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Capturing the Lost Phosphorus

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Abstract

Minable phosphorus (P) reserves are being depleted and will need to be replaced by recovering P that currently is lost from the agricultural system, causing water-quality problems. The largest two flows of lost P are in agricultural runoff and erosion (~46% of mined P globally) and animal wastes (~40%). These flows are quite distinct. Runoff has a very high volumetric flow rate, but a low P concentration; animal wastes have low flow rates, but a high P concentration together with a high concentration of organic material. Recovering the lost P in

animal wastes is technically and economically more tractable, and it is the focus for this review of promising P-capture technologies. P capture requires that organic P be transformed into inorganic P (phosphate). For high-strength animal wastes, P release can be accomplished in tandem with anaerobic treatment that converts the energy value in the organic matter to CH₄, H₂, or electricity. Once present as phosphate, the P can be captured in a reusable form by four approaches. Most well developed is precipitation as magnesium or calcium solids. Less developed, but promising are adsorption to iron-based adsorbents, ion exchange to phosphate-selective solids, and uptake by photosynthetic microorganisms or P-selective proteins.

Keywords

Phosphorus, Recovery, Precipitation, Ion exchange, Adsorption, Biological uptake

1. Introduction

Modern human society depends on a large, continuous supply of mined phosphorus (P) to sustain the global food supply (Schröder et al., 2010, Elser and White, 2010). However, the supply of mineral P is finite and also concentrated in only a few countries. Supply is decreasing while demand is increasing. Already, prices of phosphate fertilizers are rising steeply in the global market, and these rises are a significant factor for sharply rising food costs, particularly in developing countries, where fertilizer cost is a large fraction of the total cost of food production. Elser and White (2010) sum up our dilemma when they say, "Establishing a reliable phosphorus supply is essential for assuring long-term, sustainable food security...If we fail to meet this challenge, humanity faces a Malthusian trap of widespread famine on a scale that we have not yet experienced."

One of the realities with the current situation is that little of the mined P makes it into the plants and animals that humans consume. Most of the P is lost along the way, and those losses often cause serious environmental problems. When P enters surface waters, it can promote eutrophication of lakes, reservoirs, estuaries, and parts of the oceans (USEPA, 1983, USEPA, 1998, Selman, 2007). Sometimes called "accelerated aging" of a water body, eutrophication is undesirable because it eventually leads to color, odor, turbidity, loss of dissolved oxygen, and elimination of fish habitat (Duce et al., 2008). The P content of freshwater systems worldwide is at least 75% greater than pre-industrial levels, and P fluxes to oceans have increased from 8 to 22 million metric tons per year during the same time period (Bennett et al., 2001). More than 400 coastal dead zones, often found at the mouths of rivers discharging P, are known worldwide, and the number is expanding at 10% per decade (Diaz and Rosenberg, 2008).

1.1. Where the P goes

Liu et al., 2008a, Liu et al., 2008b, Cordell et al., 2009, and Schröder et al. (2010) recently provided similar estimates of the global P flows. Distributions vary significantly by country or region (Schröder et al., 2010), but the global P flows identify the large-scale trends of where P goes. Table 1 summarizes key findings based on Cordell et al. (2009). About 80% of the mined P is applied to agricultural fields, but only about 40% finds its way into harvested crops. Of that, only about 23% is incorporated into human food, and 16% is consumed by humans. Nearly all of the P consumed by humans passes through them and is conveyed as sewage to municipal wastewater-treatment plants (WWTPs). About one-half of that (8% of the mined P) is discharged by WWTPs and directly enters waterways, while most of the remainder (7% of the mined P) is disposed as sludge to landfills.

Table 1. Summary of the global P flows according to the estimates of Cordell et al. (2009).

Flow of P	Global flow in million metric tons P year ⁻¹			% of mined input	Comments
	Input to human activities	Use or internal reuse	Output to the environment		
Mined input	17.5			100	Will decline over time
Phosphate fertilizer production		14.9	2.7	85 & 15	Production losses and industrial uses are 15%
Phosphate fertilizer applied to arable soil		14.0	0.9	80 & 5	Losses are mainly in distribution
Phosphorus applied from recycled sources		10.5		60	From manure, crop, and sewage recycle
Soil erosion and runoff losses			8	46	Low concentration of P, but high volume
Crops grown		12		69	50% of P is captured and 50% lost
Crops harvested		7		40	About 58% of the crops grown is harvested
Crop residues			3	17	Some crop P is recycled to the soil
Animals produced from fertilized crops		2.6		15	Animals receive more P from grazing non-fertilized rangeland
Animals from non-fertilized rangeland	12.1			69	From vegetation on non-fertilized rangeland
Animal wastes			7	40	High concentrations of P and organics
Into human food		4.1	1	23 & 6	Losses are from the food chain
Consumed and excreted by humans		3		16	Losses are in distribution and wastage; humans retain less than 1% of their P intake
Sewage P discharged to waters			1.5	8	Relatively low concentration of P
Sewage solids			1.2	7	Now mostly disposed of to landfills; ~1% is recycled to soil

Notes: 1. Output flows that are amenable to capture by the methods in the review are highlighted in **boldface**.

2. The percentages are based on the input of mined P. Because of other inputs to the food system, such as recycling of residues and inputs from non-fertilized rangelands, the percentages do not add to 100%.

Table 1 shows that the two largest flows of lost P are soil erosion and runoff (46% of mined P) and animal wastes (40%); this estimate is only for agricultural land where mined P was applied. However, runoff from non-human fertilized land (e.g., forests) and urban areas will result in similar patterns and levels of P in surface waters. Almost all of the P in erosion and runoff goes directly into surface waters, where it accelerates eutrophication. Some P in animal wastes is reapplied to agricultural fields as fertilizers. However, most animal-waste P finds its way to surface waters, since regulations seldom control the fate of P from animal operations. The P discharged in human sewage and sewage-treatment sludge (15% combined) is significant, but considerably smaller than from agricultural runoff and animals.

Table 1 makes it obvious that most of the lost P is in agricultural runoff and animal wastes. Considerable effort has gone into assessing the separation of human urine, which contains the majority of the P from humans, from other domestic sewage flows (Ronteltap et al., 2010). While desirable, deployment of urine separation would capture only a small fraction the mined P input. We can have a greater positive impact towards generating renewable P by developing means to capture P from runoff and animal wastes. Is this possible? If yes, how?

1.2. P removal and capture

To limit eutrophication potential, P removal has been in the toolbox of wastewater-treatment engineers for several decades (Rittmann and McCarty, 2001, Tchobanoglous et al., 2003). One common approach involves chemical precipitation of the inorganic phosphate anion through addition of one or more of the cations iron, aluminum, calcium, magnesium, and ammonium. This produces a chemical sludge that is removed from the water and is usually disposed of in a landfill. A second common removal approach is called enhanced biological phosphorus removal (EBPR), which is an ecological approach that involves selecting for bacteria that store especially high amounts of P in poly-phosphate (polyP) inclusions. The P is contained in organic biosolids that are removed from the treated wastewater and usually used as a soil amendment or disposed of in a landfill.

These wastewater-treatment techniques were developed for removing phosphate from municipal wastewaters, which contain modest concentrations of P (i.e., 5–10 mg L⁻¹). While they are effective at the job they were designed to do, they are not necessarily going to be effective for the job that our society needs to have done in the future: capturing the lost P from its large P flows, which have different characteristics than domestic wastewater. Besides, the primary goal needs to shift to capturing P so that it can be reused.

The P flow from erosion and runoff usually comes as a “non-point source,” such as agricultural drainage ditches or surface storm-water flow. These sources are not easily intercepted before they reach a natural stream or river. Much of the P in runoff is associated with particulate matter that can settle out in wetlands, rivers, reservoirs, and lakes. Thus, we may need to quickly capture P from water flows that are very large in volume, but have a low P concentration. For example, total-P concentrations in the heavily agriculture-based Missouri River averaged 0.1–1 mg P L⁻¹ (orthophosphate was <0.2 mg P L⁻¹) from 1993 through 2003 (USGS, 2007). In addition, P concentrations in the Missouri River increased by over 50% between 1993 and 2003, which correlated to modifications in agricultural application of fertilizers, not to increases in suspended-solids concentrations in the river (USGS, 2007). While P concentrations are relatively low, volumetric flows vary from <0.1 to >300 m³ s⁻¹ along tributaries and the main stem; thus, annual P loads can range from 5000 kg P year⁻¹ on smaller streams to >2 700 000 kg P year⁻¹ in the main channel. Clearly, erosion and runoff present an opportunity for a large amount of P recovery, but the technical and economic challenges are serious.

The P flow in animal wastes is quite the opposite of erosion and runoff. The volumetric flow rate is not especially large, but the P concentration is high. Furthermore, the animal wastes contain high concentrations of organic material. For example, pig wastes from feedlot runoff have chemical oxygen demand (COD) and P

concentrations around 14 000 mg COD L⁻¹ and 380 mg P L⁻¹, but peak concentrations can reach 90 000 mg COD L⁻¹ and 2400 mg P L⁻¹ if the degree of dilution is smaller (USDA, 1996).

In addition to containing a large amount of P, the high COD load of animal wastes can be a substantial source of renewable energy if converted to a useful form (Rittmann, 2008). For example, the 14 000 mg COD L⁻¹ in pig waste converts to 1.6×10^8 kJ L⁻¹ of energy value at 90% conversion (Rittmann and McCarty, 2001). Fortunately, anaerobic microbiological systems are able to convert the complex organic matter in animal wastes to either methane gas (CH₄), hydrogen gas (H₂), or electricity (Rittmann, 2008). Anaerobic digestion to form CH₄ is a mature technology that can be implemented widely today (Rittmann and McCarty, 2001, Tchobanoglous et al., 2003, Rittmann, 2008, Speece, 2008), although animal wastes present certain unique challenges. The platform of the microbial fuel cell can be used to generate either electrical power or H₂ gas (Rittmann, 2008). This platform is still in the research stage, but has potential to generate renewable outputs with higher value than CH₄.

In all of the anaerobic processes, the energy in the COD is transferred from complex organic molecules to the simple forms of CH₄, H₂, or electrical power. This process releases most of the P in the organic waste as inorganic phosphate, which can then be recovered. Thus, P capture from animal wastes can be coupled naturally to energy recovery, providing a complementary means for obtaining economic value from waste materials. The simultaneous recovery of energy and P means they could subsidize one another. In contrast, other non-biological means of releasing P from animal wastes would require energy inputs (e.g., heat or an advanced-oxidation process).

In this article, we review promising new approaches to capture P from animal wastes, which have a high concentration of P in high-strength organic streams. The relative low flows and the opportunity to link energy and P capture make animal wastes a technically and economically viable option today. While we do not focus on P-capture technology for run off due to the technical and economic difficulties that make its near-term implementation unlikely, society may be pressed to recover P from run off in the future, and re-evaluation for this goal will then be appropriate.

Fig. 1 summarizes the strategy for recovering the large flow of lost P in animal waste so that the P can be used in agriculture to replace a significant fraction of mined P. The first step in P capture is to ensure that the P is in a recoverable form. Thus, we begin with a discussion of means to convert organic P into inorganic P, which is the recoverable form. Then, we look at four major approaches for removing inorganic P from the water stream in a form that can be reused: precipitation, adsorption, ion exchange, and biological uptake. In each case, we provide a succinct summary of the most promising options for recovery from high-organic/high-P streams. Table 2 summarizes all the recovery approaches and indicates whether they are ready for commercial use or require more research and adaptation. We also provide detailed information on specific technologies, their performance experiences, and commercialization status in Supplementary material.

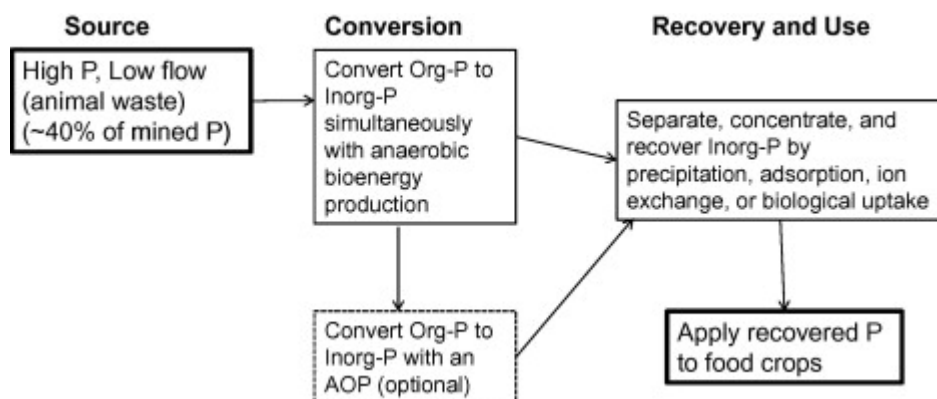


Fig. 1. Schematic of the how the major sources of lost P in animal waste can be recovered for use in agriculture.

Table 2. Technologies for phosphorus removal and recovery.

Technology	Readiness*
<i>Precipitation</i>	
Struvite or magnesium ammonium phosphate (MAP, $MgNH_4PO_4$)	1
Calcium phosphates (hydroxyapatite, HAP, $Ca_5(PO_4)_3OH$; or $CaNH_4PO_4 \cdot H_2O$)	1
Byproduct adsorbents that can be recycled as seed material (oil shale ash, alum residual, red mud, fly ash, cement kiln dust, and bone char)	2
Magnetite seeding to enable magnetic separation and removal following precipitation	2
<i>Adsorption</i>	
Iron-based adsorbents such as hybrid anion exchangers (HAIX), BluePRO [®] , and schwertmannite	1
Poly(allylamine hydrochloride) hydrogels	2
Asahi Kasei Chemical's adsorbent beads with surface micropores and an internal network of submicron pores	1
Macroporous titanium dioxide	2
Raw dolomite powder used in a fluidized bed configuration	2
Novel mixtures containing iron and manganese	2
Industrial byproducts from steel slag, blast-furnace slag, coal slag, and iron-oxide tailings	2
<i>Ion exchange</i>	
Capacitive deionization on oppositely charged electrodes	2
Iron-based layered double hydroxide compounds that release cations and/or hydroxides	2
Metal-loaded chelating resin used to selectively remove phosphate	2
Hydrotalcites	2
<i>Biological uptake</i>	
Enhanced biological phosphorus removal (EBPR)	1
Photosynthetic microbes immobilized on cellulose, ceramic, or gel carriers	2
Phosphate-binding proteins (PstS)	2

* Readiness scale: 1 = ready for commercial application today; 2 = requires further research and adaptation.

2. Conversion of organic P to inorganic P

The chemical form of P affects its removal and recovery. The P applied in fertilizer is inorganic phosphate, which has historically been the target for P removal from wastewater (Rittmann and McCarty, 2001, Tchobanoglous et al., 2003). However, organic P is often present in natural waters in the form of plant or animal tissue, nucleic acids, nucleotides, and phospholipids in the bodies of aquatic organisms (USEPA, 1983, Murphy, 2007). Furthermore, organic P is present in municipal, agricultural, and animal biosolids due to its fixation into cellular material or specific uptake and intracellular storage. Organic P has largely been grouped in the "non-reactive" and "non-bioavailable" component of total P (TP) (McKelvie, 2005). Most importantly, organic P is typically not susceptible to the removal technologies for inorganic P, and separation of P from biosolids typically requires conversion of organic P to inorganic P.

For high-organic streams, like animal wastes, digestion of organic solids in the anaerobic energy-conversion processes releases inorganic P. A number of innovations have been applied to improve the kinetics and extent of microbial conversion in anaerobic digestion (Salerno et al., 2009). These include treatments with high temperature, acid, base, enzymes, oxidants, microwaves, and pulsed electric fields (Kuroda et al., 2002, Liao et al., 2005, Wong et al., 2006a, Wong et al., 2006b, Yin et al., 2007, Yin et al., 2008, Lo et al., 2008, Kenge et al., 2009a, Kenge et al., 2009b, Salerno et al., 2009, Wang et al., 2009). Most of the methods can increase the extent

of conversion of biomass to CH₄, which also leads to more release of inorganic P. However, each of the pre-treatment approaches has challenges related to one or more of capital cost, energy consumption, chemical usage, odor, and corrosion.

Advanced-oxidation processes (AOPs) (Crittenden et al., 2005) are promising for converting organic P to the more readily removable inorganic P form in the low-concentration streams. The AOPs include ozonation, ozone/peroxide, UV/peroxide, titanium dioxide photocatalysis, and Fenton's reaction. All AOPs rely on non-specific free-radical species, such as hydroxyl radicals ($\bullet\text{OH}$), to quickly attack the structure of organic compounds. However, up to now, AOPs have mostly been evaluated for the destruction of specific P-based contaminants, such as organophosphorus pesticides (Daneshvar et al., 2004, Badawy et al., 2006, Wu et al., 2009). The non-specific nature of AOP attack means that AOP technology may be impractical for direct use with high-strength streams, such as animal wastes. In this case, radical reactions with the copious amounts of organic matter present consume too much oxidant to be practical or economical. It is possible that P-laden liquor after biological energy capture could be treated with advanced oxidation to convert released organic P to inorganic P.

3. Separation and recovery of inorganic P by precipitation

Chemical precipitation targeting the removal of P from wastewater is a well-established practice begun in the 1950s (Morse et al., 1998). Precipitation (also called crystallization) requires sufficient phosphate concentration to yield thermodynamic super-saturation. While precipitation may occur spontaneously, it normally is initiated by the addition of a divalent or trivalent metal ion: e.g., magnesium (Mg^{2+}), calcium (Ca^{2+}), aluminum (Al^{3+}), or ferric iron (Fe^{3+}). The choice of the metal ion is important because recovered P that is too tightly metal-bound cannot readily be reused in industrial and agricultural applications (Morse et al., 1998).

Table 2 lists the most common precipitation technologies to recover P for use as fertilizer. Magnesium- and calcium-based precipitation products are most commonly recycled as fertilizer, and most entries in Table 2 are based on these metal ions. Although P removal using aluminum- and iron-based precipitation is quite common in wastewater treatment (Aguilar et al., 2002, Laridi et al., 2005, Chuang et al., 2006, Georgantas and Grigoropoulou, 2007, Banu et al., 2008, Caravelli et al., 2010;), it is less appealing for recovery efforts since P recovery from these solids appears to be difficult, and aluminum is toxic to many plants and some soil organisms. The P in iron phosphates is generally considered to be unavailable to plants, although a fraction of the insoluble P may eventually become bioavailable depending on hydration or aging (Johnston and Richards, 2003). Regardless, several cities in Sweden have installed P removal and recovery pilot plants using the KREPRO sludge treatment process, which precipitates P as ferric phosphate (Levlin, 2001, Stark, 2002).

Phosphate recovery as struvite (also called magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a fairly common practice. It has multiple commercially available configurations, including PHOSNIX, Rem-Nut, and Ostara processes (Schröder et al., 2010). Struvite precipitation occurs readily once phosphate reaches 100–200 mg L⁻¹ and as long as ammonium is present (Moriyama et al., 2001, Qureshi et al., 2006, Le Corre et al., 2009). Struvite exhibits qualities comparable to standard fertilizers, such as diammonium phosphate and superphosphate (Ghosh et al., 1996, Goto, 1998, Munch and Barr, 2001, Johnston and Richards, 2003). Struvite also may be used in detergents, cosmetics, animal feed, fire-resistant panels, and cement (Gaterell et al., 2000, de-Bashan and Bashan, 2004).

Struvite precipitation already is applied to anaerobic sludge digestion, where high concentrations of inorganic P and ammonium are present (Durrant et al., 1999, Stratful et al., 1999). While precipitation may occur spontaneously (Bouropoulos and Koutsoukos, 2000, Doyle and Parsons, 2002), normally a seed material (e.g., sand, anthracite, clay, or struvite itself) is added to aid precipitation. The use of struvite as a seed material is favorable, as it increases the purity of the product (Doyle and Parsons, 2002). Chemical equilibrium models for

struvite precipitation in synthetic and actual wastewaters indicate that the resulting solids contain 27% to 100% struvite (Gadekar and Pullammanappallil, 2010). They also indicate two optimal pH and molar ratio conditions: (1) pH 8.5 at an equimolar mixture of ammonia, magnesium, and phosphate to yield 29% struvite in the solids; and (2) pH 9.8 with a 10:1.7:3.4 M ratio to yield 98% struvite.

Calcium-based precipitation is a common means of P removal based on its relatively low cost and ease of handling (de-Bashan and Bashan, 2004). Several forms of calcium-phosphate solids are possible. The most common solid form is calcium phosphate (hydroxyapatite, HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which requires the presence of Ca^{2+} and high pH (typically ≥ 10). Another alternative is $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, which is a slow-release fertilizer. For example, $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ was recovered from anaerobically digested swine wastewater by air stripping (to remove NH_3 and raise the pH) and addition of $\text{Ca}(\text{OH})_2$ (Suzuki et al., 2006, Suzuki et al., 2007, Perera et al., 2007, Quan et al., 2010). To make P more bioavailable, it may be necessary to acidify the product and/or add chelating agents (e.g., EDTA) (Zhang et al., 2010).

A wide array of byproduct materials wasted from various industrial processes offer relatively inexpensive means by which to accelerate P precipitation by providing seeding surfaces on which the precipitates can form. (Supplementary material contains information on each example.) Byproducts such as alum residual, red mud, fly ash, cement kiln dust, and bone char often contain significant fractions of divalent or trivalent metals such as aluminum, iron, and calcium, which also are able to adsorb inorganic P, the topic of the next section. Seeding is most beneficial for streams with low solids concentrations, such as runoff, as opposed to high-solids streams, such as animal wastes.

Magnetic separation of precipitated P was proposed in the 1970s by investigators as a means to improve collection of P precipitates (Karapinar et al., 2004). They exploited magnetized seed material such as aluminum sulfate, montmorillonite, iron, and calcium nitrate. In spite of potential advantages for P removal and recovery, high-gradient magnetic filtration has not superseded conventional processes. Possible reasons include the technical expenditures required for magnetite recovery and the increased energy consumption required to operate the process.

The organic material may need processing to make it available for P recovery into a useful product. For example, sludge and sludge ash, which may contain 40–95% of the P from incoming wastewater flows, require chemical or thermochemical treatment to dissolve the available P and remove heavy metals. Technologies such as KREPRO, KemiCond, Seabourne, Aqua Reci, BioCon, SEPHOS, and PRISA are used to recover P from wastewater sludge (Berg and Schaum, 2005, Montag et al., 2009).

4. Separation and recovery of inorganic P by adsorption

Adsorption refers to the transfer of liquid-phase solutes to solid-phase adsorbents (Crittenden et al., 2005). Phosphorus separation by adsorption during coagulation, followed by removal through sedimentation and filtration, was first used in the 1950s and has since been used to treat water and wastewater using a wide variety of sorbents (Morse et al., 1998, Westholm, 2006, Goh et al., 2008). The adsorption removal mechanism employed in coagulation remains the best-understood and most widely used mechanism for P removal (Morse et al., 1998, Karapinar et al., 2004). However, other P-adsorption processes are emerging. Table 2 lists important P-adsorption processes.

One advantage of P removal by adsorption as part of coagulation is that the conventional coagulants (aluminum sulfate (alum), ferric chloride, and lime) have relatively low cost, wide availability, and high adsorption capacity. The same benefits apply to several “byproduct” adsorbents, such as fly ash, steel slag, and red mud (Lan et al., 2006, Mortula et al., 2007, Xiong and Peng, 2008). Some adsorbents can be recycled for phosphate recovery (de-Bashan and Bashan, 2004).

Drawbacks of adsorption include high operational costs (energy, maintenance, sludge handling, and disposal), large reactor volumes, and possible effluent-neutralization requirements (Blaney et al., 2007, Xiong and Peng, 2008). Moreover, thermodynamics and kinetics limit conventional adsorbents to 75–90% P removal under favorable conditions (Tomson and Vignona, 1984, Bowker et al., 1987, Robertson, 2000).

Iron-based sorbents can achieve high levels of P removal due to the strong affinity of the phosphate anion for positively charged ferric iron. Iron-oxide particles successfully adsorb phosphate, and the particles themselves are effectively removed from the waste stream using microfiltration (Kang et al., 2003). Likewise, biogenic iron oxides collected from a wetland had a high affinity for phosphorous (Rentz et al., 2009). A ferri-hydrate-modified diatomite increased P-adsorption capacity by three times relative to a raw diatomite (Xiong and Peng, 2008). Another example is schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$), which is an iron-oxide sorbent that can be efficiently separated from aqueous solution using magnetic filtration (Eskandarpour et al., 2007).

Novel P adsorbents include polymeric hydrogels, which can absorb large amounts of water while remaining insoluble (Kioussis et al., 1999, Kioussis et al., 2000); small beads with surface micropores and an internal network of submicron pores (Midorikawa et al., 2008); macroporous TiO_2 that traps P within its pores (Nagamine et al., 2003); crushed dolomitic rock (Ayoub and Kalinian, 2006); and a mixed binary oxide (Fe–Mn) sorbent (Zhang et al., 2009). Iron-impregnated ion-exchange media, including a phosphate-adapted hybrid anion exchanger (HAIX), also appears promising for P adsorption and recovery (Blaney et al., 2007).

Metal oxides are found in numerous industrial byproducts, thereby making these byproducts attractive candidates for use as adsorbents for P removal and recovery. As byproducts, these adsorbents may be relatively inexpensive compared to commercial alternatives, but large-scale availability and consistent supplies may be difficult to guarantee. Additionally, the bioavailability of the resulting metal-bound compounds is variable. Sorbent-specific testing would be beneficial to ascertain P recovery potentials. Steel slag, which contains iron oxides and alumina, is the magnetically separated industrial waste from steel factories. Blast-furnace slag, which is derived from the separation of iron from ore, contains large amounts of aluminum, iron, and calcium (Yamada et al., 1986, Sakadevan and Bavor, 1998, Johansson and Gustafsson, 2000). Iron-oxide tailings derived from mineral-processing industries and coal slag are other relevant byproduct adsorbents.

5. Separation and recovery of inorganic P by ion exchange

Undesirable ions can be exchanged for solid-phase ions based on ion affinity in a process known as ion exchange (Crittenden et al., 2005). Compared to adsorption, ion exchange provides a more selective means of separating ions from solution, and it recently has gained recognition in P-removal applications (Lan et al., 2006). Ion exchange is promising for P recovery because it is generally a reversible process (Kuzawa et al., 2006). Furthermore, the concentrated ionic solution can be treated to recover P by means such as precipitation of calcium hydroxide using CaCl_2 addition. Table 2 lists some of the most promising ion-exchange processes for P removal and recovery.

Capacitive deionization (CD) is a relatively new technology developed for desalination. A charged electric field causes ions to accumulate on oppositely charged carbon electrodes. CD systems are available at the commercial scale, and several demonstration projects are on going for desalination. Although the P-removal and -recovery capabilities of CD are not currently emphasized, phosphate ions may be removed from solution by direct capture of the ions at the electrodes or by P precipitation resulting from the accumulation of multivalent metal cations (inner layer) and hydroxide or phosphate ions (outer layer) at the cathode (Dietz, 2004, CDT, 2010). The ions (and presumably precipitates) are discharged through a reversal of the applied voltage. The concentrated ionic stream would then need to be purified to recover useful P.

Iron-based layered double hydroxides (LDH) ($\text{Ma}_2+\text{Feb}_3+(\text{OH})_2(\text{a+b})\text{CO}_3\text{b}/22\text{-mH}_2\text{O}$ clay-based anion exchangers) can achieve P removal based on ion exchange between phosphate and carbonate ions. The released metal cations (Mg^{2+} , Ca^{2+} , and Fe^{3+}) and/or their hydroxides effectively enhance P removal by adsorption followed by precipitation. Metal-loaded (e.g., Zr(IV), Cu(II), Co(II), Fe(III), Al(III), Y(III), La(III), and Mo(VI)) chelating resins (ligand exchangers) have recently been promoted for their anion selectivity and trace nutrient removal capabilities in aqueous solution. While ion exchange is a proven technology for P removal (Kney and Zhao, 2004, Ruiz-Calero and Galceran, 2005, Zhu and Jyo, 2005, Wartelle and Marshall, 2006, Wu et al., 2007), only a limited number of studies have been conducted in municipal wastewaters (Safferman et al., 2004). Non-traditional ion exchange materials, including zeolites, have been suggested as alternates based on their potential specificity for phosphate (Jung et al., 2006, Yamada et al., 2006).

Hydrotalcite ($\text{Mg}_{0.683}\text{Al}_{0.317}(\text{OH})_{1.995}(\text{CO}_3)_{0.028}\text{Cl}_{0.226}\cdot 0.54\text{H}_2\text{O}$) is a positively charged brucite-like octahedral layer formed by partial substitution of divalent and trivalent metals along an inner layer consisting of anions and water molecules (Miyata, 1975). It is effective for removing P from wastewater and can recover phosphate in the form of HAP from the concentrated desorption solution using CaCl_2 additions (Kuzawa et al., 2006).

6. Separation and recovery of inorganic P by biological uptake

In EBPR, the removed P is stored as polymerized phosphate within heterotrophic biomass that is alternated between anaerobic and aerobic conditions (Rittmann and McCarty, 2001). EBPR is commonplace in treatment of domestic wastewater (Franzreb and Holl, 2000, Tam and Wong, 2000, Chae et al., 2006), because organic substrate concentrations (i.e., BOD) are sufficiently high to allow adequate synthesis of heterotrophic biomass. The product is organic P and may require additional treatment prior to recovery and reuse, although one option is to use the resulting biomass directly in agricultural settings as a slow-release fertilizer.

A serious limitation of EBPR for high-strength streams is that energy recovery must be carried out in a strictly anaerobic system (Rittmann, 2008). This is not consistent with the need to expose the microbial community to alternating aerobic and anaerobic conditions in EBPR. However, it may be possible to use EBPR to capture P in the anaerobic effluent if the BOD:P ratio is correct and aerobic biodegradation of residual COD is required.

Table 2 summarizes two novel biological processes that do not demand substantial growth and accumulation of heterotrophic biomass. The organic P must have been released from the waste organics prior to the either biological process.

Phototrophic microorganisms (i.e., photosynthetic bacteria and algae), which use sunlight as their energy source and CO_2 as their carbon source, can be grown to high biomass levels without the input of organic matter (i.e., BOD). A major challenge for using photosynthetic microorganisms is separating the microbial cells from the treated water (Talbot and Delanoue, 1993, Sawayama et al., 1998a, Sawayama et al., 1998b). While some cyanobacteria naturally aggregate and settle well, most phototrophs are difficult to remove from the water. Thus, immobilization of phototrophic microorganisms has been employed in an effort to facilitate separation (Sawayama et al., 1998a, Sawayama et al., 1998b, de-Bashan and Bashan, 2004, Shi et al., 2007).

Microorganisms in P-limited environments have evolved efficient phosphate-assimilation mechanisms. For example, the diatom *Didymosphenia geminata*, which flourishes in P-limited ($<20 \mu\text{g L}^{-1}$) waters, secretes enzymes enabling it to directly access pools of organic P (Maurer, 2008). Furthermore, large numbers of the high-affinity phosphate-binding protein, PstS, are expressed in a variety of microorganisms in low-P environments (Poole and Hancock, 1984, Wu et al., 1999). These proteins may be used in engineered systems to bind soluble inorganic phosphate.

The use of microbes expressing the PstS protein in water treatment applications requires that the microorganisms survive in the reactor. Since only certain microbes express the PstS protein, including marine cyanobacteria, their use in fresh water systems may be limited. The current development status of P removal using the PstS protein is theoretical, albeit promising. However, restrictions on the possible release of genetically engineered microbes into the environment may hinder implementation of this technology.

7. Summary

The depletion of minable P reserves will turn into a global calamity unless we find large sources of renewable P by recovering the P lost between the fertilizer applied to arable land and the food we eat. The largest two flows of lost P are in agricultural runoff and erosion (~46% of mined P globally) and animal wastes (~40%). These flows are quite distinct. Runoff has a very high volumetric flow rate, but a low P concentration; animal wastes have a high P concentration together with a high concentration of organic material that also can be converted to renewable energy. Recovering the lost P in animal wastes is technically and economically more tractable today, and we focus on that goal.

P capture begins with transforming organic P into inorganic P. For the high-organic/high-P animal wastes, P release can be accomplished in tandem with anaerobic treatment that converts the energy value in the organic matter to CH₄, H₂, or electricity. Once the P is present as phosphate, it can be captured in a reusable form by four approaches. The most well developed approach is by precipitation as magnesium or calcium solids. Less well developed, but promising are adsorption to metal-based adsorbents, ion exchange to phosphate-selective solids, and uptake by photosynthetic microorganisms or P-selective proteins.

Appendix A. Supplementary material

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Supplementary data 1.

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