

Review Article

Technological Options for Phosphate Removal and Recovery from Aqua System: A Review

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Abstract

Phosphorus is mainly removed from waste stream for the purpose of recovery for reuse in sustainable fertilizer production operations. Other reasons include eutrophication mitigation and improvement of the quality characteristics of wastewater for discharge. Furthermore, recovery of P helps to alleviate the challenges synonymous with the restrictions on the disposal of P in discarded sludge. The heightened interest in the removal and recovery of phosphate from waste streams led to the development and validation of different technological options. This paper reviewed the different technologies employed in the removal and recovery of P from waste streams and critically examined their strengths and limitations vis-à-vis the process sustainability.

Suggestions and recommendations were highlighted for present and future researchers to pursue and seek answers for better understanding and development of sustainable phosphate removal and recovery protocols.

Keywords: Environmental sustainability, phosphate removal and recovery, sewage sludge, struvite, hydroxyapatite, biosolids, wastewater treatment

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Introduction

The wide use of phosphates in agricultural and industrial applications inevitably produces large amounts of phosphates-bearing wastes, which are usually discharged into municipal and industrial effluents streams. Surface water naturally receives carbon, nitrogen, phosphorus and other nutrients from rainfall, runoff and seepage and intentional discharges. Rich nutrients input stimulate growth of algae which changes the water quality as their populations increase. This is particularly the case when they undergo population explosions referred to as "blooms" or eutrophication [1]. Approximately 50% of the lakes and reservoirs in all continents, except Africa and Oceania, are eutrophic [2]. The current knowledge of eutrophication and its concomitant effects motivated the authorities to introduce stringent laws restricting nutrient discharges from both wastewater treatment plants and other point sources of discharge contributors, thus requiring efficient removal of nutrients. Several methods have been reported for phosphate removal and recovery from wastewater including chemical precipitation and crystallization, physical methods (ion exchange and electrolysis) and biological process such as (EBPR and wetland processes). This review summarizes the different current technologies employed in the removal and recovery of phosphate from wastewater and critically examines both their strengths and limitations most especially as pertaining to sustainability.

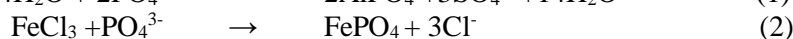
Phosphate Removal Technologies Options

P recovery from waste streams begins with its removal. Technologies for P removal from waste streams are numerous and have advanced significantly over the years. Several methods have been developed to remove phosphate from wastewater. While some are in large-scale treatment facilities, others are only experimental projects for a process-engineering system [3]. The techniques used include, chemical precipitation and crystallization [4] ion exchange, membrane filtration, electrocoagulation [5], biological processes that rely on biomass growth (bacteria, algae, plants) such as wetland and Enhanced Biological Phosphate Removal (EBPR) [6] and adsorption [7].

Chemical Methods

Chemical precipitation using salts of Ca, Al, Fe and Mg is the most effective and well-established process for removing phosphate from aqua matrix. Phosphate removal by chemical precipitation is very attractive technology as it is simple to operate and implement to achieve very low P (< 1mg P/L) in the effluent. Phosphate is removed by

converting the aqua phosphate ions into an insoluble form that is separated by sedimentation or clarification. These salts precipitate phosphates in solution forming a heavy floc blanket that settles through the water column [8]. Metal oxides are important phosphates removal sites due to their multiple charged cation and high surface charge. Four steps are usually involved in converting the soluble phosphate ions into the solid state: formation of a core solid matter, storage of precipitate, development of crystal and crystal maturation [9]. Reaction between phosphate and salts of Al, Ca and Fe respectively is given by:



Phosphate removal from wastewater by metal cations usually occurs by combination of mechanisms such as electrostatic interaction, adsorption by the Al or Fe oxide floc, and direct precipitation of Al or Fe phosphate. At low phosphate concentrations, phosphate is removed largely by adsorption (presumably outer sphere complexation) while precipitation is at work with high concentration. Several parameters influence the process of removal including solution pH, chemistry of the metal, presence of interfering ions, temperature, etc. When combined with an effective particle separation process, a high P removal can be achieved.

Although aluminium is expensive, it is a very effective precipitant. The precipitation of phosphates in solution by aluminium salts occurs almost instantly. Effective Al precipitation of phosphates occurs when both the Al and phosphate are in high concentration [10]. AlCl_3 and alum are strong precipitating agents for phosphate. Addition of polymers (cationic or anionic) enhances the efficiency of the process. This is by promoting the aggregation of the flocs formed during the process [11]. Calcium-phosphate precipitation is a common method of phosphate removal because it is cost effective and easy to handle. With respect to phosphate recovery, calcium-phosphate precipitation is preferred, as the sludge produced is useful in industrial and agricultural processes. The use of calcium compounds (CaO and CaCO_3) in the chemical precipitation of phosphate in aqua matrix is highly enhanced due to the possibilities of production of different calcium phosphate compounds that could be assessed for industrial production of fertilisers. Wastewater composition, pH, presence of interfering ions (CO_3^{2-} , NO_3^- , Mg^{2+}) and molar ratio of calcium ion to phosphate ion, determine the type of phosphate compounds produced. The presence of carbonate ions inhibit precipitation of phosphate ions by calcium by forming ion pairs with the calcium ions thereby bringing a decrease in the number of free calcium ions for phosphate precipitation [12]. Magnesium salts are rarely used as cations for phosphate precipitation, apart from intentional formation of struvite. Magnesium chloride and magnesium sulphate are effective phosphorus removal precipitants in wastewater and has been used for many years [13]. These salts remove phosphate by the precipitation of magnesium ammonium phosphate and magnesium phosphate [7, 14]. Although, Iron salts are relatively inexpensive, they are less effective precipitants for the treatment of phosphate contaminated wastewater [15]. Iron salts are usually supplied as ferric chloride (FeCl_3), ferric sulphate, ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) or ferrous sulphate ($\text{Fe}_3\text{O}_4 \cdot 7\text{H}_2\text{O}$) usually known as copperas, a cheap industrial by-product of the steel industry [15, 16].

Limitations

Removal of phosphates in wastewater treatment plants via chemical precipitation is attracting less research interest as expressed in many publicly available literatures for many reasons. Chemical precipitants imply prohibitive costs not only for the purchase but also installation of dosing equipment, operating costs for power, disposal of additional sludge, manpower and the chemicals used. Chemical precipitation is inefficient when phosphate is present only at trace concentration. Chemical precipitation technologies do not recycle phosphates as a truly sustainable product because it is removed with various waste products which are usually toxic to plants. Moreover, further application of the recovered phosphate sludges produced as fertilizers, is usually limited because recovered phosphates are too tightly metal-bounded and therefore cannot readily be reused for industrial and agricultural applications [17].

Physical Methods

Physical methods of phosphates removal include electrocoagulation [9], ion exchange [18-20]

Electrocoagulation

Electrocoagulation is very effective in a single phase to destabilize, aggregate and separate pollutants from waste stream. An electrocoagulation reactor is an electrochemical cell that consists of an electrode arrangement in contact

with the wastewater, with coagulant production in situ being their distinguishing feature [9]. The process involves the creation of metallic hydroxide flocs within the wastewater by the generation of coagulants via the electro-dissolution of a sacrificial soluble metal [21]. The coagulant is released by applying a potential difference across the electrodes. Coagulation and precipitation processes are conducted by the electrodes in the reactor instead of chemical coagulants. Characterized as being simple, the process involves easy-to-operate equipment, short operation time, none or negligible amount of chemicals usage, low energy requirement and decreased amount of sludge production [22]. The flocs (colloids, suspension or emulsion) formed by electrocoagulation (EC) are relatively large, contained less bound water, stable and easily amenable to filtration because they are influenced by electric charges. Electrocoagulation is comparatively a suitable process for phosphate removal using either aluminum or iron plate electrodes [23]. An increase in the supply of the electrical charges to the charged particles via appropriate electrodes causes a neutralization of the surface charge of the particles thereby causing them to combine into larger and separable agglomerates. The electrode assembly is the heart of the treatment facility and therefore selection of the appropriate electrode is very important. They are cheap, readily available and proven effective [24]. In effect, the effectiveness of the EC techniques depends on pH, current density, type of metal electrodes, number of electrodes, size of electrodes, and configuration of metals [25].

Ion exchange

Undesirable ions can be exchanged for solid-phase ions based on ion affinity in a process known as ion exchange. Ion exchange is promising for phosphate recovery because it is generally a reversible process [26] and the recovered phosphate could be collected in the form of high-grade fertilizer (struvite). A formidable competition posed by sulphate contained in the wastewater limits the phosphate removal capacity of many commercial anion exchangers. A selective anion exchanger, Polymeric Ligand Exchanger (PLE), is very selective toward phosphate in the presence of competing sulphate ions was developed by [27].

Membrane Filtration

Membrane filtration technologies are increasingly used nowadays for solid-liquid separation purposes in water and wastewater treatment plants. Membrane filtration is advantageous over chemical treatment in that it involves low energy consumption, small land area requirement, easy up-grading of existing facilities, continuous separation, better effluent quality and avoidance of chemical addition. Based on the pore sizes, membrane filtration methods are classified as, Micro-membrane filtration, MF (0.1 μm - 1 μm), Ultra-membrane filtration, UF (1nm - 0.1 μm), Nano-membrane filtration, NF (1nm - 0.01 μm) and Reverse osmosis, RO (> 1nm). MF will remove suspended matter and bacteria. UF is well suited for the removal of some natural organic matter and viruses. NF has the capability to remove organic micro-pollutants, multivalent ions and some monovalent ions while RO is suitable for the removal of all the ions and dissolved salts [20, 28]. Operational factors such as flux, cross flow velocity, concentration of phosphorus in feed water, pH and ionic strength affects the efficiency of the membranes [29].

Limitations

Phosphates removal by physical method suffers several limitations. The electrocoagulation (EC) technique is limited in its application based on the following: constant replacement of electrodes, difficulty with removal of suspended solids, high cost for electricity generation, development of an impermeable oxide film on the cathode leading to loss of efficiency of the EC unit, requirement of high conductivity in the wastewater suspension before treatment and in some cases, new species such as Cl^- , SO_4^{2-} are introduced into water. The application of ion exchangers in the removal of phosphate is highly impeded by several factors such as requirement of high regeneration costs, sludge disposal problems created via precipitation or coagulation processes. A major limitation in the efficiency of the membranes is the fouling by solid particles [30, 31]. Fouling increases the resistance of the membrane thereby reducing its ability to remove ions. Fouling of the membrane system are of different types namely, inorganic, organic, particulate, colloidal and bio-fouling [32]. Pre-treatment can easily be used to control all types of fouling with the exception of bio-fouling [33]. A higher operating pressure system, more frequent chemical cleaning and shorter membrane life is required when bio-fouling sets in, thus, increasing the cost of operation and maintenance [19]. Although RO and NF can be used to remove phosphate substantially from waste stream, its utilization is becoming too unpopular because membrane treatment is expensive and not suitable for mainstream phosphate removal.

Biological Methods

Biological phosphate removal process is much popular nowadays over chemical methods due to its simplicity, reduced chemical cost, less sludge production and several environmental benefits. Biological process involves removing phosphates by accumulating it with biomass (algae, bacteria, plants). Two major research areas of biological methods are the Enhanced Biological Phosphate Removal (EBPR) and wetland processes. Wetland systems (natural or constructed (engineered) are systems, which employ wetland vegetations to assist in treating wastewater [34]. Wetland systems are characterized by moderate capital costs, low energy consumption and maintenance requirements [35]. The Wetlands plants or macrophytes include *Scirpus* (bulrush), *Lemna* (duckweed), *Eichornia crassipes* (water hyacinth), *Pistia stratiotes* (water lettuce). The macrophytes enhance wastewater treatment either by acting as a medium for bacterial growth, filtering/adsorbing suspended particulate matter or removing inorganic nutrients from the wastewater [35, 36]. The EBPR process is a promising area of research that is based on the cultivating of natural microbes in a P rich- side stream. Simply put, it relies on the enhancement of the ability of microbes to uptake more phosphates into their cells. The process consists basically of alternating conditions of anaerobic zone followed by an aerobic zone. The organisms that help achieve the process by accumulating the poly-P reserves are called Polyphosphates Accumulating Organisms (PAOs). In the anaerobic conditions, the PAOs decompose their poly-P and create adenosine triphosphate (ATP) and use the ATP to adsorb volatile fatty acids (VFAs) in water and store as Poly- β -hydroxyalkanoates (PHAs) in the bacterial body. Thus, organic matter uptake and phosphate release take place under the anaerobic condition [37]. In the aerobic conditions, PAOs will decompose the stored PHAs to be a carbon and energy source for aerobic activities and use ATP to adsorb phosphate as well as other nutrients in water. Thus, phosphate uptake takes place in the aerobic condition. Therefore, the phosphate will be in the sludge after the aerobic condition. The phosphate accumulated in the sludge will then be removed by sedimentation. The higher the concentration of PAOs, the higher the concentration of phosphate removed in the reactor sequence [38]. The accumulated phosphate in the sludge is a high energy poly-P reserves, usually released in the form of orthophosphate from the cells of the PAOs as organic matter. P removal via EBPR is favourable, as the P can be readily recovered along with good quality sludge.

Limitations

P removal via biological process can remove up to 97% of the total phosphates, but the process can be highly variable due to operational difficulties. The process however is usually limited based on infrastructural availability. A huge amount of energy is also needed for the maintenance of the complex conditions (anaerobic, aerobic and anoxic) involved. Moreover, conventional biological methods have limited phosphate removal capacity as microbes utilize phosphate during cell synthesis and energy transport; therefore, some of the soluble phosphates are still present in the effluent [3, 39].

Adsorption Methods

The change in concentration of a substance at the interface as compared with the neighbouring phases is referred to as adsorption. Among the treatment methods discussed so far, adsorption method has been found to be more superior for phosphate removal on the basis of cost, flexibility, simplicity of design, ease of operation and maintenance. The use of cost-effective adsorbents with wide availability and high phosphate sorption capacity to remove phosphate in wastewaters has become popular worldwide recently. The adsorption technique is usually described by several phenomenon such as adsorption equilibrium and kinetics and thermodynamics. Many investigations have been carried out on phosphate removal using low cost materials. These materials removed phosphate ions from aqueous solutions either through adsorption on iron and aluminium (hydr)oxides or precipitation as phosphate salts by Ca^{2+} and Fe^{3+} ions. Most studies have shown that excellent and efficient phosphate adsorbents are all characterized by their high aluminium, iron or calcium contents which can effectively remove phosphate from wastewaters by the adsorption and/or precipitation to chemically stable phosphate phases [40]. These adsorbents are categorized as: (a) Natural inorganic minerals (b) Industrial wastes / by- products and (c) Biogenic derived materials.

Natural inorganic Minerals

These include raw minerals such as zeolite, sepiolite, calcite, dolomite and soil (laterite and marl). The adsorption of phosphate is attributed to a ligand exchange reaction on the adsorbent surface, in which the phosphate ion is exchanged with structural hydroxyl groups on the surface of the adsorbents [41, 42]. Zeolites are naturally occurring hydrated aluminosilicate minerals, known as tectosilicates; consisting of a three-dimensional framework structure

bearing SiO_4 and AlO_4 tetrahedral. They belong to the class of minerals. Karaprina, [43], achieved a 93% phosphate removal at the pH of 7.2 within 120 minutes. Karageorgiou et al [1], reported orthophosphate species uptake from aqueous solutions using calcite. The results showed that the process was more effective in the highly basic pH region, resulting in complete removal of the various orthophosphate species. Sepiolite, a hydrated magnesium silicate clay mineral with a fibrous chain structure, non-toxic and relatively inexpensive has a high sorption capacity for phosphate [44]. Sepiolite has a unique property over other clay materials in that it does not exhibit swelling properties, and as such, difficulties such as clogging of hardware or jamming of filters in treatment systems does not occur with its usage [45].

Industrial Wastes and By-Products

Several research groups have investigated the use of industrial wastes and their by-products for phosphate sequestration. Metal oxides are found in numerous industrial by-products, thereby promoting them as attractive candidates for use as adsorbents for phosphate removal. As by-products, they are usually relatively inexpensive. These include calcium and iron oxides from steel making slag [46], calcium and aluminium silicate minerals [47], iron and aluminium oxides from water treatment residuals [48] and coal combustion fly ash. Blast-furnace slag, a residue from the steel-iron processing, has high percentage of alumina and silica, and is relatively available abundantly for large scale use [49]. Among the slag materials, converter slag has competitive advantage as seed crystals for phosphate crystallization and as adsorbent for phosphate removal in terms of its cost-effectiveness and high performance [50]. The use of converter slag is limited because it easily aggregate together in water phase or moisture conditions making the hydraulic conductivities of a column reactor to decrease and reduce the efficiency of treatment [51]. Coal cinder is an inorganic waste produced in coal combustion. Coal cinder is often mixed with other materials like red clay, in soil treatment systems for improving the permeability and enhancing nutrient removal caused by its complex porous structure and high hydraulic conductivity. The combination of coal cinder and converter slag as filter media for wastewater treatment enhances higher phosphate removal ability of the converter slag and an improved effluent quality caused as a result of removing the nutrients. Fly ash is a residue and particulate substance containing metal oxides, carbon and other microelements that results from the combustion of coal in a power plant. Fly is a widely available and cheap adsorbent and its alkaline properties make it interesting for use in wastewater treatment for precipitation of phosphates [52]. Fly ash releases free lime in solution thus producing an insoluble or low solubility salt when combined with phosphate [53]. Gas concrete is produced from different mixtures of silica, sand, cement, lime, water, and aluminium cake, which produce gas. One of the main advantages of phosphate removal by gas concrete is that it does not produce any chemical sludge [54].

Biogenic derived materials.

Biogenic materials are particulates or dissolved organic compounds such as carbohydrate, fats or proteins of living organisms and their remains or inorganic compounds such as shells or skeletons. On the basis of waste minimization and cost reduction, many biogenic materials have found utilization as adsorbents for phosphate removal from waste streams. These include, scallop shell synthesised ceramic biomaterial [55], thermally treated recycled oyster shell [56], Corbicula shells [57], Gastropod shells [58], calcined eggshell [59]. These materials are characterised with high affinity for phosphate due to their high contents of metallic oxides, especially CaCO_3 and large surface areas.

Limitations

Adsorptive treatment technology of phosphate removal is limited by several factors including high operation cost of energy, maintenance, sludge handling and disposal. Although, biogenic materials are inexpensive, their availability and accessibilities impedes their usage as sorptive materials. Huge cost may have to be incurred for the transportation of these materials from their natural habitat. Large-scale availability and consistent supplies of industrial materials and by-products is difficult to guarantee. Moreover, bioavailability of the metal-bound phosphate to plant is highly variable.

In summary, this review shows that the various techniques of phosphate removal has attracted the attention of scientists and has been extensively studied by researchers. Comparison of the different techniques is rather difficult to undertake because of the inconsistencies and paucity of necessary information in the data presentation and variations in the experimental processes. Phosphate removal was evaluated at different experimental conditions such as pH, initial phosphate concentration, temperature, type of wastewater (synthetic, industrial, seawater, agricultural etc), reactor system (batch, continuous, column etc). All these make comparison to be rather difficult and complicated.

Therefore, the comparison among the techniques is done based on their strength /advantages and weakness/ disadvantages of the removal methods discussed (**Table 1**).

Phosphates Recovery Technological Options

Need for Phosphate Recovery

Phosphorus is a vital, non-renewable, finite resource that is being depleted at an alarming rate. Its recovery has become a necessity for sustainable development as phosphate rock prices have risen and access to good grade phosphate rock diminishing [35, 60]. The perspective of viewing P in wastewater as contaminants rather than a resource has begun to change recently. A simple and practical solution to P shortage lies in recovering and recycling P. The main current focus of P recovery is to extract the maximum amount of P from recoverable sources such as wastewater, sludges and sewage sludge ash for fertilizer production [61, 62]. Other focuses include: water pollution prevention (eutrophication), improved wastewater treatment [63, 64] and Industrial P application [65]. Furthermore, recovery of P would help to alleviate the restrictions on sludge disposal of minimal levels of P in discarded sludge.

Technological Processes of Phosphate Recovery

The processes and techniques applied for P recovery and reuse vary greatly and are dependent on the source, composition of the waste stream and reuse of P [61]. P recovery from wastewater treatment plants is possible using existing technologies [3, 66]. Numerous approaches to the recovery of P from wastewater or sludge exist. The processes and technologies of the recovery approaches could be categorized based on (a) the type of material source (b) technological methods and (c) P recovered products.

Material Sources of P recovery

The primary source of P is phosphate rock, mined at just limited locations in the world, including USA, China, Morocco and Western Sahara [67]. Alternative sources of P include municipal waste stream, agricultural (animal husbandry and vegetable processing plants) and industrial by-products. P recovery technological processes are highly dependent on and specific to the form and type of the waste streams [68]. P can be recovered from three basic sources, namely, side stream/sludge liquor (Liquid phase), sewage sludge (digested, non-digested or dewatered) and sewage sludge ash [69].

Table 1 Strengths and Limitations of the Various Phosphates Removal Techniques

Techniques	Strength	Weakness
Chemical Precipitation	<ul style="list-style-type: none"> Highly Effective Well understood High Removal Capacity Fast 	<ul style="list-style-type: none"> Expensive pH dependent Not appealing for recovery purpose Not effective at low concentration Sludge handling and disposal problem.
Physical Methods Membrane Filtration	<ul style="list-style-type: none"> Low energy demand Less time consuming Less space requirement High selectivity Low energy demand No sludge generation 	<ul style="list-style-type: none"> Membrane fouling Low chemical stability Low thermal stability Swelling and clogging
Ion exchange	<ul style="list-style-type: none"> Highly selective Energy efficient Low maintenance Easy regeneration 	<ul style="list-style-type: none"> High cost (Resin) Solution concentration must be maintained High energy demand Selection of appropriate electrode

Electrochemical (Electrocoagulation)	<ul style="list-style-type: none"> • Low cost • High selectivity • Ease of operation • Negligible use of chemicals 	<ul style="list-style-type: none"> • Huge sludge generation • Solution concentration must be maintained • Replacement of electrode
Biological	<ul style="list-style-type: none"> • Low cost • Effective at low concentration • Reduction in sludge production • Negligible use of chemicals • Possibility of recovery 	<ul style="list-style-type: none"> • Large space requirement • Process is highly variable • Requirement of large amount of microorganisms • Environmental pollution from microbes
Adsorption (Natural inorganic minerals, Industrial by-products, biogenic derived materials)	<ul style="list-style-type: none"> • Low cost • High quality treated effluent • Negligible use of chemicals • High sorption capacity • Fast 	<ul style="list-style-type: none"> • Sensitivity to operation conditions: pH, ionic strength • Sludge handling and disposal • Non – availability and easy access to sorbents • Limited supply of sorbents.

P recovery from P rich side stream/ effluent wastes (Liquid phase) Recovery of P from runoffs and animal wastes is promising as these two sources contain enormous amount of P [70]. P recovery from waste stream is usually limited and ranged between 10-40% [71] this is because P concentration in waste streams are relatively low (<100mg/l) and therefore need to be accumulated for a beneficial recovery [68]. This is usually achieved by accumulation of the nutrient. Accumulation of soluble P from waste streams of low concentration can be achieved via biological, chemical or physical treatment. A common and efficient way is usually based on the use of EBPR process on P rich side streams, which leads to easy release of P from the sludge followed by crystallization as struvite or calcium phosphate [60]. Wastewater treatment plants facilities are capable of removing phosphate from municipal wastewater with low P concentration (5–10 mg P/L) and animal husbandry with high P concentration (excess of 200mg P/L).

P recovery from Sewage sludge Recovery of P from sewage sludge is generally very efficient with almost 85% of the soluble P is incorporated in the sludge, which account for about P recovery potential from the sludge of about > 94% [71]. The biosolids from wastewater treatment plants contains considerable amount of P. P recovery from sewage sludge has attracted a lot of research interest [62, 70]. However, sourcing sewage sludge for P, deserves great care; sewage sludge contain high load of toxic organic compounds, pathogens and heavy metals which renders the products obtained unfit for agricultural and industrial use. Decontamination of the product involves redissolution and selective precipitation of the phosphate product, a costly and complex process. Several technologies are used to recover P from sludges including, bioleaching, crystallization, gas-permeable membrane and wet chemical technologies [60].

P recovery from Sewage sludge ash Sludge incineration is the controlled combustion of sewage sludge at high temperature in a furnace. Incinerated sewage sludge produces what is called sewage sludge ash. If sludge is incinerated, P recovery from ash is a promising prospect as it contains almost 95% of the P load to the WWTP. However, it should be noted that only mono- incinerated sludge is useful for P recovery because incineration of the sewage sludge with other wastes lowers the P concentration and increase the level of contaminated in the ash. Incineration of the sludge reduces sludge volume, organic pollutants and pathogens content and produces an ash containing the highest concentration of P from the waste stream. Sourcing P from sewage sludge ash is attractive because of ease of transport because of reduction in volume [72]. However, the ash contains a high concentration of heavy metals which must be separated before P recovery.

Limitation and Potentials

P recovery from the liquid phase can be done on a small or large scale nearly at every WWTP, whereas the use of sludge and sewage sludge ash implies higher energy and material cost and as such are limited. The presence of metals, pathogens and toxic organic matter limit the use of sewage sludge which requires huge cost of amount of chemicals to redissolve and precipitate the recovered P from the sludges. Sewage sludge and sewage sludge ash can produce fertilizer product for direct use in agriculture but products of P recovery from liquid phase need further

treatment before its reuse [73]. P recovery from sludge ash is considered with a greater potential than its extraction from sludge such as: higher recovery strength (90%), lower amount of toxic waste and heavy metals, saved cost of sludge and ash disposal to landfills [60]. A summary of the different sources limitations and potentials are presented in **Table 2**.

Technological options for P recovery

There are numerous technological approaches to P recovery [3, 60, 61]. The three significant recovery technologies include: Crystallization, Wet chemical treatment and thermal treatment.

Table 2 Limitations and Strengths of the different sources for P recovery

Phosphorus Recovery Source	Concentration of phosphorus	Recovery Potential	Applicable technology	Limitations	Strengths
Liquid Phase	Less than 100mg/l	40%	<ul style="list-style-type: none"> Crystallization 	<ul style="list-style-type: none"> Low recovery rate Huge volume of sludge Presence of heavy metals and toxic substances Products require further treatment before use 	<ul style="list-style-type: none"> Easy to operate Applicable to both low and high scale Low cost Production of compact reusable pellets
Sewage sludge	About 10g/kg	90%	<ul style="list-style-type: none"> Crystallization Wet Chemical 	<ul style="list-style-type: none"> High pollutant load. High capital cost Limited to low scale application 	<ul style="list-style-type: none"> High P recovery potential Product can be applied directly in agriculture
Sewage sludge ash	64g/kg	90%	<ul style="list-style-type: none"> Wet chemical Thermo-chemical 	<ul style="list-style-type: none"> High energy consumption Dependent on P removal method Dependent on mono incineration 	<ul style="list-style-type: none"> High P recovery potential Negligible amount of toxic materials Product can be applied directly in agriculture Ease of transportation Reduced volume of sludge

Crystallization Methods Crystallization technological methods are commonly used to recovery P from P-rich side stream effluents. Wastewater effluent or liquor (anaerobically digested or dewatered) with P concentration greater than 100mg/l have proven economically rewarding and is been operated in several plants in full -scale [71]. A sufficient phosphate concentration is usually required for crystallization to occur. Comparably to conventional precipitation, crystallization technology involves dosing of the water with a metal salt (Ca, Mg, Al and Fe) until supersaturation occurs and subsequent transformation of the phosphate salt into solid crystal materials from the aqueous solution. On the basis of recovery, the choice of the metal ion used is important, because recovered P that is too tightly metal-bound (Al-P and Fe-P) cannot readily be reused in industrial and agricultural applications [74]. There are 3 stages involved in the process namely; supersaturation, primary and secondary nucleation and crystal growth [60]. Phosphate crystal pellets produced are usually air- dried, readily handled, highly pure and with a typical size of 1mm. Magnesium- and calcium-based precipitation products are most commonly recycled as fertilizer [75, 76]

Wet chemical Methods The wet chemical treatment involves the use of chemicals (acids/base), pressure and/or temperature for the dissolving, leaching, release or extraction of bound P from the sewage sludge or sewage sludge ash. When chemicals are used for the dissolution, heavy metals are dissolved along with the phosphate and need to be removed from the solution before the recovery of P. Recovery of the redissolved P is achieved using several treatment

methods such as, ion exchange, adsorption, membrane filtration but crystallization technique is the most popular [71]. The heavy metals can be subsequently removed as precipitated metal sulphides using sodium sulphide salt [77]. This method of recovery is considered as the most expensive and complex due to the huge amount of chemical usage and various processing steps involved [60].

Thermochemical Methods The main focus of this method is to remove heavy metals present in the sewage sludge ash as well as increasing the bioavailability of the P in the ash to the plant. The technology is based on recovery of P from the ash obtained from the incineration of the sewage sludge. The ashes and chlorine compounds ($MgCl_2$, or $CaCl_2$) are usually fed into a furnace operated at 250-800°C [68]. The processes involved include, pyrolysis, wet oxidation, incineration, gasification and hydrolysis. The P recovery potential of this technique is very high (>90%). Moreover, the technology is independent on the characteristics of the sewage sludge ash, unlike the wet chemical treatment [72]. However, the method is limited to only ashes that were mono-incinerated and not applicable on large scale due to huge amount of energy consumption.

Limitations and Potentials

The crystallization process is a cheap, easy to operate and efficient way to recover P from wastewater as useful products [78] but suffers some setbacks including, heavy metal ions and toxic substances remain bound in the sludge requiring further treatment for the removal before P can be efficiently recover for reuse. This requires intensive use of chemicals leading to increase in cost of treatment. Other limitations of the crystallization techniques include increased sludge production, inhibitory effects on the biological process as a result of increased salinity [68].

Table 3 Limitations and Strengths of the different Methods of P Recovery

Technology	P recovery Potential	Limitations	Strengths
Crystallization	Fair	<ul style="list-style-type: none"> Metals remain in the sludge P recovery rate is 40% maximum Sludge handling and disposal problem 	<ul style="list-style-type: none"> Process is very simple Cost effective Applicable to treating liquid phase Maximum of 2 processing steps Applicable on both small and large scale treatment
Wet chemical	Excellent	<ul style="list-style-type: none"> Process is complex Huge financial investment is required Requires digestion/ fermentation of the sludge Requires large amount of chemicals Requires many process steps Not economical on small scale 	<ul style="list-style-type: none"> Applicable to sewage sludge and sewage sludge ash Metals are dissolved from the sludge Can work on any sludge Suitable for large scale treatment
Thermochemical	Excellent	<ul style="list-style-type: none"> Process is complex Requires incineration of the sludge Requires huge amount of energy Operated only on large scale, not economical on small scale Limited to only mono-incinerated sludge Amount of P recycled is limited because of mono-incineration 	<ul style="list-style-type: none"> Heavy metals and toxic organic pollutant are eliminated from the sludge Produces ashes that could be applied directly in agriculture High recovery potentials

A higher integration and binding strength of P exist in sewage sludge and sewage sludge ash, this implies that recovery of P via wet chemical and thermochemical methods are more expensive. The thermochemical treatment can

greatly reduce bulk volume of wastes and pollutants. The technologies are limited by high operating and capital costs. A summary of the limitations and potentials of the various technologies are presented in **Table 3**.

P Recovery Products

Until recently, P has been economically produced by leaching apatite minerals (phosphate rocks) with sulphuric acid. The processes involve include beneficiation, drying, calcining and grinding. Mined rock phosphate is a relatively cheap source of phosphate for fertilizer production. According to several reports [3, 62, 67] the high quality resource will near depletion within the next 100-120 yrs. Increase in price and worsening accessibility has therefore heightened the need for sustainable P recovery studies among researchers. P can be recovered as different products; however, application in agricultural purposes determines majorly the product type. P can be recovered as struvite ($\text{MgNH}_4.6\text{H}_2\text{O}$, MAP), hydroxyapatite and sewage sludge / sewage sludge ash.

Struvite P recovery as struvite (magnesium ammonium phosphate hexahydrate) is very promising and preferred [13]. Struvite is normally recovered from EBPR plants in a wastewater treatment facility. Struvite crystallizes as a stable white, orthorhombic substance in a molar ratio of magnesium, ammonium and phosphate of approximately 1:1:1 in the pH range of 8. Factors such as temperature, mixing energy, presence of other ions (especially, Ca^{2+}) affect the process. Struvite crystallization is applicable where the waste stream being treated is low in solids contents. A valuable agricultural fertilizer, it is sparingly soluble in water with reduced potential to cause eutrophication to water bodies and highly comparable in performance to commercial fertilizer in terms of dry matter production, P uptake and extractable residual P. Furthermore, struvite crystallization helps to reduce chemical costs of WWT as it reduces sludge generation and disposal problem. Struvite is easy to handle and transport when recovered in a granular form, as a slow-release fertilizer, requiring less frequent application and decrease in loss of nutrient via surface run-off [79] and contains low amount of heavy metals and pathogens [80]. Struvite production is a favourable reaction in many wastewater treatment plants because of the presence of inherent nutrients (N and P) in the wastewater [81]. Magnesium concentration is usually low relative to ammonium and phosphate in wastewater, therefore the addition of magnesium is necessary to achieve struvite crystallization. Sources of magnesium include MgCl_2 , $\text{Mg}(\text{OH})_2$ and MgO [82]. Sparingly water soluble crystal of struvite forms when the concentration of Mg, NH_4^+ , and P reaches supersaturation; seeding materials can also be added to the reactor to induce crystal growth. Most industrial wastewater treatment full-scale with crystallization process produces struvite.

Calcium phosphates P recovery as calcium phosphates products includes dicalcium phosphate dihydrate (DCP), tricalcium phosphate (TCP), hydroxyapatite (HAP) and whitlockite. HAP, with chemical formula $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is the most thermodynamically stable form amongst them. Calcium phosphates recovery is suited for Ca rich wastewater having high concentration of P and low NH_3 concentration and high pH of 8-9 [83]. Lime is usually added as a source of calcium to the wastewater which is economically cheaper than magnesium. However, other seeding materials such as sand, calcite or calcium silicate hydrate have been used to crystallize pellets of calcium phosphate at high supersaturation [78]. Calcium phosphate is used as direct substitute in industrial application as fertilizer and also by mixing with other nutrient, where a slow-release fertilizer is obtained for agricultural purposes. Calcium phosphates recovery is recently gaining much attention as other promising sources of calcium are being investigated [42, 58, 84].

Sewage Sludge/ Sewage Sludge Ash P recovery as sewage sludge/ sewage sludge ash is produced via wet chemical and thermochemical treatment of sludge from wastewater treatment respectively. Sewage sludge is also referred to as biosolids. Inherent fertilizer contents found in biosolids is of great importance in direct land application as soil conditioner in sustainable agricultural practices. Sewage sludge builds and maintains higher soil organic matter contents which leads to improved soil physical condition, rejuvenate soil health and stimulate its biological activity. The major drawback in the application of sewage sludge in agriculture as fertilizer is environmental and human health concern due to its high pollutant load of heavy metals, organic compounds, pharmaceutical and pathogens. The use of ash from thermochemical treatment is becoming increasingly popular because of various benefits, with the major benefit being negligible amount of contaminants found in the sewage sludge [68]. Further treatment of the sewage/ash by mixing with other nutrients such as NH_4NO_3 , K_2SO_4 , KCl produces a multinutrient fertilizer in industrial and agricultural application.

Limitations and Potentials

Spontaneous formation of struvite fouls pipes and inner surfaces of wastewater treatment plant leading to an inefficient and expensive process. A deliberate and controlled recovery of P as struvite in WWTPs would therefore, alleviate unwanted struvite deposits in anaerobic digestion and post digestion processes, and also ensures environmental sustainability [3]. Recovered P products as struvite can be of superior quality than currently available phosphate rock. Application of sewage sludge in agricultural land is becoming less popular because of its pollutant load of heavy metals, which implies further treatment (costs) before they can be used in agriculture [60]. Over 90% of the P load to a WWTP is usually contained in the sewage sludge ash. Treated ash can be used directly as fertilizer. Biosolids (sewage sludge/ sewage sludge ash) reduces run-off and increase surface retention of water by soil. Sewage sludge is a good alternative source with a high phosphate potential. During CaP recovery, a high pH, excessive Ca^{2+} concentration is needed. A major limitation of struvite and Hydroxyapatite is very low organic matter (contents). A major limitation with sewage sludge is the expense associated with transportation to the site of application/disposal; sewage sludge has a high volume of moisture content (>89%). Summary of the limits and strengths of the different recovered products is presented in **Table 4**.

Table 4 Limitations and Strengths of the Different P Recovered Products

Recovered Products	Strengths	Limitations
Struvite	<ul style="list-style-type: none"> • Production is relatively simple and easy • Process is very easy to scale -up • Applicable to both municipal and agro-industrial wastewater • Negligible heavy metal content • Low moisture content • Easy to handle and transport • Production reduces chemical and operation cost of WWT • Low amount of sludge production. 	<ul style="list-style-type: none"> • Low organic matter content • Spontaneous production fouls and clogs pipes
Calcium phosphates	<ul style="list-style-type: none"> • Production suitable for wastewater with high P concentration and low NH_3 content. • Easy to handle • Reduced cost 	<ul style="list-style-type: none"> • Not suitable for municipal wastewater • Production affected by the presence of carbonate • A high pH and excessive Ca^{2+} concentration is needed. • Low organic matter content
Sewage sludge/ Sewage sludge ash	<ul style="list-style-type: none"> • Production saves cost of disposal • High organic matter content • An important biological organic fertilizer and soil conditional • Add micro and macro nutrients to soil • Reduces surface run off and increases surface retention capacity of soil 	<ul style="list-style-type: none"> • High heavy metal content in sewage sludge • Increased cost for treatment (incineration) to produce ash

Current Technological Approaches of P Recovery

Several P recovery processes have emerged recently, while some are already in full blown large industrial scale, some are still in development stage and some are only applicable at the laboratory stage. In **Table 5**, the basic recovery processes and products obtained from the different sources available on the internet and existing literatures are summarized.

Table 5 Current Technological P Recovery Processes and Recovered Products

Process Name	Input Source	Recovery Potential	Technology	Recovered Product	Technological Purpose	Stage	Reference
Ostara Pearl	Mixed Wastewater	80-90%	Crystallization with addition of $MgCl_2$	Struvite	P recovery from waste stream	Industrial scale	61, 85
Unitika Phosnix	P-rich side stream	80-90%	Crystallization with addition of $Mg(OH)_2$	Struvite	P recovery from waste stream	Industrial scale	86
Ash Dec	Sewage sludge ash	>90%	Thermochemical with use of $CaCl_2$ or $MgCl_2$ to remove heavy metals	Sewage sludge ash	Heavy metals removal	Pilot scale	63,87,90
MEMPHREC	Sewage sludge ash	>90	Thermal (Incineration) treatment in a blast furnace	CaP fertilizer	Heavy metals removal	Semi industrial scale	88
BioCon	Sludge	>85	Wet chemical (Extraction with H_2SO_4 , removal of heavy metal via ion exchange)	Phosphoric acid	Removal of organic matter, dissolution of P and heavy metals	Semi industrial scale	89
SEPHOS	Sludge	>85	Wet chemical (leaching with acid and precipitation with base)	CaP/ AIP	Heavy metal removal	Lab-scale	89

Conclusion

Overall, this review has highlighted the various removals and recovery technologies options applied for P. Chemical phosphates precipitation, though highly understood, is besieged with numerous problems stated in the review. Biological phosphate removal is highly variable in operation, sensitive and subject to many fluctuations and uncertainties. The use of cost-effective absorbents and high phosphate sorption capacity to remove phosphate in wastewaters, though has become popular worldwide, is limited by availability in terms of quantity and accessibility. Tertiary wastewater facility that removes P via chemical or biological treatment as a non-recyclable metal-phosphate losses the P forever with numerous other waste materials as sludge. A recovery technology that can efficiently separates P from other waste components, so that it can be recycled as a fertilizer or an ingredient in other valuable phosphorus products is highly needed for sustainability. Combination of P removal via EBPR and P recovery as struvite and hydroxyapatite are appropriate sustainable technologies. The combination of these technologies, apart from being simple and easy to operate, implies reduction of chemicals for precipitation, reduction of size of the treatment facility, and reduction of the volume of effluent to be treated and consequently reduce costs. The other technologies discussed herein are only suitable at large scale operation, because they require huge amount of chemicals and operation processes and an in-depth engineering knowledge and skill by the operators. Future researchers may need to undertake several lines of research to assist our understanding of these techniques.

References

- [1] Karageorgiou K, Paschalis M, Anastassakis G.N, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, *J. Hazard. Mater.* A139 (2007) 447-452.
- [2] Sengupta S, Pandit A, Selective removal of phosphorus from wastewater combined with its recovery as a solid phase fertilizer, *Water Res.* 45 (2011)3318-3330.
- [3] de-Bashan, L. E. and Y. Bashan (2004). "Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003)." *Water Research* 38 (19): 4222-4246.

- [4] Ruixia L, Jinlong G, Hongxiao T, Adsorption of fluoride, phosphate and arsenate ions on a new type of ion exchange fiber, *Journal of Colloid and Interface Science* 248 (2002) 268–274.
- [5] Koparal, A.S, Yavuz, Y, Ogutveren , U, (2002). Electroadsorption of Acilan Blue Dye from textile effluents by using activated carbon-perlite mixtures. *Water Env. Res* 74 (6) 521-525
- [6] Sommariva C, Converti A, Borghi M.D, Increase in phosphate removal from wastewater by alternating aerobic and anaerobic conditions, *Desalination* (1996) 255–260.
- [7] Chitrakar, R., Tezuka S, Sonoda A, Sakane K, Ooi K, Hirotsu T , Phosphate adsorption on synthetic goethite and akaganeite. *Journal of Colloid and Interface Science*, 2006. 298 (2) 602-608.
- [8] Kroiss, H., H. Rechberger & L. Egle (2011) Phosphorus in Water Quality and Waste Management.
- [9] Chen G, Chen X, Yue P.L., Electrocoagulation and electroflotation of restaurant wastewater, *J. Environ. Eng.* (2000) 858–863.
- [10] Sawsan A. M. M and Haider A. S, 2009 Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride *Iraqi Journal of Chemical and Petroleum Engineering* Vol.10.(2) 35-42
- [11] Ozacar M, Adsorption of phosphate from aqueous solution onto alunite, *Chemosphere* 51 (2003) 321–327.
- [12] Song Y, Hahn H.H, Hoffmann E, Effects of solution conditions on the precipitation of phosphate for recovery. A thermodynamic evaluation, *Chemosphere* 48 (10) (2002) 1029–1034.
- [13] Wang, H., Brown, S. L., Magesan, G. N., Slade, A. H., Quintern, M., Clinton, P. W., and Payn, T. W. (2008). Technological options for the management of biosolids. *Environ. Sci. Pollut. Res.*, 15(4), 308–317.
- [14] Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2009. Phosphorus recovery from wastewater by struvite crystallization: a review. *Crit. Rev. Environ. Sci. Technol.* 39, 433–477.
- [15] Zheng, L., Xiaomei, L., Liu, J., 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research* 38, 1381. adsorption onto goethite. *Journal of Colloid and Interface Science* 308, 40–48.
- [16] Genz A, Kornmuller A, Jekel M, Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide, *Water Res.* 38 (2004) 3523–3530
- [17] Sibrell, P.L., 2007. Method of Removing Phosphorus from Wastewater. U.S. Patent 7,294,275.
- [18] Levlin, E., 2001. Recovery of phosphate and separation of metals by ion exchange. In: *Proceedings of a Polish-Swedish Seminar. Wastewater, Sludge and Solid Waste Management*
- [19] Martin B.D, Parsons S.A, Jefferson B. Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Sci Technol* 2009 60 (10) 2637-45
- [20] Paul, D.H., 2011. Reverse Osmosis: scaling, fouling and chemical attack. *International Desalination & Water Reuse* 1, 8–11.
- [21] Balmér, P. 2004. Phosphorus recovery – an overview of potentials and possibilities. *Water science and technology*, 49(10): 185.
- [22] Berg, U., G. Knoll, E. Kaschka, P.G. Weidler, and R. Nuesch. 2006. Is phosphorus recovery from waste water feasible? *Environmental Technology* 28: 165–172
- [23] Irdemez S, “Phosphate removal from wastewaters by electrocoagulation”, Ph.D. Thesis, School of Natural and Applied Science, Atatürk University, Erzurum, 2005.
- [24] Behbahani, M, Mohammad Reza, Alavi Moghaddam, Mokhtar Arami, Phosphate removal by electrocoagulation process: optimization by response surface methodology method *J. Environmental Engineering and Management* 2013 (12) :12, 2397-2405
- [25] Miranzadeh M.B, Rabbani D and Dehqan S (2012) Electrocoagulation process for removal of adenosine-5'-monophosphate and sodium hexamethaphosphate from the synthetic wastewater *International Journal of Physical Sciences* Vol. 7(10), pp. 1571 – 1577,
- [26] Sukalyan Sengupta, and Jeffrey W. Beaudry 2013 Selective Removal of Phosphate from Wastewater using Ion Exchange Resin Beads . *Book of Abstract Sigma Xi Research competition*
- [27] Mitsch, W. J. And Gosselink, J. G. 2000. *Wetlands*. John Wiley and Sons, Toronto, ON.
- [28] Van Dijk, J.C., and H. Braakensiek. 1984. Phosphate removal by crystallization in a fluidized bed. *Water Science and Technology* 17: 133–142.
- [29] Piekema, P. & A. Giesen (2001) Phosphate recovery by the crystallisation process: Experience and developments. *Environmental Technology*, 21, 1067-1084.

- [30] Paul, E., M.L. Laval, and M. Sperandio. 2001. Excess sludge production and costs due to phosphorus removal. *Environmental Technology* 22: 1363–1372.
- [31] Khedr. M.G., 2011. Membrane fouling problems in reverse osmosis desalination plants, *Desalination & Water Reuse* 10 (3), 8–17.
- [32] Stratful, I., Brett, S., Scrimshaw, M.D., Lester, J.N., 1999. Biological phosphorus removal, its role in phosphorus recycling. *Environ. Technol.* 20, 681–695.
- [33] Schwartz, M.F., Boyd, C.E., 1995. Constructed wetlands for treatment of channel catfish pond effluents. *Progr. Fish-Cult.* 57, 255–267.
- [34] Kayombo S., Mbwette T.S.A. Katima J.H. Y, Ladegaard N., and Jorgensen S.E. (2000) “Waste Stabilisation Ponds and Constructed Wetlands Design Manual UNEP-IETC and DANIDA
- [35] Mann, R.A., 1997. Phosphorus adsorption and desorption characteristics of constructed wetland gravels and steelworks by-products. *Aust. J. Soil Res.* 35, 375–384.
- [36] Snow A.M and Ghaly A.E, (2008) A Comparative Study of the Purification of Aquaculture
- [37] Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S., Nakamachi, K., 2001. Development of artificial seed crystal for crystallization of calcium phosphate. *Environ. Technol.* 22, 1245–1252.
- [38] Bassin J.P, Winkler M.-K.H, Kleerebezem R, M. Dezotti M , van Loosdrecht M.C.M. Improved Phosphate Removal by Selective Sludge Discharge in Aerobic Granular Sludge Reactors *Biotechnology and Bioengineering*, 2012: 342 - 348
- [39] Oehmen, A., Lemos, P.C., Carvalho, G., Yuan, Z.G., Keller, J., Blackall, L.L., Reis, M.A.M., 2007. Advances in enhanced biological phosphorus removal: From micro to macro scale. *Water Research*, 41 (11): 2271–2300.
- [40] Johansson L, and Gustafsson J.P, Phosphate removal using blast furnace slags and opoka-mechanisms, *Water Res.* 34 (2000) 259–265.
- [41] Déry P and Anderson B (2007), ‘Peak phosphorus’, *Energy Bulletin*, 13 August 2007 (www.energybulletin.net/node/33164).
- [42] Oladoja, N.A., Ahmad, A.L., Adesina, O.A., Adelagun, R.O.A., 2012. Low-cost biogenic waste for phosphate capture from aqueous system. *Chem. Eng. J.* 209,170–179.
- [43] Karapinar N, Hoffmann E, Hahn H.H, P-recovery by secondary phase nucleation and crystal growth of calcium phosphates on magnetite mineral, *Water Res.* 40 (6) (2006) 1210–1216.
- [44] Oladoja, N.A., Adesina, A.O., Adelagun, R.O.A., 2014. Gastropod shell column reactor as on-site system for phosphate capture and recovery from aqua system. *Ecol. Eng.* 69, 83–92.
- [45] Hrenovic J, Tibljas D, Ivankovic T, Kovacevic D, Sekovanic L, Sepiolite as carrier of the phosphate-accumulating bacteria *Acinetobacter junii*, *Appl. Clay Sci.* 50 (2009) 582–587.
- [46] Drizo A, Forget C, Chapuis R.P ,Comeau Y, Phosphorus removal by electric arc furnace steel
- [47] Donnert, D., Salecker, M., 1999a.Elimination of phosphorus from wastewater by crystallization. *Environ. Technol.* 20,735–742.
- [48] Deng Y.X , Xu H, Huang L, Application of steel slag in the process of phosphorus wastewater treatment, *Non-ferrous Min. Metall.* 18 (2002) 43–45 (in Chinese).
- [49] Ensar oguz, Ahmet Gurses and Mehmet Yalcin Removal of phosphate from wastewaters by adsorption *Water, Air, and Soil Pollution* 148: 279–287, 2003.
- [50] Sakadevan K, and Bavor H.J, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems, *Water Res.* 32 (2) (1998) 391–399.
- [51] Choi S.S, Chung J.H, Yeom S.H, Removal of phosphate using coal fly ash from a thermal power station, *J. Ind. Eng. Chem.* 11 (2005) 638–642.
- [52] Levlin, E., Löwén, M., Stark, K. and Hultman, B., 2002. Effects of phosphorus recovery requirements on Swedish sludge management. *Water science and technology*, 46(4-5): 435-440.
- [53] Oladoja, N.A, Adelagun, R.O.A, Ahmad, A.L, Ololade, I.A. 2015 Phosphorus recovery from aquaculture wastewater using thermally treated gastropod shell. *Process Safety and Environmental Protection* 98: 296–308
- [54] Oguz E, Removal of phosphate from aqueous solution with blast furnace slag, *J. Hazard. Mater.* B114 (2004) 131–137.
- [55] Driver J, Lijmbach D, Steen I, Why recover phosphorus for recycling, and how? *Environ Technol.* 20 (7) (1999) 651–662.

- [56] Ratnapriya, E. A. S. K., Mowjood, M I M, De Silva, R P, and Dayawansa, N D K (2009) "Evaluation of constructed wetlands for efficiency of municipal solid waste leachate treatment in Sri Lanka" Presentation at DAAD_GAWN Alumni Expert Seminar,
- [57] Onoda, 2013 Wastewater Using Water Hyacinth, Water Lettuce and Parrot's Feather American Journal of Applied Sciences 5 (4): 440-453,
- [58] Oladoja N.A, Ololade I.A, Adesina A.O, Adelagun R.O.A, Sani Y.M, Appraisal of gastropod shell as calcium ion source for phosphate removal and recovery in calcium phosphate minerals crystallization procedure, Chem. Eng. Res. Des. 91 (5) (2013) 810–818.
- [59] Kose T.E, Kivanc B, Adsorption of phosphate from aqueous solutions using calcined waste eggshell, Chem. Eng. J. 178 (2011) 34–39.
- [60] Sartorius, C., Von Horn, J., and Tettenborn, F. (2012). Phosphorus recovery from wastewater-expert survey on present use and future potential. *Water Environ. Res.*, 84(4), 313–322.
- [61] Schröder, M., Cordell, D., Smith, A. L., Rosemarin, A. 2010. Sustainable Use of Phosphorus. Report 357, Plant Research International, Part of Wageningen UR, The Netherlands.
- a. Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: global food security and food for thought. *Global Environ. Change* 19, 292–305.
- b. Cordell, D., Rosemarin, A., Schroder, J. J., and Smit, A. L. (2011). Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. *Chemosphere*, 84, 747–758.
- [62] a. Hermann, L. 2009a. Recovery of phosphorus from wastewater treatment. A review. (Rückgewinnung von Phosphor aus der Abwassereinigung. Eine Bestandesaufnahme). *UmweltWissen* Nr. 0929. Bundesamt für Umwelt (BAFU). Bern. (In German)
- b. Hermann, L. 2009b. Prec recovery from sewage sludge ashes by thermochemical treatment. Presentation in BALTIC 21 Phosphorus Recycling and Good Agricultural Management Practice, September 2830, 2009.
- [63] Uysla, A., Yilmazel, Y. D., and Demirer, G. N. (2010). The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester. *J. Hazard. Mater.*, 181, 248–254.
- [64] Schipper, W.J. and Korving, L. 2009. Fullscale plant test using sewage sludge ash as raw material for phosphorus production. Proceedings of International conference on nutrient recovery from wastewater streams, May 10 – 13 2009, Vancouver, British Columbia.
- [65] Bhuiyan, M.I.H., Mavinic, D.S., and Beckie, R.D. (2006). Solubility and thermodynamic study of struvite. *Environmental Technology*, Submitted (December, 2006).
- [66] a. US. Geological Survey. 2010. Mineral commodity summaries 2010, Phosphorus. United States Government Printing Office. Available: http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/
- b. US Geological Survey, 'Mineral commodity summaries', January 2010 on Phosphate rock'
- [67] Mehla, C.M.,Khubjarb , W.O., Nguyenb, S.T., Batstones, D.J, (2014) Technologies to Recover Nutrients from Waste Streams: A critical Review . *Critical Reviews in Environmental Science and Technology* pg. 366-418
- [68] a. Stark K. (2002). Phosphorus release from sewage sludge by use of acids and bases. Dep. Land and Water Resources Engineering, KTH, licentiate thesis, ISBN 91-7283-307-6.
- b. Stark, K., E. Plaza & B. Hultman (2006) Phosphorus release from ash, dried sludge and sludge residue from supercritical water oxidation by acid or base. *Chemosphere*, 62(5), 827-832.
- [69] Rittmann, B.E., Mayer, B., Westerhoff, P., Edwards, M., 2011. Capturing the lost phosphorus. *Chemosphere* 84, 846–853.
- [70] Cornel, P., and C. Schaum. 2009. Phosphorus recovery from wastewater: needs, technologies and costs. *Water Science & Technology* 59 (6): 1069–1076.
- [71] Petzet, S. and Cornel, P. 2009. P recovery from sewage sludge and sewage sludge ashes. Presentation in BALTIC 21 Phosphorus Recycling and Good Agricultural Management Practice, September 2830, 2009.
- [72] Montag, D., K. Gethke, and J. Pinnekamp. 2009. Different strategies for recovering phosphorus: Technologies and costs. In *International conference on nutrient recovery from wastewater streams*, 3ed. London, UK: IWA Publishing.
- [73] Gaterell, M.R., Gay, R., Wilson, R., Gochin, R.J., Lester, J.N., 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environ. Technol.* 21, 1067–1084.

- [74] Banu, J.R., Do, K.U., Yeom, I.T., 2008. Effect of ferrous sulphate on nitrification during simultaneous phosphorus removal from domestic wastewater using a laboratory scale anoxic/oxic reactor. *World J. Microb. Biotechnol.* 24, 2981–2986.
- [75] Caravelli, A.H., Contreras, E.M., Zaritzky, N.E., 2010. Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. *J. Hazard. Mater.* 177, 199–208.
- [76] a. Hultman B. Levlin E. Mossakowska A. and Stark K. (2001b). Effects of wastewater treatment technology on phosphorus recovery from sludges and ashes. 2nd International Conference on Recovery of Phosphates from Sewage and Animal Wastes, Holland, NL, 12-13 March 2001.
b. Hultman B., Levlin E., and Stark K. (2000). Phosphorus recovery from sewage sludges: Research and experiences in Nordic Countries, *Scope Newsletter CEEP*, (41), 29-32.
- [77] Whang, J.A., Young, D., Pressman, M., 1982. Soluble sulfide precipitation for heavy metals removal from wastewaters. *Env. Prog* 1 91) 110-113
- [78] Giesen, A. 2009a. Presentation: P recovery with the Crystalactor® process. Presentation in BALTIC 21 Phosphorus Recycling and Good Agricultural Management Practice, September 28-30, 2009. Berlin.
- [79] Munch, E.V., and K. Barr. 2001. Controlled struvite crystallization for removing phosphorus from anaerobic digester side streams. *Water Research* 35: 151–159.
- [80] Doyle J.D, Parsons S.A, 2002 Struvite formation, control and recovery. *Water Res* (36) 3925–3940.
- [81] Molinos, M., F. Hernandez, and R. Sala. 2010. Economic feasibility study for wastewater treatment: A cost benefit analysis. *Science of the Total Environment* 408: 4396–4402.
- [82] Tchobanoglous, G., M. Abu-Orf, G. Bowden & W. Pfrang (2014) *Wastewater Engineering: Treatment and Resource Recovery*. McGraw-Hill Education, New York.
- [83] Wang, J., J. G. Burken & X. Zhang (2006) Effect of Seeding Materials and Mixing Strength on Struvite Precipitation. *Water Environment Research*, 78(2), 125-132.
- [84] a. SCOPE (2003a) Germany, Sweden –National objectives for P-recovery announced. *SCOPE Newsletter*, (50), 3.
b. SCOPE (2003b) Sewage sludge management in Europe. *SCOPE Newsletter*, (50), 3 pp 2-3.
c. SCOPE (2004a) P-recovery seminar summary. German Environment Agency (UBA) *SCOPE Newsletter*, (54), 3. pp.2-6.
d. SCOPE (2009) The International Conference on Nutrient Recovery and Recycling. *SCOPE Newsletter*, (74).
- [85] Ostara (2013) Company Website [online]. <http://www.ostara.com> [accessed 18-12 2013]
- [86] Ueno, Y. & M. Fujii (2001) Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology*, 22(11), 1373-1381.
- [87] Schaum, C., Cornel, P., Jardin, N. (2005): Possibilities for a Phosphorus Recovery from Sewage Sludge Ash, proceedings, Conference on the Management of Residues Emanating from Water and Wastewater Treatment, 09.-12.08.2005, Johannesburg, South-Africa
- [88] Scheidig, K.; Schaaf, M.; Mallon, J. (2009). Profitable recovery of phosphorus from sewage sludge and meat & bone meal by the Mephrec process – a new means of thermal sludge and ash treatment. Proceedings of the International Conference on Nutrient Recovery from Wastewater Streams. Vancouver, Canada 10.-13. March 2009.
- [89] Schaum, C. (2007). Verfahren für eine zukünftige Klärschlammbehandlung Klärschlammkonditionierung und Rückgewinnung von Phosphor. Dissertation an der TU Darmstadt.
- [90] ASH DEC. 2009. ASH DEC Umwelt AG. Available: http://www.ashdec.com/eng_index.html.

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