

Phosphorus Recovery in Sustainability Frame

Engin GÜRTEKİN

Faculty of Engineering, Department of Environmental Engineering Firat University, Turkey

Abstract

In working towards a sustainable society, recycling and recovery of products together with handling of scarce resources must be considered. The known reserves of phosphorus are estimated to be consumed in about 100 years. Phosphate may be recovered from different sources (urine, wastewater, sewage sludge). The technologies to recover phosphorus from different sources are in an initial phase of development and it is reasonable to believe that further improvements are possible. Phosphorus recovery is an economically feasible process as long as environmental benefits are considered. In this study, the sources for phosphorus recovery, phosphorus recover yields and the cost of phosphorus recovery are investigated.

Key Words: Phosphorus recovery, sustainability, wastewater, sludge.

1. Introduction

There is still a long way to go to achieve a sustainable society. One aspect of sustainability is to economise with scarce resources [1]. Sustainability means recycling of resources without supply of harmful substances to humans or the environment. Phosphate recovery is very important. Phosphate fertiliser is produced by mining of phosphate ores. More than 300 different phosphate minerals are available, but only apatite (calciumphosphate, $\text{Ca}_3(\text{PO}_4)_2$) is used for production of fertiliser. In 1995 the world phosphate rock production was 160.000 ton per year (as P_2O_5), having tripled over the last 40 years. About 90% of this is used as fertiliser [2]. The phosphate production is concentrated in only a few countries, based on geological conditions (Figure 1).

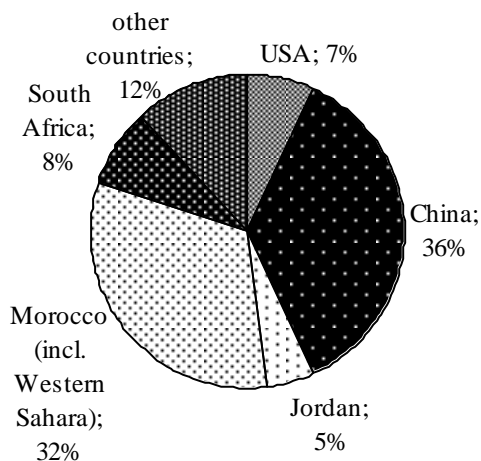


Figure 1. Global allocation of phosphate reserves

European countries do not have any phosphate ore deposits and are, therefore, dependent upon the import of phosphates [3]. At this rate of consumption the known apatite reserves have been estimated to last for a period up to 1000 years. However, if the present increase in world population and the increasing need for fertiliser for food production is taken into account, the supply of phosphate may well be crucial within a century [2, 4-6].

Phosphate recovery by chemical or microbiological/chemical precipitation in the water line and recovery from the sludge is possible. The technologies to recover phosphorus from wastewater and sludge are in an initial phase of development and it is reasonable to believe that further improvements are possible [7]. The driving force parameters for phosphorus recovery vary in the national context, in early stage there seems to be driven by legislation and technical feasibility (some cases also economic feasibility), while for next stage, full-scale implementation the most important factors seems to that economic feasibility, the environmental sustainability, and the social acceptance [8]. Phosphate may be recovered from different waste streams (urine, wastewater, supernatant, sewage sludge) by direct use or by different technologies (Figure 2) [9].

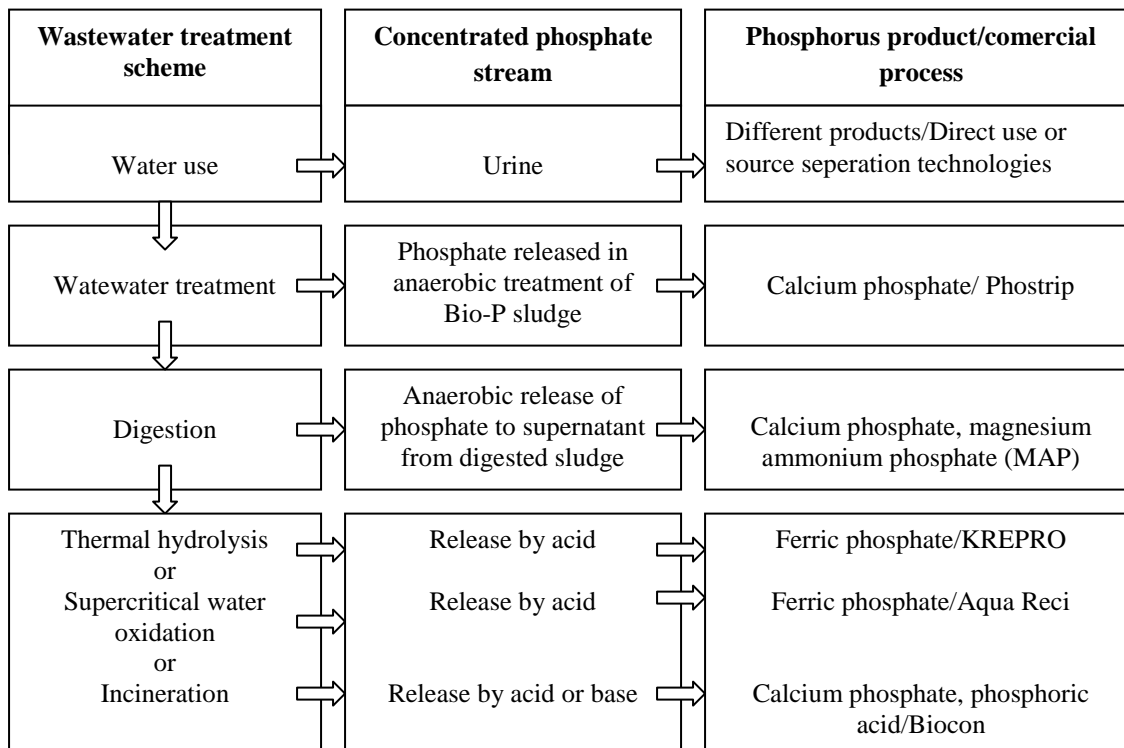


Figure 2. Possible pathway for phosphorus recovery

In this study, the sources for phosphorus recovery, phosphorus recover yields and the cost of phosphorus recovery are investigated.

2. Phosphorus Recovery Sources

2.1. Urine

Urine that does not come into contact with feces is a good nutrient and infectious disease risk is less than fecal. [10]. In addition, the nutrients dissolved in urine is form that can be easily by plants. Although source separation is beneficial, there are some disadvantages. The transforming the urinary nutrients into solid state is a useful process [11]. Phosphorus recovery is achieved by passing solid phase in the form of struvite precipitation to phosphate dissolved in urine [12,13]. Mihelcic et al. [14] reported that the total phosphorus available in excreted human waste (urine and feces) in 2009 is approximately 22% of global phosphorus demand. The phosphorus available in urine alone could account for 11% of the total global phosphorus demand assuming 50% of phosphorus is present in urine.

2.2. Anaerobic sludge digestion

Stabilization of sludge at large wastewater treatment plants is usually carried out by anaerobic digestion. In this process, organic matter is transformed into CH_4 and CO_2 by the action of different groups of bacteria. The main advantages of this process are the reduction in the volume of waste sludge and the production of methane gas that can be utilised to supply energy. The rejected liquors from anaerobic digestion of enhanced biological phosphorus removal sludges show high phosphorus concentration which makes these streams very appropriate to recover phosphorus [15].

2.3. Sludge and sludge ash

The phosphate in sludge is used directly as fertiliser in agriculture. However, because there are heavy metals, harmful pollutants such as endocrine nutrient together with phosphate, the direct use in agriculture is limited. Therefore, the development of different technologies to obtain phosphate from sludge is important.

In processes for a recovery of phosphorus from sewage sludge and sewage sludge ashes, chemical or chemical/thermal treatment takes place. All processes (Krepro, Kemicond, Seaborne, Aqua Reci, Biocon, Sephos) are under development, and have not yet been tested on a large technical scale [16]. There has been increasing interest in sludge fractionation, which includes sludge volume reduction, product recovery and separation of toxic substances into a small stream. Different options for sludge fractionation are summarized in Table 1 [17].

It is gradually limited to deposition of waste and sludge on landfill. Incineration and Super Critical Water Oxidation (SCWO) are methods that eliminate all organic content and the potential energy of the organic material can be utilised. SCWO occurs in water of a supercritical phase at a pressure higher than 22 Mpa. Sludge incineration requires that sludge have to be dried to 40% dry substances.

Table 1. Different options for sludge fractionation

Methods	General purpose
Physical Heat/pressure	Solution of sludge components, sludge conditioning
Mechanical Mechanical devices, ultrasonic	Disruption of cells for improved sludge degradation
Biological Enzymes	Solution of sludge components, increased biodegradability of the sludge
Anaerobic aritm Sulphate reducing bacteria	Production of organic acids, release of phosphates
Sulphur, sulphide and ferrous oxidation bacteria	Production of sulphides for release of phosphates and precipitation of metals Production of hydrogen ions for release of metals from sludge
Chemical Acids, bases, oxidizing agents (ozone, hydrogen peroxide, etc.)	Hydrolysis of sludge, release of different sludge components, conditioning of sludge, increased biodegradability of sludge
Complexing agents	Release of metals, etc. from

Phosphorus recovery from wastewater treatment plant sludges occur generally three steps: (i) Transfer of soluble phosphorus into sludge by use of biological and chemical methods, (ii) Solubilization of sludge by use of physical, mechanical, biological or chemical methods, (iii) Recovery of solubilized phosphate by methods as chemical precipitation, crystallisation or ion exchange. Leaching with acid and base is a promising method for phosphorus recovery from wastewater treatment of sewage sludge. Samples of ash taken from the co-incineration of sludge with municipal waste, sludge incineration plant and SCWO residues have been leached with acid, hydrochloric acid and base, sodium hydroxide. The metal and phosphorus content before leaching has been analyzed as well as the metal and phosphorus content in the leachate. Leaching with acid gives a higher release of phosphorus compared to leaching with base. The largest degree of leached phosphorus (80 – 100 % at acid concentrations below 0.5 M) was obtained by leaching SCWO residue with acid. Acid leaching of sludge incineration ash gave 75 – 90 % leached phosphorus at the concentration 1 M. Alkaline leaching of sludge incineration ash and SCWO-residue gave 50 – 70 % leached phosphorus at the concentration 1 M. When leaching with base, the calcium content in the sludge binds phosphorus as calcium phosphate. On leaching with acid it is difficult to recover phosphorus as other products than iron phosphate. However, iron phosphate has no commercial value as raw material for the phosphate industry, and the low solubility makes it less favorable to use as fertilizer [18].

For improve phosphorus release by leaching with acid and base, a two-step leaching process has been tested. Ash and SCWO-residues are in the first step leached with acid, with the main purpose to dissolve calcium. In the first step, sulphuric acid cannot be used since calcium sulphate has a very low solubility. After leaching experiments with hydrochloric acid and acetic acid at different pH-levels from 3 to 6 leaching with acetic acid at pH-level 4 was chosen as the first

leaching step. With a weak acid the dissolution reaction can occur at the desired pH-level without limitation caused by insufficient amount of acid. Two-step leaching gave for SCWO-residue 23% higher leaching of phosphate and for sludge incineration ash 11% higher leaching. [19].

The composition of the sludge affects the leaching results and, thus, the recovery. The metal/phosphorus ratio was higher with acid than with base. This means alkaline leaching will preferentially dissolve phosphorus with a lower metal contamination compared to acid leaching. The difference shown in leaching with acid or base may be due to the fact that the calcium phosphate in the case of alkaline leaching. When leaching SCWO residues with sodium hydroxide, sludge with 3% calcium released 90% of the phosphorus content, while sludge with 8% calcium only released 65% phosphorus. Another reason could be that the precipitation of calcium hydroxide can be favourable at high pH in systems containing calcium [9].

In many cases, higher temperatures increase the reaction process. However, at room temperature, 100% of the phosphate was released at 0.1 M HCl and only 1% iron, while at 90 °C, 64% phosphate was released and 71% iron. A possible reason is that the metal bonds break at different rates. The higher temperature together with acid dissolved the strong iron precipitates and caused precipitation of phosphate with dissolved ions. In the case of alkaline leaching, the release was similar at both temperatures. [9].

2.4. Phosphate Rich Streams

To obtain a stream with a high phosphate concentration, the process must be operated according to biological phosphorus removal principle. Biological phosphorus removal processes, can be changed to achieve phosphorus without increasing effluent phosphorus concentration and without requiring expensive new investment.

PhoStrip process is a side-stream process and the phosphorus is recovered by anaerobic treatment of a part of the return sludge flow in a stripper (Figure 3). Through addition of acetic acid the bacteria's are induced to release phosphorus, thereby a concentration of 60-80 mg P/l is achieved. After separation of the sludge phase the dissolved phosphate is precipitated with lime. Calcium phosphate produced from a side-stream in the treatment plant has a sufficient enough content of pollutants to be used as raw material in the phosphate industry. Chemical consumption for PhoStrip process is organic acids as acetic acid for the stripper and lime for the calcium phosphate precipitation. To precipitate apatite with lime about 3 g is needed per g precipitated calcium phosphate precipitation [20].

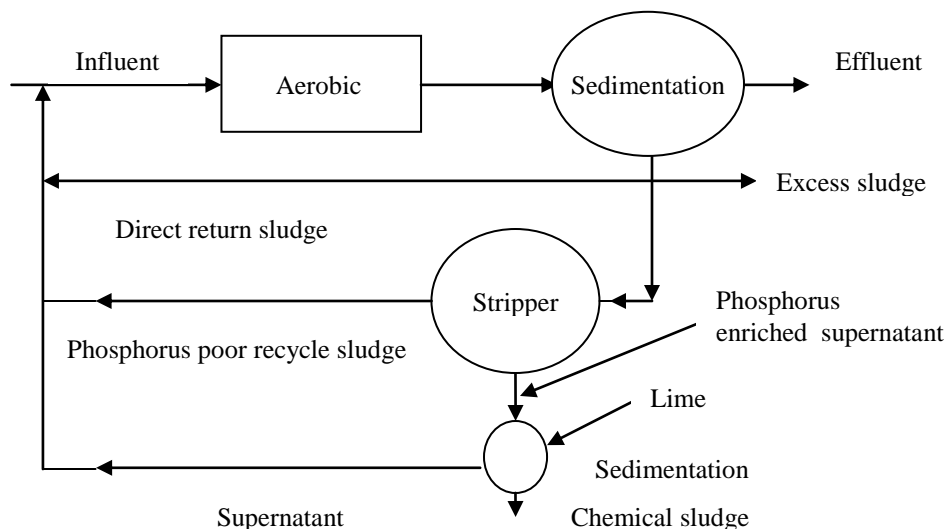


Figure 3. Phostrip process flowsheets.

Phosphorus and/or ammonium rich side streams can also be achieved from sludge. From processes similar to PhoStrip a side-stream with a high phosphate content can be obtained. After dewatering of digested sludge a supernatant with a high content of ammonium is obtained. If the phosphate rich stream is combined with the ammonium rich supernatant there is good possibilities for producing struvite. Phosphate rich streams also contain a high content of magnesium since in phosphate release also magnesium and potassium are released to maintain the ion [20].

3. Phosphorus Recovery Products

Phosphate can be obtained through methods such as crystallization of apatite and magnesium ammonium phosphate precipitation from high phosphate concentration waters as a result of sludge disintegration and from recycle sludge of biological phosphorus removal process as phostrip. Possible phosphate precipitations are listed in Table 2 [2]. However, phosphorus is usually obtained with struvite and calcium phosphate.

Table 2. Phosphate precipitations

Precipitation	Name	pKs	Precipitation rate	Optimum pH
$MgNH_4PO_4$	Magnesium ammonium phosphate (MAP)	12.6	Medium	7-8
$Ca(PO_4)_3OH$	Hydroxide apatite	57	Very low	9.5-11
$Mg(PO_4)_2 \cdot 8H_2O$	Bobierite	-	Very low	-
$CaHPO_4$	Calcium hydrogen phosphate	6.6	-	-
$Ca_3(PO_4)_2$	Tricalcium phosphate	25	-	-

3.1. Struvit

Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Struvite precipitation can be separated into two stages: nucleation and growth. Nucleation occurs when constituent ions combine to form crystal embryos. Crystal growth continues until equilibrium is reached [21]. Struvite precipitation is controlled by pH, degree of supersaturation, temperature and the presence of other ions in solution such as calcium [22].

Struvite can be a problem in wastewater treatment plants although it is more prevalent at those with sludge digestion processes. However, struvite has the potential use as a fertiliser [23,24]. Struvite has been suggested to display excellent fertiliser qualities under specific conditions when compared with sandart fertilisers [25]. Other benefits of precipitating struvite include reducing the phosphorus and nitrogen load of side-stream and sludge liquors recirculated to the head of wastewater treatment works [26]. Another incentive for consciously forming struvite is its impact on sludge disposal as the recovery of phosphorus can reduce the volume of sludge generated by 49% [27].

3.2. Calcium phosphate

Most wastewater are supersaturated with respect to calcium phosphate compounds. However, spontaneous precipitation of calcium phosphate seldom occurs. The fundamental idea of the crystallisation technology is to lower the interfacial energy by the supply of suitable seed material and thus to trigger the deposition of calcium phosphate compounds onto the seed material surfaces in order to achieve equilibrium between Ca ions and phosphate. Up to now crystallisation has been realised in pilot-scale (i) using sand in fluidised bed technology – the DHV Crystalactor process which requires an initial CO_2 –stripping followed by an adjustment of the pH value to optimise the calcium phosphate precipitation, and (ii) using calcite in a stirring reactor. In addition, promising laboratory and pilot plant scale results were obtained in Japan by the use of tobermorite pellets as seed material for the deposition of phosphorus minerals in a fluidised bed. This technology is mainly suitable for side stream Bio-P processes as the pH exceeds $\text{pH} > 9.5$ [28].

4. Cost

Phosphorus recovery can be seen as technically feasible but the economic feasibility of phosphorus recovery from sewage can still be judged as dubious [29]. Most important reason is that the prices of the available nowadays techniques (in Euro/tonne P) are much higher than compared to the prices of phosphate rock. Hultman et al., (2003) has estimated that phosphorus recovery would increase the total services of potable water and sewage by 1% [30]. Balmer [1] writes that if the economy of a system, which may look environmentally attractive, is miserable, this may at least be an indication that precaution is recommended before such a system is adopted [1]. The economic feasibility analysis proposed taking into account the environmental benefits by

Molinos-Senante et al. [31] shows that the phosphorus recovery is viable not only from sustainable development but also from an economic point of view.

5. Conclusions

Phosphorus is produced by mining of phosphate ores. Phosphorus is an essential nutrient, which cannot be substituted by any other element and about 90% of this is used as fertiliser. Present phosphorus reserves will presumably exhaust at present utilisation rates. The recovery of phosphorus discharge to the environment is both to reduce commitment to the phosphate rocks and to ensure sustainable development by providing phosphorus supply for the future. The technologies to recover phosphorus from waste streams are in an initial phase of development and it is reasonable to believe that further improvements are possible. Phosphorus recovery is an economically feasible process as long as environmental benefits are considered.

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