieves and precipitators, so an improved method for capturing crystals was needed. Nitrogen removal and recovery efficiencies were 93 % and 85 %, respectively. The analysis of the composition of the produced fertilizers showed that struvite is the dominant sediment, and the quality of ammonium sulfate meets European standards.

Xu et al.,¹⁶⁴ presented an innovative strategy for the selective separation of P from synthetic urine containing a high concentration of Cl⁻, by simply adjusting the filling and emptying process of the flow electrode capacitive deionization unit (FCDI). During the charging process, both P and Cl⁻ are transported to the anode chamber where they are adsorbed by charged carbon particles.

The inevitable Faraday reactions caused the formation of H⁺ and led to the conversion of charged P ions into H₃PO₄ and spontaneous desorption into electrolyte. When the polarity of the electrode is reversed, constantly charged species such as Cl⁻ are generally pushed back into the spacing chamber, while neutral H₃PO₄ is selectively trapped in the anode chamber due to slow pH variations (especially when higher carbon content is used), forming a P-rich solution. The results showed that FCDI can be a promising technology for efficient removal of P and recovery from urine separated from the source without the use of additional chemicals.

**Nanonucleation**

One of the main challenges in phosphorus recovery is its relatively low concentration in liquid waste, which complicates adsorption and precipitation reactions. In addition, although several procedures have been developed to remove P from waste streams, none of these conventional techniques has been identified as entirely cost-effective for recovering P for subsequent use as a nutrient source.

Nucleation by nanomaterials (nanonucleation) is effective in the crystallization and recovery of dissolved substances from unsaturated aqueous solutions. Nanomaterials can be naturally found in the soil, with particle size ranging from 1 to 10 nm,
which allows them to have a high sorption capacity for P. They bind P mainly by surface complexation, but particle aggregation can also occur by encapsulating sorbed surface species into the material. One such material is allophane clay. Its particle size range is 3–3.5 nm, and its specific surface area is 900 m² g⁻¹. Allophane effectively removes P from a wide range of P concentrations, and is recommended as a low-cost, environmentally friendly nanomaterial for regenerating P from waste streams. Other nanomaterials used to recover P are cerium oxide, iron oxide, and magnetite.

**Conclusions**

The paper provides an overview of phosphorus recovery technologies from waste streams as good practice examples combining sustainable development and circular economy. The need for phosphorus has become even more urgent and more evident by the fact that phosphate ore has been included on the list of critical raw materials formed by the European Commission. Initially, the removal of phosphorus from waste streams was not primarily aimed at its recovery in usable form, but rather at preventing pollution. Recently, many developed countries have adopted legislation that encourages the widespread use of chemical precipitation and biological treatment systems for wastewater treatment and combating the harmful phenomenon of eutrophication. In the last couple of decades, waste streams rich in phosphorus have been increasingly recognized as a promising secondary source of this element, providing the possibility of restoring it in a usable, bioavailable form. Therefore, the focus has shifted from P removal to P recovery and recycling.

A local, sustainable, and practically inexhaustible source of phosphorus that can be used as a raw material or directly as fertilizer would greatly alleviate the phosphorus crisis. Significant efforts have been made in the development of phosphorus recovery technologies, and the progress is evident. However, there is a lack of commercially operational processes, and most of them are based on chemical precipitation and obtaining struvite. The reason behind the relative success of the struvite technologies is the fact that struvite removal solves another issue: the issue of unwanted struvite precipitation in pipes for biological wastewater treatment. Controlled removal of struvite can prevent costly maintenance, which provides additional economic incentives for targeted struvite deposition.

Based on the reviewed technologies, it seems that the recovery of phosphorus from sewage sludge is more promising compared to other methods/technologies. The recovery from sewage sludge ash is five to ten times greater than the recovery from sludge and leachate. The downside is that such technologies are economically viable only in large wastewater treatment plants. This is mainly due to the high capital costs of the construction, considering the fact that the facility must meet all environmental criteria for sludge incineration. Still, there are several such plants globally.

As thermal treatment is often costly for the phosphorus recovery from raw solid waste (primarily manure), direct wet extraction has been used as an alternative. The advantage of this method over thermal pretreatment is the low content of heavy metals in the regenerated P product.

Nanoparticle nucleation (nanonucleation) is effective in the crystallization and recovery of dissolved substances from unsaturated aqueous solutions. Nanomaterials are naturally found in the soil, and their particle sizes range from 1 to 10 nm. These materials have a high sorption capacity for phosphorus. These include allophane clay, cerium oxide, iron oxide, and magnetite, to name only a few.

One of the widely used techniques to remove P from wastewater in treatment plants is phosphorus adsorption on different adsorbents. Low-cost materials can be used for this purpose, such as industrial by-products and natural materials. Another potential treatment is ion exchange. Ion exchange enables the precise separation of dissolved substances from waste streams. The advantage of ion exchange compared to adsorption is the possibility of renewal and reuse of ion exchange material.

Adsorption and assimilation of phosphorus by algae is another promising method. Photosynthetic algae use CO₂ and nutrients for their growth and produce oxygen, at the same time. Heterotrophic bacteria use these algae for their metabolism, thus forming NH₄⁺, NO₃⁻, and PO₄³⁻ ions. The advantage of this method is the value of the produced biomass. The collected biomass can be used in various industries, and as a raw material in the production of liquid biofuels.

Recovery of phosphorus using membrane technologies is a relatively new procedure and is still under development. Early results are very promising in terms of phosphorus recovery efficiency. This technology, however, is still not widely used due to the high operating costs of the entire process (cleaning, maintenance, and deposition chemicals).
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