Phosphorus is a key pollutant in municipal wastewater. To minimise eutrophication, treatment facilities must often reduce phosphorus levels to less than 1 mg L\(^{-1}\). Two main approaches to achieving this are chemical precipitation and enhanced biological uptake. Chemical precipitation is widely used and relatively simple; biological phosphorus removal is more complex but relies less on the addition of chemicals and also offers the opportunity to reuse the phosphorus. Phosphorus can be released from cells and converted to calcium phosphate or the mineral struvite. While the products have been shown to be excellent fertilisers, the economic drivers for recovery are still not clear.

INTRODUCTION

Phosphorus (P) enters municipal wastewater treatment facilities from both domestic and industrial sources. Domestic contributions come from human waste and detergents. Load is estimated to be 0.60 kg P capita\(^{-1}\) y\(^{-1}\) from human waste, 0.30 kg P capita\(^{-1}\) y\(^{-1}\) from laundry detergent and 0.10 kg P capita\(^{-1}\) y\(^{-1}\) from other household cleaning products. Without specific P removal during wastewater treatment, approximately 75% of this load would end up in rivers. In the UK, it is estimated that 41% of all P in surface waters originates from treatment facilities (Defra 2003), while the remaining portion comes primarily from agriculture, through run-off and animal husbandry.

Excess P leads to eutrophication of lakes and rivers, adversely affecting biological diversity and water quality. Efforts have been made, starting in the 1970s and 1980s, to reduce P input from both urban and industrial point sources. The amount of sodium tripolyphosphate used in detergents was decreased, and zeolite became a non-phosphate alternative. Phosphorus in municipal wastewater occurs in dissolved and particulate forms. Most occurs as dissolved phosphate and consists of ~50% orthophosphate, 35% condensed phosphates and 15% organic phosphates. Typically, total P concentration in municipal wastewater is between 6 and 8 mg L\(^{-1}\). While such averages can be useful for predicting annual loads, concentrations at the treatment sites can vary from 2 mg L\(^{-1}\) to 16 mg L\(^{-1}\) over a 24-hour period.

PHOSPHORUS REMOVAL

Phosphorus can be removed from wastewater by transforming it from a soluble form into a solid that can be removed by sedimentation. Two widely used processes are chemical precipitation and enhanced biological removal. Both typically achieve effluent concentrations of 1 to 2 mg L\(^{-1}\) and, if combined with filtration processes, levels as low as 0.2 mg L\(^{-1}\) are possible.

Chemical Precipitation

Chemical precipitation, the most commonly applied process, can remove up to 90% of all influent P (Thistleton et al. 2002). It is relatively simple and needs little equipment aside from a chemical holding tank and a pump. Figure 1 shows an example of chemical dosing into the influent wastewater. The chemicals used are either iron (Fe) or aluminium (Al) chlorides or sulphates; Fe\(^{3+}\) and Fe\(^{2+}\) are preferred. At first glance, the chemical process looks simple. If pH is not too low, addition of Fe\(^{3+}\) to water results in formation of ferric hydroxide, a loose precipitate known as Fe ‘floc’:

\[
\text{Fe}^{3+}(aq) + 3\text{H}_2\text{O}(l) \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+
\]

If there is soluble phosphate in the water, it reacts with the Fe\(^{3+}\) to form an insoluble salt, ferric phosphate, which removes one mole of P for every mole of Fe\(^{3+}\):

\[
\text{Fe}^{3+}(aq) + \text{PO}_4^{3-}(aq) \rightarrow \text{FePO}_4(s)
\]

In practice, however, the precipitate formed is complex – a mixture resulting from the two reactions – so the relationship between the metal salt required and the P in solution is not stoichiometric (Fytianos et al. 1998).

\[
\text{Fe}^{2+}(aq) + \text{yH}_2\text{O}(l) + \text{xPO}_4^{2-}(aq) \rightarrow \text{Fe(OH)}_x(\text{PO}_4)_y(s) + \text{yH}^+
\]

Because the reaction of Fe with water is very fast, mixing at the addition point needs to be thorough. Once Fe hydroxide has formed, the rate at which it absorbs P is quite slow. The better the mixing, the more P is removed per unit Fe added. The optimum pH for Fe coagulation is around 5. Higher pH increases the tendency for Fe hydroxide formation, thus requiring even more rapid mixing.

The precipitate settles and is removed as a sludge. As a result of chemical dosing up to 95% more sludge is generated (Yeoman et al. 1988), and it contains more inert material (e.g. Fe phosphate) and less soluble P. These differences in composition have been shown to impact on downstream sludge treatment processes such as anaerobic digestion. Anaerobic digestion is a widely used process in municipal wastewater treatment works as it converts organic matter in sludge into a biogas rich in methane, which can be used in onsite combined heat and power plants to generate renewable energy. When anaerobically treated, sludge generated from chemical precipitation results in approximately 12% less biogas and 8% less methane as compared to sludge which has not been chemically treated (Smith 2006).
Enhanced Biological Removal

Phosphorus can also be removed biologically from wastewater by incorporation into cells; these cells are then removed as a sludge. Conventional biological treatment typically removes only 20% of the P present, whereas encouraging the establishment of bacteria that can take up and store more P than they need for their normal metabolic requirements can increase this to 90%. This process is termed enhanced biological phosphorus removal (EBPR) and relies on establishing a community of phosphorus-accumulating organisms (PAO) that take up 20–30% of their dry weight as P compared to 2% for conventional organisms. To establish PAO requires both a change in process and also a sufficient quantity of readily biodegradable organic matter in the influent wastewater. A typical process flowsheet and the mechanisms involved in EBPR are shown in Figure 2; the process requires the combination of both anaerobic and aerobic stages to encourage P uptake and release. Wastewater is typically reported according to its organic strength (total concentration of organic material) as either biological oxygen demand (BOD) or chemical oxygen demand (COD), and the type and quantity of the organic matter are key to the success or failure of EBPR. Sufficient quantities of readily biodegradable matter, specifically volatile fatty acids (VFAs), are required. Wastewater contains VFAs, but from the experience of many operating EBPR plants, the addition of chemicals such as acetate is required before they achieve good removal rates.
Increased P levels in the sludge and sludge liquors can lead to formation of magnesium ammonium phosphate hexahydrate, more commonly known as the mineral struvite. Struvite formation in pipes carrying supernatant liquors from the downstream anaerobic digesters was reported by Rawn et al. (1937) and on anaerobic digester walls by Borg erding (1972). The main problem associated with the formation of struvite is that it significantly reduces pipe diameter (Fig. 3). There have been many studies made to develop ways to minimise or eliminate struvite formation (e.g. Doyle et al. 2002).

PHOSPHORUS RECOVERY

A promising technology to help remove P from concentrated wastewater streams is the production of recyclable compounds such as calcium phosphate and struvite \((\text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O})\) (Le Corre et al. 2007). This concept has gained particular interest because both compounds have been identified as marketable fertilisers (de-Bashan and Bashan 2004). The composition of struvite in particular, where nitrogen (N), phosphorus (P) and magnesium (Mg) occur in equal molar concentrations, makes it a potentially interesting product in the fertiliser industry. It has been found to be as good a fertiliser as commercial mono calcium phosphates in plant-growth trials (Johnston and Richards 2003). A benefit is struvite’s low solubility, which prolongs nutrient release during the growing season, minimising the danger of burning crop roots. Recently, struvite research has gained momentum (Doyle and Parsons 2002), with studies on scale prevention, alternative methods for phosphorus removal and recovery from wastewater, and potential exploitation to the benefit of both wastewater treatment and the fertiliser industry.

The majority of recovery strategies are based on phosphorus crystallisation as hydroxylapatite or struvite, using sludge liquors generated in anaerobic digesters. These techniques can be classified into three main categories:

- Selective ion exchange (i.e. RIM NUT® process)
- Precipitation in stirred reactors
- Precipitation in fluidised bed reactors (FBR) or air-agitated reactors

The most common method for recovering struvite from wastewater is via the fluidised bed reactor or the air-agitated reactor. Struvite particles precipitate spontaneously from the supernatant liquor following the addition of chemicals such that the molar proportions are Mg:P:N = 1:1:1. Once nucleation starts, growth takes place either by agglomeration or on seed materials (e.g. sand or struvite) derived from the initial bed of particles (Fig. 4).

Japan is the only country where complete P removal and struvite recovery from anaerobically digested sludge liquors have been implemented and the resulting product sold to fertiliser companies (Ueno and Fujii 2001). Plants are in construction in Canada, and a full-scale pilot plant has been established in Italy (Fig. 5; Battistoni et al. 2004). In the UK, large-scale pilot plant trials have recently been conducted at the Slough wastewater treatment facility (Jaffer et al. 2002), and they demonstrated the potential to produce up to 100 tonnes of struvite per year (Fig. 5).
The processes required to form and capture struvite are at a stage of development where utilities can have confidence in their performance. There are still barriers to overcome before phosphorus recovery moves away from single demonstration plants to widespread use. Such barriers include the economics of the process, the logistics of the supply chain and the overall life-cycle assessment compared to processes such as land application of sludges.

ACKNOWLEDGMENTS

Jen Smith would like to acknowledge research funding under EPSRC grant number GR/S8550/01. Jen Smith would like to acknowledge research funding under EPSRC grant number GR/S8550/01.

REFERENCES


Borgerding J (1972) Phosphate deposits in digestion systems. Journal of the Water Pollution Control Federation 44: 813-819


Rawn AM, Perry Banta A, Pomeroy R (1937) Multiple-stage sewage sludge digestion. American Society of Civil Engineers 2116: 93-132


Based on this value, treating 400 m³ per day of liquors from the Slough facility and producing struvite from them could generate a potential income of about €25 000 under optimum conditions (Jaffer et al. 2002). Unfortunately, this income would only cover about a third of the cost of the chemicals needed for struvite crystallisation. Nevertheless, struvite removal reduces other operational costs: for example, significant savings are attained because of decreased costs of sludge handling and disposal (Shu et al. 2006) and lower plant maintenance costs by avoiding struvite scaling (Neethling and Benisch 2004).

CONCLUSIONS

The removal of phosphorus from municipal wastewater by chemical and biological processes is widely applied and successful. Both processes have pros and cons, and the selection of the process is controlled by local conditions such as the population served and the strength of the wastewater. Biological phosphorus removal does, however, offer the possibility to recover the phosphorus in the form of struvite or calcium phosphate, which have proven value as fertiliser. The processes required to form and capture struvite are at a stage of development where utilities can have confidence in their performance. There are still barriers to overcome before phosphorus recovery moves away from single demonstration plants to widespread use. Such barriers include the economics of the process, the logistics of the supply chain and the overall life-cycle assessment compared to processes such as land application of sludges.

The main issue preventing widespread recycling of phosphorus is the cost of producing struvite compared to its value as fertiliser. For example, in Japan, struvite has been sold as fertiliser at a price of nearly €250 per tonne (Köhler 2004).