Removal and recovery of phosphate from water using sorption

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ABSTRACT

Sorption is an effective, reliable, and environmentally friendly treatment process for the removal of phosphorus from wastewater sources which otherwise can cause eutrophication of receiving waters. Phosphorus in wastewater, if economically recovered, can partly overcome the future scarcity of phosphorus resulting from exhaustion of natural phosphate rock reserves. The authors present a comprehensive and critical review of the literature on the effectiveness of a number of sorbents, especially some novel ones that have recently emerged, in removing and recovering phosphate. Mechanisms and thermodynamics of sorption, as well as regeneration of sorbents for reuse using acids, bases, and salts, are critically examined.

KEY WORDS: adsorption, phosphate sorption, phosphate desorption, phosphate recovery, sorption mechanism, sorption thermodynamics, sorbent, water treatment, wastewater treatment

RUNNING HEAD: Phosphate removal and recovery from water

CONTENTS

1. Introduction

Globally, clean water for domestic, agricultural, and recreational uses, as well as for potable supply, is increasingly endangered due to water pollution, climate change and rising human needs. Stringent legislation and regulations exist in many countries to reduce pollutants bolstered by anthropogenic activities that thresten natural water bodies. Because of the limited availability of high quality water resources, reclamation and reuse of treated wastewater have become important in the sustainable management of this natural resource.

Phosphorus (P) is a major nutrient contaminant in water. It enters water bodies through mining, industrial and agricultural activities, and sewage discharges. Excessive concentrations of P in water cause eutrophication (Hussain et al. 2011; Paleka and Deliyanni 2009; Xu et al. 2010a), which is defined as the enrichment of water bodies by nutrients and the consequent deterioration of quality due to the luxuriant growth of plants such as algae and its repercussions on the ecological balance of the waters affected (Yeoman et al. 1988). Although both nitrogen (N) and P are considered to be the limiting nutrients for eutrophication, some algae are efficient in the fixation of atmospheric N and hence P often becomes the potentially limiting nutrient in freshwaters (Yeoman et al. 1988; Zeng et al. 2004). In advanced stages of eutrophication, dissolved oxygen can become depleted to dangerously low levels causing fish death when algae decay (Awual et al. 2011; Long et al. 2011). The large algae biomass produced by eutrophication can also affect water treatment by blocking filters or passing through them causing bad odour and taste in treated water (Collingwood 1977). Blue-green algae can produce compounds that are toxic to fish and other aquatic life (Davis 1980). These conditions are also potentially risky to human health, resulting from consumption of shellfish contaminated with algal toxins or direct exposure to waterborne toxins (EPA 2009).

To control eutrophication the US EPA has recommended that total P should not exceed 0.05 mg P/L in a stream at a point where it enters a lake or reservoir and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs (Mueller and Helsel 1996). The European Union (EU) considers that the cut-off for total P concentration between at risk and not risk of eutrophication in lakes is < 10 µg/L to > 100 µg/L, and for rivers, total P concentration below 0.01-0.07 µg/L is considered excellent waters (European Commission 2009). The Australian and New Zealand water quality guidelines recommend that Australian upland rivers, depending on the region, should have a total P concentration < 0.01-0.02 mg P/L, low land rivers < 0.005-0.01 mg P/L, freshwater lakes and reservoirs < 0.01-0.025 mg P/L, and estuaries < 0.02-0.10 mg P/L (ANZECC 2000). The corresponding limits for New Zealand are 0.026 mg P/L for upland rivers and 0.033 mg P/L for lowland rivers (ANZECC 2000).

Phosphorus commonly originates from human and animal wastes, food-processing effluents, commercial fertilisers, agricultural land runoffs and household detergents. In water and wastewater, P is present in the form of orthophosphate, polyphosphates and organic phosphorus. Polyphosphates and organic P are converted to orthophosphate by hydrolysis/or microbial mobilisation (Weiner 2008). Orthophosphate is soluble and considered to be the only type of P that is directly assimilated by most plants, including algae. Due to their strong adsorption onto inorganic particles they also occur adsorbed onto particulate matter/sediments in water. A proportion of P in detergents and cleaning compounds contains tripolyphosphate, which is slowly mineralised to orthophosphate (Zhou et al. 2011). Early work by Clescere and Lee (1965) showed that the hydrolysis of condensed phosphates to orthophosphate can take hours or days in the presence of various microorganisms. The chemical form and ionic charge of orthophosphate change with the pH of water in accordance with their pK values ($pK_1 = 2.15$, $pK_2 = 7.20$, $pK_3 = 12.33$) (Chitrakar et al. 2006b; Streat et al. 2008; Weiner 2008). The pH also influences the surface charge characteristics of soils and sediments, thereby controlling P sorption onto these materials. Raising pH decreases the positive charges and increases the negative charges on the surfaces of soils and sediments, affecting the energies (coulombic attraction vs coulombic repulsion) of P binding. Consequently, pH is expected to influence the physicochemical behaviour of P in water.

Phosphorus in wastewater sources must be removed or reduced to avoid eutrophication of receiving waters such as rivers and lakes. The ecological recovery of the receiving water bodies after prolonged eutrophication can be very slow even after the solution P is reduced (Vollenweider 1968; Yeoman et al. 1988). This is because much of the P may be temporally trapped in the sediments in water bodies and released slowly into the water.

Phosphorus removed from water can be a source of raw material for the phosphate industry, especially the production of phosphate fertilisers for agriculture. If a successful method is developed for effective and economical recovery of P, the current thinking that P is a contaminant will change to one that deems it is a resource. This view has increased in recent years because some have argued that P is a limited and non-renewable resource and the reserves of high grade phosphate rock that are used to make phosphate fertilisers will be largely exhausted before the end of this century, unless another source of high-grade phosphate is identified (Cordell et al. 2011; De-Bashan and Bashan 2004; Isherwood 2000). However, others have reported that, assuming current rates of production, phosphate rock concentrate will be available for the next 300-400 years (Van Kauwenbergh 2010).

A recent global P scenario analysis indicates that meeting the increasing long-term P demand would require cutting the projected demand by two-thirds through more efficient use of P and meeting the remaining third through a high recovery rate of P from human excreta, manure, food waste and mining waste (Cordell et al. 2011). A significant proportion of P in these materials, especially human excreta and manures end-up in wastewaters (e.g. dairy shed effluent, municipal discharges). Devising suitable technologies to effectively recover P from wastewater could significantly contribute to meeting the future P demand. In some countries, attempts have already been made to recover P from wastewater in the form of struvite and hydroxyapatite and to use them as fertiliser (De-Bashan and Bashan 2004; Le Corre et al. 2009; Midorikawa et al. 2008).

There are numerous methods for removing phosphate from water (Fig. 1). Of these, the sorption process is generally considered to be an effective water treatment option because of convenience, ease of operation, simplicity of design and economics, provided low-cost sorbents are used (Bhatnagar and Sillanpää 2011). (As the phosphate removal mechanism is not always at the surface of the sorbent, the term ‘sorption’ is used in this paper to denote phosphate removal both at the surface and interior of the sorbent). However, sorbents are not commonly used in wastewater treatment plants due to the necessity to regenerate sorbent, and discharge the regeneration solution. With more emphasis on recovering the removed phosphorus and the need for very low P concentration in the effluent, sorption is an attractive process for wastewater plants in the future. Sorbents are used as filter media in filter-based systems and as bed media in constructed wetlands. After a period of usage they become saturated with phosphate and their efficiency of phosphate removal decreases. At this point the sorbent can either be used directly as a source of P if it has no contaminants or can be regenerated by removing the adsorbed phosphate. The phosphate so removed can be recovered by precipitation with calcium/or magnesium salts and employed as phosphate fertilisers. Alternatively they can be diluted with irrigation water for fertilising irrigated crops.

Although there have been several reviews on the removal of pollutants from water and waste water (see references in this paragraph), to our knowledge no comprehensive review on removing phosphates from water and wastewater by sorption process has been published. One exception is that by Westholm (2006), which covered many sorbents but not ones extensively researched in recent times (e.g. layered double hydroxides). Early reviews on this subject focused on the removal of phosphates by chemical precipitation, biological treatment and constructed wetlands (De-Bashan and Bashan 2004; Le Corre et al. 2009; Morse et al. 1998; Yeoman et al. 1988). Some reviews concentrated only on specific types of sorbent such as red mud (Wang et al. 2008), layered double hydroxides (Goh et al. 2008) or low-cost sorbents (Gupta et al. 2009). This paper presents a critical and comprehensive review of the literature on the effectiveness of various sorbents, especially those that have emerged in recent years, in removing and recovering phosphate from water. The mechanisms and thermodynamics of sorption/desorption of phosphate during the removal and recovery process, and environmental factors influencing the effectiveness are also discussed.

2. Sorption mechanisms

The capacity, energy and kinetics of sorption of phosphate are controlled by the mechanisms of sorption. Understanding the mechanisms can provide useful information on the optimisation of the sorption process and the subsequent desorption/regeneration process. There are five mechanisms of phosphate sorption: (1) ion exchange (outer-sphere surface complexation), (2) ligand exchange (inner sphere surface complexation), (3) hydrogen bonding, (4) surface precipitation, and (5) diffusion into the interior structure of the sorbent. The predominant type of mechanism operating in a sorption process depends on the physical and chemical characteristics of the sorbent and the environmental/operational conditions. The five mechanisms are briefly discussed below and summarised in Fig. 2.

2.1. Ion exchange

Ion exchange is a stoichiometric process where any counter ion leaving the ion exchange surface (diffuse double layer) is replaced by a chemically equivalent number of another counter ion to maintain electro-neutrality of the ion exchanger. In other words, one ion is sorbed onto and another ion is desorbed from the sorbent or ion exchanger. In this paper, ion exchange is considered to be a type of sorption unlike some others where they are treated separately. The force of attractive between the ion and the sorbent is coulombic or electrostatic and the sorption process is reversible. The ions are sorbed physically by fully retaining their inner hydration shell. Ion exchange materials or sorbents tend to prefer counter ions of higher valency, higher concentration and ions of smaller hydrated equivalent volume (Helfferich 1995). Phosphate exchange with chloride ion in an ion exchange resin and layered double hydroxide (LDH) is illustrated in Fig. 2.

2.2. Ligand exchange

In ligand exchange the sorbing anion such as phosphate forms a covalent chemical bond with a metallic cation at the sorbent surface resulting in the release of other potential determining ions such as OH ions previously bonded to the metallic cation. Thus phosphate is said to form an inner sphere complex at the sorbent surface. The sorption creates a negative charge on variable charge surfaces, thereby shifting the zero point of charge to a lower pH (Fig. 3). The development of spectroscopic techniques such as X-ray absorption fine structure (EXAFS) spectroscopy, fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron (XPS) spectroscopy and their application to ion sorption process during the last decade has provided useful information on the structure of the surface complex at the molecular level (Elzinga and Sparks 2007; Sparks 2001).

Ligand exchangers have the particular advantage of combining high sorption capacity with high selectivity for the anions. These exchangers can remove large proportions of anions having higher selectivity for sorption from very dilute solutions of the anions even in the presence of competing anions of lower selectivity. Examples of the phosphate sorption process following ligand exchange mechanism are presented in Fig. 2 for metal oxide sorbents commonly used for removing phosphates from water (Antela et al. 2005; Deliyanni et al. 2007; Kasama et al. 2004; Xue et al. 2009; Yan et al. 2010; Zhang et al. 2009, 2011).

2.3. Hydrogen bonding

Hydrogen bonding (H bonding) is a strong dipole-dipole attractive force between bonding of the strong electropositive H atom in a molecule in a sorbent or sorbate and a strong electronegative atom such as oxygen in another molecule (Weiner 2007). However, the energy of sorption in H bonding is weaker than in the inner sphere complex formation in ligand exchange. H bonding occurs in the sorption of phosphate on metal oxides (see Fig. 2 of ligand exchange) and organic molecules (Saha et al. 2009).

2.4. Surface precipitation

Sorption of phosphate is commonly measured by the decrease in the amount of phosphate in solution phase after a period of time the solution was in contact with the solid phase. The decrease in phosphate content, results not only from sorption but also from precipitation of phosphate in solution phase if the product of the solution concentrations of the constituents of the precipitate exceeds the solubility product of the precipitate.

Surface precipitation of metal phosphates can occur even at solution concentrations of phosphate and metals lower than those expected to form metal precipitates in solution phase according to the thermodynamic solubility product principle (Sparks 2001). In such cases, a finite volume adjacent to the mineral surface exists that is oversaturated with respect to precipitate formation (Ford 2006). X-ray diffraction and scanning electron microscopic data provided evidence for the formation of surface precipitates of phosphate compounds of Ca, Fe, Al, and Zn on sorbents containing components of these metals (Bowden et al. 2009; Khadhraoui et al. 2002; Koilraj and Kannan 2010; Oguz 2005; Roques et al. 1991) (Fig. 2). Using scanning electron microscopy, Nagamine et al. (2003) showed that when a phosphate solution was mixed with an equal volume of a $CaCl_2$ solution having the same concentration as phosphate with pH adjusted to 8.8 to 9.0 and passed through a macroporous TiO_2, calcium hydroxyl phosphate was crystallised inside the pores. The phosphate sorbed to TiO_2 in the pores was deemed able to provide nuclei for this crystallisation process.

2.5. Diffusion

Sorption of phosphate on many microporous sorbents (e.g. hydrous metal oxides, especially those having amorphous structure) is recognised as a 2-step process: firstly, an initial rapid sorption (within an hour) that reaches a pseudo-equilibrium at the solid-solution interface; and secondly, a much slower process (days to months) where the phosphate ions move by intra-particle diffusion into the interior pores and channels of the sorbent (Trivedi and Axe 2006) (Fig. 2). For example, studies on removal of phosphate from aqueous solutions by date palm fibres showed that phosphate moved into the internal cells of the fibres by diffusion (Riahi et al. 2009). Evidence for this process was provided by scanning and transmission electron microscopy and energy dispersive spectroscopy.

Intra-particle diffusion rate is directly related to the square root of time of sorption. Therefore if a straight line relationship is obtained between the rate of sorption and square root of time at longer times of sorption it can be inferred that the diffusion process controls sorption at these times. Such a relationship was found in many studies concerning the sorption of phosphate on different sorbents (Anirudhan and Senan 2011; Babatunde and Zhao 2010; Benyoucef and Amrani 2011; Long et al. 2011; Zach-Maor et al. 2011).

Outer-sphere (ion exchange) and inner-sphere (ligand exchange and H-bonding) sorption processes (Fig. 2) are also known as non-specific and specific sorption processes, respectively. There are differences in these processes according to Bolan et al. (1999), and they are presented in Table 1.

3. Sorption efficiency measurement methods

Numerous sorbents have been used to remove phosphate from water (Table 2-5). The efficiency of removal by not only different but also similar adsorbents varies widely depending on the chemical and physical characteristics of the sorbents (surface functional groups, surface area, porosity), environmental conditions such as pH, solid/solution ratios, competitive ions present in solution, temperature and method used for determining sorption. Studies do not always report such information and sometimes this makes it difficult to compare the removal efficiencies of sorbents. However, if a number of studies on the same sorbent were carried out, an assessment can be made on the efficiency of the sorbent based on the average results of the studies as suggested by Westholm (2006). In addition to removal efficiency, other factors such as sorbent cost, local availability and regeneration potential need to be considered in the selection of the most appropriate sorbent.

Assessment of the phosphate sorption efficiencies of sorbents is generally based on two types of investigations: static batch sorption and dynamic column leaching studies. These methods and a continuous-flow stirred tank reactor method are discussed below.

3.1. Batch method

In a batch system, predetermined amounts of an sorbent are mixed with solutions containing a known of concentration phosphate in containers for a given contact period and subsequently the sorbate is separated by sedimentation or filtration. The liquid phase phosphate is then analysed to determine the amount sorbed. The batch mode of sorption is static and conducted in closed system and therefore the data obtained are generally not applicable to most real systems. However, the method is simple and quick information can be obtained on the effects of many solution variables on sorption by conducting a number of batches of sorption experiments simultaneously. The batch method is used mainly to examine the mechanism of sorption and to compare the sorption capacity of various sorbents. Perhaps for these reasons most studies reported in the literature used the batch method (Tables 2-5).

Data obtained from batch experiments have generally been fitted to sorption models such as Langmuir, Freundlich, Temkin, Redlich-Peterson, Langmuir-Freundlich equations (e.g. Hamoudi et al. 2007; Zeng et al. 2004). Furthermore, information on maximum sorption capacities has been obtained to compare the efficiencies of phosphate removal using different adsorbents. Langmuir and Freundlich models proved to be satisfactory in describing the sorption process in a majority of the studies (Tables 2-5). Time-wise sorption data obtained from these studies have been fitted to kinetic models such as pseudo-first order, pseudo-second order, Elovich and diffusion models; these provided information on the possible mechanisms of sorption. Of these models the pseudo-second order model has been found to fit the sorption data in most of the studies (Tables 2-5).

3.2. Column method

In most large-scale applications of the sorption process, water flows continuously through a column of sorbent or a packed bed where dynamic sorption of phosphate and other solutes occurs. The column operation allows efficient utilisation of the sorptive capacity than the batch process (Akratanakul et al. 1983; Faust and Aly 1987; Tor et al. 2009). Akratanakul et al. (1983) explained this as due to the amount of ions in solution phase decreasing with time as more and more ions are sorbed in the closed batch system whereas in flow systems, the sorbent is exposed to the same concentration of sorbate at all times. They also reported that the maximum amount of ions that are exposed to the sorbent in a batch system is equal to the product of concentration and volume. In a dynamic system, the product of concentration, flow rate, and exposure time gives the amount of ions exposed to the sorbent. A schematic comparison of the two processes is illustrated in Fig. 4.

In column sorptive removal of solutes, initially the solute is rapidly sorbed at the top layer of the column until the amount sorbed is in equilibrium with the solute concentration in the influent solution. When adsorption in this layer reaches the capacity of the sorbent the solute starts to sorb in the next layer which is called the mass transfer zone (Faust and Aly 1987). As time passes this mass transfer zone moves down the column until it reaches the bottom causing the solute concentration to rise. This point is called the breakthrough point, as shown in Fig. 5. At breakthrough the bottom layers are not completely saturated with the solute. The breakthrough capacity is therefore less than the overall sorption capacity. When the sorbent reaches exhaustion the breakthrough curve takes on the classic S-shape that is controlled by the shape and length of the mass transfer zone (Faust and Aly 1985). Decreasing influent flow rate and the concentration of the solute and increasing the volume capacity of the sorbent will reduce the movement of the mass transfer zone to the bottom of column resulting in a higher degree of column utilisation (Helfferich 1995).

Smooth S-shaped breakthrough curves are obtained for solutions containing only phosphate anion. However, in natural water systems where there are many competing anions for sorption the typical S-shaped curves are not obtained due to chromatographic peaking, where a strongly sorbing anion displaces the previously sorbed phosphate. This causes a higher concentration of the latter in the effluent compared to the influent (Bae et al. 2002; Bajracharya and Barry 1995; Gupta et al. 2012; Pan et al. 2009).

Although the dynamic column studies are closer to the operational conditions in the real full-scale treatment system, they experience the problem of filters being clogged. This issue can be overcome by using prefilters to remove suspended solids and organic matter

(Chazarenc et al. 2007; Johir et al. 2011), using large sized media (Shilton et al. 2006) or using a mixture of fine sized media (to have high sorption capacity) and coarser sized media (to reduce clogging) (Yang et al. 2009). In dynamic column removal of phosphate the filter media selected should not only have favourable physico-chemical properties to remove phosphate but also maintain sufficient permeability (Johansson 1999a; Westholm 2006; Yang et al. 2009).

Xu et al. (2011) reported that a decrease of flow rate (15, 10, 5, 3.3 mL/min) of a phosphate solution through a column containing giant reed-based sorbent increased the breakthrough volume or breakthrough time for phosphate and explained this as due to an increase in empty bed contact time (EBCT). The higher the EBCT, the higher the effective diffusion process becomes, resulting in higher sorption capacity for phosphate. Xu et al. (2011) also stated that the breakthrough process was saturated earlier at high flow rate because the front of the sorption zone quickly reached the bottom of the column. In contrast, lower flow rates and longer contact times resulted in a shallow sorption zone. Hussain et al. (2011) also reported that higher flow rate of phosphate solution through a column containing a mixture of limestone and granular activated carbon resulted in shorter column saturation /exhaustion time. When the flow rate increased, the residence time in the column decreased (lower column utilisation, column saturation time, and bed capacity).

3.3. Continuous-flow stirred tank reactor method

Continuous-flow stirred tank reactor (CFSTR) system is another type of dynamic continuous-flow sorption system used to overcome the problem of clogging in columns and to enhance the diffusion/convection process (Jellali et al. 2010; Wahab et al. 2011). Wahab et al. (2011) reported a high removal efficiency (80%) of phosphate from synthetic solution containing 50 mg P/L using a plant-waste sorbent in CFSTR. They stated that the CFSTR system has many operational and economic advantages because: firstly, the amount of sorbent used is less than in column mode; secondly, contact between the sorbent particles and phosphate in solution is more homogeneous; and thirdly, the rate of transport of phosphate to the solid/liquid interface is faster than in column mode. As mentioned earlier the clogging problem inherent in the column mode does not occur in the CFSTR system. More studies on the use of this system on different sorbents are required, especially in field conditions so that the efficiency of this method can be assessed.

4. Sorbents

4.1. Inorganic sorbents

The efficiencies of removal of phosphate by various inorganic sorbents, the methods used, and the kinetic and equilibrium models best explaining the sorption data are presented in Table 2.

4.1.1. Metal oxides and hydroxides

Oxides and hydroxides, also called hydrous oxides or oxyhydroxides, of trivalent and tetravalent metals such as Fe, Al, Mn, Ti and Zr are used to remove both anionic and cationic contaminants from water and wastewaters because of their strong tendencies to sorb these ions (Zhou and Haynes 2011). The capacity of sorption depends on the affinity of the ions to the sorbent surface, the relative concentrations of ions and pH in solution.

The predominant mechanism of sorption of phosphate on oxides and hydroxides is ligand exchange by the formation of inner sphere complexes (specific sorption) as discussed in section 2 (Antelo et al. 2005; Chitrakar et al. 2006a,b; Elzinga and Sparks 2007). Therefore simple non-specifically sorbing ions such as nitrate and chloride which form outer sphere complexes have little influence on the sorption of phosphate. Ionic strength of solution also has little influence on phosphate sorption on oxides and hydroxides because anions of the indifferent electrolytes have little influence on phosphate sorption (Antelo et al. 2005). However, ionic strength can influence surface charge thereby affecting specific sorption of anions such as phosphate (Bolan et al., 1986).

Several anions co-exist with phosphate in wastewater, and they can compete for sorption. Chitrakar et al. (2006a) showed that the tendency for sorption of anions on goethite at pH 8 followed the selectivity order, Cl^-, NO_3^-, $SO_4^{2-} << CO_3^{2-}$, HPO_4^{2-} and on akaganeite the order was Cl^-, $CO_3^{2-} < NO_3^- < SO_4^{2-} < HPO_4^{2-}$. Similarly, Genz et al. (2004) reported that the sorption sequence for removing anions from membrane bioreactor (MBR) filtrates was $Cl^- < NO_3^- < SO_4^{2-} < HCO_3^- < PO_4^{3-}$ for granulated ferric hydroxide sorbent and $Cl^- \sim NO_3^- < SO_4^{2-} \sim HCO_3^- < PO_4^{3-}$ for activated aluminium oxide sorbent.

Of the oxides and hydroxides of metals used to remove phosphate, Fe and Al oxides and hydroxides have been studied the most. Iron oxides occur as goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ -FeOOH), haematite (α -Fe_2O_3) and magnetite (Fe_3O_4). Of these goethite is the most widespread iron oxide in natural systems, and this material has been used in many sorption studies, including studies on phosphate (Chitrakar et al. 2006a). Aluminium oxides and hydroxides occur as gibbsite, boehmite and bayerite (Makris et al. 2005).

Sorption of phosphate onto laboratory synthesised goethite with surface area 316 m^2/g and average particle size < 70 µm and a commercial sample of Al oxide with surface area 200 m^2/g and average particle size of 50-200 µm was studied in batch experiments at temperatures of 25, 45 and 65°C by Paleka and Deliyanni (2009). The sorption data at 25°C and the optimum pH of 5 fitted the Langmuir model with a maximum sorption capacity of 144 and 35 mg P/g for goethite and Al oxide, respectively. For both the sorbents the sorption capacity declined with higher temperature, indicating that sorption is an exothermic process.

Genz et al. (2004) investigated the removal of phosphate from membrane bioreactor effluents using a subsequent fixed-bed sorption process to meet Berlin's expected regulation aiming at an effluent phosphate concentration limit of 50 µg P/L. They compared the effectiveness of phosphate removal from an MBR effluent spiked with phosphate by using an Fe-based sorbent (granulated ferric hydroxide (GFH)) with akaganeite (β-FeOOH mineralogy, specific surface area 280 m^2/g) and an Al-based sorbent (activated aluminium oxide (AA), Al_2O_3, specific surface area 230-300 m^2/g) in batch and column experiments. In both types of experiments, GFH was more efficient than AA. In the batch experiment, sorption at low phosphate concentration (<3 mg P/L) fitted the Langmuir model with maximum sorption capacities of 23 mg/g at pH 5.5 and 17 mg/g at pH 8.2 for GFH. The corresponding values for AA were 14 mg/g at pH 5.5 and 12 mg/g at pH 8.2. For high phosphate concentrations (> 4 mg P/L) at pH 8.2, there was a steep increase in phosphate sorption on both sorbents. Because the MBR had a high concentration of Ca (120-140 mg/L) the steep rise in sorption was explained in terms of possible co-sorption of Ca and P leading to calcium hydroxyl phosphate precipitation. In the column experiment the effluent criteria of 50 µg P/L was reached after a throughput of 8000 bed volumes for GFH and 4000 for AA, thus confirming the batch study results that GFH is a superior sorbent for removing phosphate.

The steep rise in phosphate sorption in the presence of high Ca concentration at high pH was also reported by Bastin et al. (1999) in their study on sorption of phosphate by a formulation called OX containing a mixture of iron oxide (ferrihydrite) and gypsum at pH > 8. The increased phosphate sorption was attributed to calcium phosphate precipitation. It could also be due to an increase in positive surface charge caused by Ca^{2+} sorption (Bolan et al. 1993). In the pH range 4-8, phosphate sorption remained constant contrary to reports showing a decrease of sorption with increase in pH (Hingston et al. 1972; Ryden et al. 1977). This was explained as due to the presence of gypsum in the sorbent. Calcium in gypsum might have mediated phosphate adsorption. The OX had much higher phosphate removal efficiency (39.1 mg P/g) than hematite (0.7 mg P/g), and this was explained by the disordered structure of ferrihydrite in OX in contrast to the crystalline nature of hematite. Poorly ordered iron oxides are more reactive than their crystalline counterparts (Parfitt 1989).

Common filter media such as sand and perlite cannot achieve significant P removal efficiencies. Sansalone and Ma (2009) used an aluminium oxide coated media (AOCM), a porous soil-type substrate coated with Al_2O_3, to provide large number of surface sites to selectively sorb phosphate. The coating was carried out by adding a 0.5-1 M aluminium salt to a heated (1000°C) clayey soil and reheating the Al-coated soil to dryness and washing. Sorption studies on synthetic phosphate solutions showed that most of the final equilibrium concentrations were below 0.1 mg P/L with 90% reduction or higher for initial phosphate concentration below 2.5 mg P/L and pH 5-8. Increase of pH from 5 to 9 consistently decreased phosphate sorption with a maximum adsorption of 2.5-3.0 mg P/g at pH 5. At all pH values, nitrate had no significant effect on phosphate sorption but sulphate reduced phosphate sorption. This was explained as being due to phosphate and sulphate sorbing mainly through ligand exchange mechanism (specific sorption), whereas nitrate sorption occurred through electrostatic attraction (non-specific sorption). In contrast to sulphate the presence of Ca increased phosphate sorption in the basic environment (pH 8 to 9) as a result of surface complex formation involving Ca and phosphate, as discussed earlier. Sansalone and Ma (2009) concluded that the use of Al oxide coated media (substrate containing clay soil, concrete/brick rubble or any other comparable material) in removing phosphate from stormwater can meet most surface water discharge requirements.

Nano-sized iron oxides that have very high surface area and therefore high ion sorption capacity are expected to be highly efficient in removing phosphate from aqueous solutions. However, because of their very small particle size they cannot be separated from aqueous solutions by gravitational sedimentation. They need a supporting matrix when used in water treatment. Recently, Zach-Maor et al. (2011) used granular activated carbon (GAC) as a support for nano-sized magnetite (Fe_3O_4) particles (nFeGAC) that was prepared from ferric chloride. Phosphate removal efficiency (specific surface area 1024 m^2/g) was examined in batch studies in solutions containing 250, 500 and 1000 mg PO_4^{3-}/L. The sorption data was fitted to the Langmuir model giving an sorption maxima of 16 mg P/g nFeGAC, which was considered to be much higher than that of most other sorbents. It was suggested that the sorption of phosphate on nFeGAC involves two steps: initial (within 1 h) sorption on active surface sites and subsequent diffusion into the interior pores of the magnetite.

Manganese oxides generally have low ZPC (Healy et al. 1966; Loganathan et al. 1977) but they can remove phosphate even at neutral pH where the oxide surface is negatively charged, and therefore do not sorb phosphate by anion exchange process. The mechanism of sorption in this case is inner-sphere complexation. A natural MnO_2 (ZPC 4.7) was reported as having a maximum sorption capacity of 0.4 mg P/g in a solution of pH 7 (Ouvrard et al. 2002). Manganese oxides are also mixed with iron oxides to improve the phosphate removal efficiency from waters. For example, Zhang et al. (2009) reported that a Fe-Mn binary oxide with a Fe/Mn molar ratio of 6.1 was more effective for phosphate removal than Fe-Mn oxides having other ratios and pure amorphous FeOOH. This binary oxide (specific surface area 309 m^2/g) had a Langmuir sorption maximum of 11 mg P/g at pH 5.6. The presence of Cl^-, SO_4^{2-} and CO_3^{2-} at 1.0 and 10 mM had no effect on phosphate sorption from a solution containing 5 mg P/L. FTIR spectra showed that surface OH groups were replaced by phosphate groups during sorption.

Zirconium (Zr) (Chitrakar et al. 2006b), lanthanum (La) (Ou et al. 2007) and titanium (Ti) (Nagamine et al. 2003) oxides and hydroxides have also been used to remove phosphate from water. Chitrakar et al. (2006b) investigated the sorption of phosphate from sodium phosphate solution, sea water and waste water on a synthetic amorphous zirconium hydroxide in batch experiments. Based on the distribution coefficients (ion uptake (mg/g)/ion concentration in solution (mg/L)), the selectivity order for sorption of ions was found to be Na^+, K^+, $Ca^{2+} < Cl^- < SO_4^{2-} << PO_4^{3-}$. The maximum sorption of phosphate from sodium phosphate solution, sea water and waste water were 30, 10, and 15 mg P/g at equilibrium pH of 5.0, 7.7 and 8.8, respectively. The lower sorption values for sea water and waste water were reported to be due to the higher pH and presence of competing anions in these solutions. The sorption capacities of phosphate from sea water and waste water emerged as being much higher than the values obtained for these solutions on many other sorbents.

Chitrakar et al. (2006b) also showed that phosphate sorption from sodium phosphate solution decreased progressively from pH 2 to 9. In contrast, phosphate sorption from sea water increased from pH 2 to 6 and then decreased progressively to 9. In the pH range 2-4, sulphate in sea water was considered to affect phosphate sorption greatly because the sorbent preferred divalent SO_4^{2-} to monovalent $H_2PO_4^-$.

Although finely divided zirconium hydroxides and oxides have good P sorption characteristics they suffer from the difficulty in separating them from water. One method of overcoming this difficulty is making the sorbents magnetic and then separating them using a magnet. Long et al. (2011) prepared such a magnetic material by combining Zr with Fe (Fe-

Zr binary oxide) and showed that this material was magnetic and had a high phosphate sorption capacity of 13.65 mg P/g at pH 4.

Ordered mesoporous silica (OMS) doped with various metal (La, Zr, Ti, Fe and Al) oxides has been studied for the removal of phosphate from water using sorption. OMS has proven to be a good substrate sorbent material because of its high surface area, controlled pore diameters, controlled morphology (spheres, rods and discs), mechanical robustness and non-toxic nature (Delaney et al. 2011). Ou et al. (2007) reported that La doped OMS had much higher phosphate removal capacity (> 90%) than undoped OMS (~ 4%) in a solution containing 0.992 mg P/L at pH 7.3 even though undoped OMS had higher surface area than doped OMS.. The study indicated that the lower the molar ratio of Si to La (ratios tested were 5, 10, 20, 30) the greater was the phosphate removal capacity. The Langmuir maximum sorption capacity for a molar ratio of 10 was 23.1 mg P/g. Delaney et al. (2011) also showed that undoped OMS had little or no affinity for phosphate, however when Zr, Ti, Fe or Al oxide was grafted to the surface it proved to be an efficient sorbent with removal percentages of up to 100%. The maximum sorption capacity was found to be 1.5 mg P/g.

Phosphate removal from water was studied using a La doped vesuvianite by Li et al. (2009). Vesuvianite, which consists of feldspar, pyroxene and other minor mineral components, has a low density (< 800 kg/m^3), which makes it float on water. Therefore, it can be easily recycled. Lanthanum doping at a ratio of 1:1 La to vesuvianite had a sorption capacity of 1.3 mg P/g after a contact time of 50 h with phosphate compared to 0.3 mg P/g for undoped vesuvianite. A maximum sorption capacity of 6.7 mg P/g was obtained for the doped vesuvianite.

Ultra-low P concentrations in the effluents of wastewater plants may be required in some circumstances in the future that cannot be economically achieved by conventional treatment methods such as chemical precipitation. A highly porous sorbent bead (average diameter 0.55 mm, porosity 85%) was manufactured in Japan from a mixture of a metal oxide and a polymer (MOP) and tested for P removal from wastewaters to produce very low P concentrations in the effluents (Omori et al. 2007; Midorikawa et al. 2008; Fitzpatrick et al. 2011; Tsuji et al. 2011). The exterior surface of the sorbent was reported to have a multitude of submicron pores while the interior had cavities opened to the surface. However, the chemical composition of the sorbent was not reported. A column packed with MOP had a breakthrough capacity of 12 mg P/g at a flow rate of 20 space volume (bed volume)/h, and consistently removed P from a synthetic P solution containing 1.0 or 3.1 mg P/L to produce effluent P concentration below the detection limit of 0.02 mg P/L (Omori et al. 2007). When municipal wastewater was first passed through a sand filter, and then through MOP the breakthrough sorption capacity was 8.4 mg P/g. Competitive sorption of the coexisting anions, which were present at much higher concentrations than phosphate probably diminished phosphate sorption, although the selectivity for phosphate sorption was 100 times greater than for sulphate and > 1000 times greater than for chloride and nitrate.

Midorikawa et al. (2008) extended the study of Omori et al. (2007) to field trials where a wastewater secondary effluent containing 0.1-2.1 mg P/L, previously filtered through an activated carbon column, was passed through two columns in series containing MOP. After the breakthrough from the first MOP column to reach an effluent P concentration 0.05 mg P/L the second column was used as the new first column instead, and a fresh column was used as new second column. While the P removal process continued with the new pair of columns the old column was regenerated by washing with NaOH to desorb the sorbed P and kept ready for later use. With this arrangement of columns the P concentration in the treated water was maintained at 0.02-0.04 mg/L for 8 days of treatment. This system of P removal from wastewater was tested in pilot plants in Japan and USA with two columns in series with a third column on standby, all containing MOP (Fitzpatrick et al. 2011; Tsuji et al. 2011). To avoid fouling of the sorbent media with solids and excessive backwashing of the media columns, a sand filtration step was introduced before the MOP columns. For 33 days of treatment at a space velocity of 20/h, the P concentration of the pilot plant effluent remained at 0.023-0.059 mg P/L, while the P concentration in the sand filter effluent was 0.10-3.7 mg P/L. With an introduction of a microfiltration system as a pre-treatment step the P concentration in the effluent was further reduced to 0.006-0.027 mg P/L.

Very low P concentration (< 0.03 mg P/L) in the effluent of wastewater containing 1.84 and 6.9 mg P/L after treatment with a sorption filter media was also reported in Ireland by Clean Water Technology Ltd (2010). However, the chemical characteristics of the sorbent were not reported. After 53 hours of operation using 179 kg of filter media, an ultimate breakthrough exceeding 0.03 mg P/L occurred when over 72 m^3 water passed through the filter media. The breakthrough sorption capacity was 1.8 mg P/g, and this value was reported to be higher than those of gravel, bottom ash, steel slag, blast furnace ash, fly ash, shale, laterite, and zeolite. However, many sorbents reported in Tables 2-5 had higher sorption capacity than that of the sorbent of Clean Water Technology Ltd (2010).

4.1.2. Calcium and magnesium carbonates and hydroxides

Calcium and magnesium carbonates and hydroxides have been used to remove phosphate from water. The mechanisms of removal are generally considered to be sorption followed by precipitation of Ca and Mg phosphates. Calcium and magnesium carbonates and hydroxides partially dissolve in aqueous solutions releasing Ca and Mg cations which combine with phosphate and form Ca and Mg hydroxyl phosphates. Their dissolution causes an increase in pH (Johansson 1999b; Hussain et al. 2011; Roques et al. 1991), which helps in the precipitation. Johansson (1999b) found that at low phosphate concentrations (< 15 mg P/L) only 40-50% phosphate was removed by limestone ($CaCO_3$) probably by the sorption process. Elevating the phosphate concentration above 15 mg P/L progressively increased the phosphate removal to 90% at 25 mg P/L. Precipitation explained the higher phosphate removal at the higher phosphate concentration. However, the maximum phosphate sorption at this particular concentration was only 0.3 mg P/g. The low phosphate sorption capacity was explained as due to the coarse particle sizes of limestone used in the study (median diameter 0.9 mm, < 5% of particles < 0.074 mm).

Roques et al. (1991) investigated the removal of phosphate from synthetic wastewater using dolomite ($Ca,Mg(CO_3)_2$) burned at 650-750°C to produce a material containing equal moles of MgO and $CaCO_3$, and mean particle size of 0.5 mm. The maximum phosphate sorption capacity of this material was found to be 10 mg P/g. In a column experiment the effluent solution initially had pH greater than 10, but with time, the pH stabilised between 8 and 9. Formation of a non-stochiometric calcium phosphate on the surface of the grains, probably an amorphous type, was suggested as the main mechanism for the removal of phosphate. Since the pH of the effluent solution after treatment with calcium and magnesium carbonates and hydroxides sorbents is generally alkaline, these sorbents have the potential to remove phosphate from acidic wastewaters (mining wastewater, acidic leachates from wet chemical P-recovery process).

Removal of phosphate from water by surface precipitation inside macropores of coal was noted in a study using a composite sorbent containing bentonite, coal and $Ca(OH)_2$ (Khadhraoui et al. 2002). Bentonite in the sorbent acted as a carrier and coal provided macropores for phosphate precipitation. The function of $Ca(OH)_2$ was to chemically react with phosphate to form the precipitate. Phosphate removal increased with Ca content of the sorbent. X-ray diffraction data revealed that the precipitate was crystalline hydroxyapatite.

A novel method of removal of phosphate and many other oxyanions from synthetic wastewater via carbonation of $Ca(OH)_2$ was proposed by Montes-Hernandez et al. (2009). They analysed the removal of oxyanions from an aqueous solution of $Ca(OH)_2$ by carbonation under moderate pressure (carbon dioxide pressure of 20 bar) and temperature ($30^{o}C$) and demonstrated that this process successfully removed approximately 100% of phosphate. Techniques using transmission and scanning electron microscopy equipped with energy dispersive X-ray analyser were applied to show that phosphate was incorporated into the structure of calcite formed during the carbonation process by substitution of carbonate ions by phosphate. It was stated that the proposed carbonation process could be an economic and ecological method for removing phosphate from waters, if the $Ca(OH)_2$ source derived from alkaline waste such as fly ash, waste concrete and cement, alkaline paper mill waste, etc.

4.1.3. Layered double hydroxides

Most of the clay minerals, such as kaolinite, mica, montmorillonite, vermiculite and zeolite, carry predominantly negative charges and therefore adsorb very little amounts of anions. During the last two to three decades, another type of clay mineral having positive charges and therefore able to adsorb anions, has received much attention in the removal of anionic contaminants such as oxyanions (e.g. arsenite, arsenate, chromate, phosphate, selenite, selenate, nitrate, etc.) and monoatomic anions (e.g. fluoride, chloride) from aqueous solutions (Goh et al. 2008). This type of clay, called layered double hydroxide (LDH) or hydrotalcite (HTlc), occurs naturally and has been synthesised in the laboratory. Structurally, LDHs are composed of positively charged brucite-like sheets with intercalated anions in the hydrated interlayer regions to balance the positive charges (Goh et al. 2008; Zhou et al. 2011;

Khan and O'Hare 2002). Isomorphous substitution of trivalent or tetravalent cations for Mg^{2+} in the brucite-like layer produces the positive charges. Charges can also be produced by the ionisation of the surface OH groups in LDHs. The ZPC of LDHs is in the region pH 9-12 (Goh et al. 2008) and therefore at the neutral pH of natural water, LDHs are positively charged and act as anion exchangers.

There are four mechanisms for removing anions by LDHs, namely, surface sorption, interlayer anion exchange, surface precipitation and reconstruction of calcined LDH precursors by the 'memory effect' (Cheng et al. 2010; Goh et al. 2008; Koilraj and Kannan 2010; Zhou et al. 2011). When LDHs are calcined at high temperatures they lose their layer structure and form active composite metal oxides which when placed in aqueous solution reconstruct its original structure with rehydration and sorption of anions. This process is known as the 'memory effect'.

The type of cations in the brucite-like sheets of LDHs has a significant effect on phosphate sorption. Zhou et al. (2011) compared the ability of Mg_2Fe-Cl-LDH and Ca_2Fe-Cl-LDH to remove tripolyphosphate (TPP) from water. They found that the Mg form of LDH removed 10.5 mg P/g corresponding to 10-15% of the theoretical anion exchange capacity (67 mg P/g) estimated on the basis of the amount of Cl ions in the interlayer space. In contrast, the Ca form removed a higher amount of 56.4 mg P/g. It was also found that the Ca-LDH was unstable in water losing its LDH structure and became amorphous with release of Ca whereas the Mg-LDH was stable in water maintaining its LDH structure. The removal of TPP by the Mg-LDH was considered to be through surface sorption and the near-edge intercalation. The large size TPP could not penetrate into the interlayer space to exchange with all the Cl ions. A comprehensive analysis of the Ca-LDH with and without TPP using XRD/XPS/FTIR revealed that Ca-LDH dissolved first releasing Ca^{2+} which reacted with TPP to form insoluble Ca-TPP precipitate. Based on the information obtained from the two LDHs, a Ca and Mg combined LDH (Mg-Ca-LDH) was produced which removed large amounts of TPP (84.2 mg P/g).

Similar results were obtained by Xu et al. (2010a) for the removal of orthophosphate from water by Ca and Mg forms of LDH. They found that the Ca-based LDHs were more soluble than the Mg form. The dissolved Ca reacted with phosphate to form hydroxyapatite. Phosphate removal by Ca-LDH was higher at pH 5 than at pH 9 because of its higher dissolution at lower pH. Structural analysis by XRD revealed that phosphate sorption on Mg-LDH occurred by way of intercalation into the interlayer spaces while that over Ca-LDH occurred by means of precipitation.

Higher valency cations incorporated into the brucite-like layer of LDH can produce more positive charges in the interlayer for increased removal of phosphate. Koilraj and Kannan (2010) introduced Zr^{4+} into ZnAl-LDH and obtained a greater phosphate removal from aqueous solutions in a batch study. They found that in addition to the increased sorption on the positive charges in the interlayer, another major mechanism improved the removal of phosphates. Using XRD, SEM, and FTIR it was demonstrated that the increased sorption of phosphate resulted from the formation of a zinc phosphate mineral on the surface of the sorbent by surface precipitation of dissolved Zn with phosphate sorbed as an outer-sphere complex on the LDH. The presence of Zr^{4+} was considered to produce instability in the LDH structure thus caused the release of Zn.

Chitrakar et al. (2010) synthesised a Zr-modified MgFe-LDH(CO_3) from a mixed solution of Cl salts of Zr, Mg, and Fe and compared the phosphate removal efficiencies from pure phosphate solution and P-enriched sea water with those of MgFe-LDH(CO_3), ZrO, and other materials. XRD, FTIR and elemental analysis showed that the synthesised material was a nanocomposite of MgFe-LDH and amorphous $Zr(OH)_4$. Sorption data showed that this material had the highest selectivity for phosphate removal from P-enriched sea water and pure phosphate solution at pH 4. The maximum removal capacities from pure phosphate solution (pH 3-4) (80 mg P/g) and sea water (20 mg P/g) were higher for this material compared to those for eight other commonly used sorbents. The presence of $Zr(OH)_4$ particles on LDH sheets of this material was considered to be the reason for this high phosphate sorption capacity.

LDHs are calcined to increase their anion sorptive capacity. The increased sorption capacity of calcined LDHs is attributed to an increased surface area (calcined LDHs 198-287 m^2/g compared to 5-84 m^2/g for uncalcined LDHs, Goh et al. 2008) and the structural ‘memory effect’. Peleka and Deliyanni (2009) found that increase of calcination temperature up to 500^oC increased phosphate sorption capacity of the LDH. Maximum sorption capacities of 245 and 193 mg P/g were obtained for LDH calcined at 500 and 400^oC, respectively. The uncalcined LDH had a maximum sorption capacity of 60 mg P/g. Cheng et al. (2010) also reported increase in phosphate sorption with calcination of Zn-LDH up to 300^oC, but the phosphate sorption decreased when the LDH was calcined at 600^oC. This was explained as being due to the ‘memory effect’ operating at 300^oC, whereas the calcined product formed at 600^oC was unable to recover the original LDH structure by incorporating phosphate ions. Instead, a spinal $ZnAl_2O_4$ was formed.

4.2. Organic sorbents

The efficiencies of removal of phosphate by various organic sorbents, the methods used, and the kinetic and equilibrium models best explained the sorption data are presented in Table 3.

4.2.1. Activated carbon

Activated carbon (AC) is an effective sorbent for the removal of a wide range of aquatic pollutants. It is commonly used as an sorbent in the treatment of wastewaters due to its exceptionally high surface area (500-1500 m^2/g), highly developed internal microporosity, presence of a range of functional groups, low cost, and easy availability (Chingombe et al. 2005; Yin et al. 2007).

Activated C is prepared from a wide range of materials such as shells, hulls and cobs of plant produces, coal, lignite, and wood (Pollard et al. 1992) using one of two basic activation methods (Gupta et al. 2009). The first method is carbonization at 600-900^{o}C in an inert atmosphere resulting in the formation of char that is normally non-porous, followed by calcining at 600-1200^{o}C in oxidising environment to produce porous material with high surface area. The second method is impregnation with chemicals followed by heating to 450-900^{o}C. Activated C used in water treatment is available in two main forms, namely, powdered AC (PAC) and granular AC (GAC). Use of GAC is usually preferred because it can be easily separated from water after use.

The main functional groups on the AC surface are phenolic (hydroxylic), carbonyl, carboxylic, ether, and lactones (Chubar 2010; Faust and Aly 1987). The type and number of functional groups on AC matrix can be manipulated by thermal and chemical treatments to produce sorbents that are tailored for a particular function (Chingombe et al. 2005). The functional groups have negative or positive charges depending on the pH of the solution where the AC is exposed to. Faust and Aly (1987) reported a ZPC range of 4.75 to 7.10 for five types of AC whereas Mahmudov and Huang (2011) found that the ZPC of GAC made from bituminous coal was 7.9. At pHs less than the ZPC, AC carries predominantly positive charges and at pH above the ZPC, it carries predominantly negative charges.

Ma et al. (2011) obtained a Langmuir maximum sorption capacity of 0.4 mg P/g for GAC compared to 0.003, 0.04, and 2.6 mg P/g for perlite, zeolite, and a composite adsorbent containing perlite and activated alumina (perlite/Al), respectively for phosphate sorption from a solution containing KH_2PO_4 in a batch study. The sorption capacities determined from a column experiment were < 0.004, 0.11, and 0.25 mg P/g for zeolite, GAC, and perlite/Al, respectively. Despite GAC having a much higher specific surface area of 863 m^2/g than for perlite/Al (28.8 m^2/g) the sorption capacity was lower because of the non-specific nature of sorption of phosphate on GAC compared to a predominantly specific type of sorption on Al oxides in the perlite/Al composite material.

Sorption capacity of AC can be increased by impregnating AC with suitable chemicals (Yin et al. 2007). Shi et al. (2011) prepared a composite sorbent by loading iron oxide onto GAC (15.05 mg Fe/g) and compared the sorption capacity of this material with that of unamended AC in a batch experiment using NaH_2PO_4 solution at pH 3. They found that the Langmuir sorption capacity of the composite material (3.2 mg P/g) was higher than that of AC (2.5 mg P/g), despite the specific surface area being lower for the composite sorbent (668 m^2/g for composite material compared to 1039 m^2/g for AC). Phosphate sorption on the composite sorbent decreased drastically with increasing pH, from pH 2 to 5 and levelled off when the pH was over 6. The decrease in sorption with increase in pH was considered to be due to a reduction in the positive charges on the surface of the sorbent and increased competition for adsorption from hydroxyl ions at high pH. Namasivayam and Sangeetha (2004) obtained a different trend for the pH effect on phosphate sorption on a Zn-doped AC prepared by carbonisation of coir pith at 700^{o}C in a batch study. They showed that phosphate sorption remained constant between pH 2 and 11 but decreased below 2 and above

11. They explained the reduction in sorption below 2 as a result of phosphate present as uncharged H_3PO_4, and reduction above 10 as due to OH^- competition with PO_4^{3-} species for sorption on a highly negatively charged sorbent surface.

Zhang et al. (2011) loaded AC fibres (specific surface area 1326 m^2/g) with different doses of La oxide and investigated their phosphate sorption capacities in batch experiments. They found that phosphate sorption from a KH_2PO_4 solution containing 30 mg P/L and sorbent concentration of 5 g/L increased from 79.9% to 96.0% with increasing La loading rate from 5 to 15% and the amount sorbed remained constant thereafter up to 25%. The maximum sorption capacity was 5.85 mg P/g. The inability of the La loaded AC fibres to remove phosphate beyond 15% La was considered to be because the AC fibres had a fixed amount of sites for reaction with La and they could not react with the excess dosage of La to produce further sorption of phosphate. The pH at the initial stages of sorption increased sharply with a rapid increase in phosphate removal and this was explained as due to ligand exchange between phosphate in solution and OH groups on the sorbent surface.

4.2.2. Anion exchange resins

Ion exchange resins are an important class of ion exchangers used to remove cationic and anionic pollutants from water and wastewater. Their framework or matrix consists of irregular, macromolecular, three dimensional network of hydrocarbon chain (Helferich 1995). The cation exchange resins have negatively charged functional groups whereas the anion exchange resins have positively charged functional groups such as $-NH_3^+$, $=NH_2^+$, $\equiv N^+$, $\equiv S^+$. The matrix of the resin is generally cross-linked poly (styrene) exhibiting hydrophobicity (Awual et al. 2008; Helferich 1995). Therefore the resins prefer less hydrated anions such as NO_3^-, SO_4^{2-} to highly hydrated anions like $H_2PO_4^-$.

Recently, it has been shown that a type of anion exchange resin called Purolite A500P consisting of $R(CH_3)_3N^+$ functional group removed more than 80% nitrate and phosphate from a wastewater containing 3.1 mg P/L of phosphate and 11 mg N/L of nitrate whereas another anion exchange resin called Purolite A520E consisting of quarternary ammonium group removed nearly 90% of nitrate but only 30-40% of phosphate (Johir et al. 2011). Das Gupta et al. (2012) also found that Purolite A500P with Langmuir sorption capacities of 64 mg N/g and 7 mg P/g removed a higher percentage of nitrate than phosphate from synthetic water and wastewater in batch and column studies. Because the resin was not able to effectively remove phosphate, they used hydrated ferric oxide (HFO) adsorbent to remove the phosphate in the effluent from the resin. Similarly, Blaney et al. (2007) used a hybrid anion exchange media called HAIX containing a mixture of an anion exchange resin beads and HFO to remove phosphate and other anions from water.

Because the conventional anion exchange resins with hydrophobic character were not effective in removing phosphate from water, recently, Awual et al. (2011) produced a novel fibrous anion exchanger named FVA containing aliphatic cross-linked polymer matrices having primary amino groups which showed hydrophilic character to effectively remove phosphate. Using a batch study, they found that this resin had a high sorption capacity and selectivity for phosphate at pH 2.0-8.3 (74 to 216 mg P/g) in the presence of chloride, nitrate and sulphate. Using data from a kinetic study and FTIR spectra, they proposed that the mechanisms of sorption of phosphate to the resin were ion exchange and H-bonding.

4.2.3. Other organic compounds

There are many other organic compounds with functional groups that can sorb phosphate. Their sorptive characteristics can be further improved by surface modification through grafting specialised organic molecules and metals. For example, Anirudhan and Senan (2011) used cellulose and its derivatives to efficiently remove phosphate from water. They grafted iron coordinated amino-functionalised polymers on to cellulose and studied the structure, porosity, anion exchange capacity and phosphate sorptive capacities of cellulose (cell), amine polymer grafted cellulose (amine-cell) and iron (Fe) coordinated amine product (Fe-amine cell). The anion exchange capacity of the cell was found to be 0.71 meq/g and that of the Fe-amine cell was 1.28 meq/g. XRD and SEM data showed that the structure of amine-cell was more porous and less crystalline than the cell while that of the Fe-amine cell was even more porous and amorphous with many cavities for enhanced sorption of phosphate. The maximum sorption capacity as determined by the Sips equation was 23 mg P/g for the Fe- amine cell which was higher than the value of 13 mg P/g obtained for the anion exchange resin Dowex.

Benyoucef and Amrani (2011) prepared a chemically modified Aleppo pine saw dust containing lignocellulosic materials by acid prehydrolysis and urea addition and showed that this material had more pores and higher phosphate adsorptive capacity than the unmodified material. The sorption capacity did not change much between pH 3 and 10. A maximum phosphate sorption capacity of 23 mg P/g was found at pH 7.5.

In the last two to three decades a new class of porous materials called mesostructural materials was developed for use as sorbents in separation techniques. Surface functionalization of these materials via the tethering of organic functional groups has attracted much attention because it allows one to introduce several functionalizations onto the internal pore structure through post-synthesis grafting and co-condensation (Schumacher et al. 1999). Hamoudi et al. (2007) produced an ammonium functionalized mesoporous silica compound called MCM-48 and tested its effectiveness in removing nitrate and phosphate from aqueous solutions. Mesoporous silica functionalized with amine groups designed for the removal of metallic cations were converted into positively charged ammonium groups for the sorptive removal of anions. The material was shown to have a maximum sorptive capacity of 0.7 mmole/g for nitrate and 0.5 mmole/g (15.5 mg P/g) for phosphate at 5^0C. These values suggested that only 45% of the grafted functionalized groups were involved in the sorption process.

Materials with transitional metal organic complexes bound to the pore walls inside mesoporous silica have also been tested for the removal of phosphate. Chouyyok et al. (2010) compared the effectiveness of phosphate removal by Cu and Fe ethylene diamine complexes anchored inside mesoporous silica compounds in batch studies. Based on the distribution coefficients (mass-weighted partition coefficient between solid and solution phases of the phosphate concentration) Chouyyok et al. (2010) found that the Fe-based sorbent had higher sorption capacity than the Cu-based sorbent. The Langmuir sorption capacity of phosphate on Fe-based adsorbent was 15 mg P/g. In the presence of 1000-fold molar excess of Cl^- and NO_3^- the phosphate removal by the sorbent was not affected.

Carboxylic acid coated alumina (Saha et al. 2009) and surfactant coated nano crystalline iron oxide (akaganéite, β-FeO(OH)) (Deliyanni et al. 2007) were tested for their effectiveness in removing phosphate by sorption. Though the carboxylic acid coated alumina had low phosphate sorption capacity (1.7 mg P/g) it was highly selective in removing phosphate in the presence of Cl^- , Br^- and NO_3^-. It emerged that the phosphate sorption capacities of akaganéite (ak) and the surfactant modified akaganéite (ak_s) were extremely high (60 and 451 mg P/g for ak and ak_s, respectively). Based on FTIR data the sorption mechanism on both these materials was considered to be inner sphere complexation of phosphate with FeOH groups. The high sorption capacities were reported to be due to the high surface area of the nanosized materials. The negatively charged surfaces created by the inner sphere complexation process were neutralised by the positively charged surfactant, thereby facilitating further sorption of phosphate, hence the higher sorption capacity of ak_s.

Phosphate sorption by organic compounds is discussed in a later section on biological wastes.

4.3. Industrial by-products

The efficiencies of removing phosphate by various industrial by-products, the methods used, and the kinetic and equilibrium models best explaining the sorption data are presented in Table 4.

Many industrial by-products are wastes that need to be disposed of. Any beneficial use of them can save disposal costs, prevent environmental pollution and release disposal lands for alternative and productive use. Several types of industrial by-products have been used for the sorptive removal of pollutants including phosphate from water (Bhatnagar and Sillanpàà 2011; Gupta et al. 2009; Mohan and Pittman Jr 2007; Pratt et al. 2007; Westholm 2006). Most of them are mining industry (e.g. red mud), steel industry (e.g. slag materials), and power plant industry (e.g. fly ash and bottom ash) by-products. The methods and efficiency of removing phosphate depend on the chemical and physical characteristics of these by-products. In general they are composed mainly of oxides, hydroxides and/or carbonates of Si, Al, Fe, Ca, Mg and Ti in different proportions. Therefore the predominant mechanisms of phosphate removal are ligand exchange and solution and surface precipitation as discussed for these metal oxides, hydroxides and carbonates in section 4.1. The phosphate removal capacities of each of these by-products, however, varied between studies because of the variation in the composition of the by-products used and the differences in the experimental methodology (Table 2). Utilising these by-products has the additional advantage of simultaneously removing other pollutants such as heavy metals from water as they have strong sorptive capacity for these pollutants as well.

4.3.1. Red mud

Red mud is the finely grained waste residue produced after the caustic digestion of bauxite ores during the production of alumina. Red mud is a highly alkaline waste material with a pH 10-13 because of the residual sodium hydroxide solution employed in the refining of alumina (Bhatnagar et al. 2011). The high alkalinity can be neutralised by sea water to reduce the pH to around 9. The resulting product is called Bauxsol and the pH can be further reduced by acid treatment. Akhurst et al. (2006) found that phosphate removal efficiency of these materials increased in the order, red mud < Bauxsol < acid treated red mud. The optimum phosphate removal was achieved at a pH of around 5.2. They postulated that a combination of ligand exchange (inner sphere complex formation), together with surface precipitation by the abundant Fe, Al, Ca, and Mg compounds were the likely phosphate removal mechanisms.

In reviewing the studies on the use of red mud as an sorbent for phosphate, Wang et al. (2008) and Bhatnagar et al. (2011) reported that red mud generally exhibits low sorption but activation by acid treatment or heat treatment can improve the sorptive capacity. For example, Li et al. (2006) studied the phosphate sorptive capacities of red mud acidified with different concentrations of HCl (0.001-2 mole/L) and heating temperatures varying from 200 to 1000^{o}C. They found that the sorptive capacity was highest with 0.25 mole/L HCl and 700^{o}C heating treatments. The increase of sorption with increase of acidity up to 0.25 mole/L and temperature up to 700°C was explained as due to increase surface area and porosity. Acid treatment also reduces the pH of solution which is known to increase phosphate sorption. But at very high acid concentration and temperature, phosphate removal decreased due to dissolution/decomposition of certain phosphate sorbing minerals in red mud.

Because red mud is finely divided, it needs to be granulated for column techniques. Red mud granular sorbents have been produced by mixing red mud with starch and bentonite at different ratios and sintering temperatures. These will determine the best conditions needed for producing granular materials that have good phosphate removal capacities (Yue et al. 2010b).

4.3.2. Slags

Most studies on steel industry by-products like blast furnace slag, electric arc furnace slag, basic oxygen furnace slag and converter slag have shown that these materials are highly promising for removing phosphates from water (Bowden et al. 2009; Westholm 2006; Xue et al. 2009). This ability is due to the presence of oxides of Ca, Fe, Al, Mg, and Mn.

Studies have found big differences in phosphate removal capacities of slag materials because the methods used differed, and furthermore the slag materials’ chemical and physical characteristics varied. For example, Johansson (1999b) reported that phosphate sorption capacity decreased following the order, coarse crystalline blast furnace slag (BFS), fine crystalline BFS, amorphous fine BFS, and amorphous coarse BFS. This was explained by the difference were suggested to be a difference in surface area and surface structure resulting in different amounts of reactive calcium. Bowden et al. (2009) reported that basic oxygen furnace slag (BOFS) had higher phosphate removal capacity than many other steel slags because of a higher Ca content (42-44% CaO) and free lime content (4-6%). XRD, E-SEM, and EDX data showed that at low phosphate concentrations the mechanism of phosphate sorption was chemisorption (inner-sphere complexation) but at high phosphate concentration the mechanism was surface precipitation of several calcium phosphate compounds. Similarly, Xue et al. (2009) reported that the phosphate sorption capacity of BOFS was higher than that of BFS. Their study also showed that BOFS modified by milling and acid treatment had higher phosphate sorption capacity than the unmodified BOFS. This was due to the increase in surface area and porosity caused by these treatments and the acid treatment reducing the negative charges on the sorbent surface thus favouring sorption of anions like phosphate.

Gong et al. (2009) showed that the sorption capacity of BFS can be improved by surface modification with hydrated lime. They investigated phosphate sorption on different weight ratios of BFS and hydrated lime, finding that combining these two materials had higher sorption capacity than BFS or hydrated lime alone. Improved pore structure with higher surface area of the combined BFS and hydrated lime material provided more sorption sites for phosphate to produce surface precipitation of Al, Ca, and Fe phosphates.

Titanium/Al rich metal slags produced as a by-product from steel mills have been used with 54-84% efficiency of removing P from farm effluent treatment ponds (Miller 2005). Pratt et al. (2007) investigated the mechanisms of P removal by these slags in order to understand the large variation in P removal efficiency. The following mechanisms for P removal were suggested: (1) P sorption onto metal oxides/oxy-hydroxides, which are ubiquitous throughout the porous slag matrix and its surface film; (2) P precipitation, mainly as Fe-phosphates (determined by SEM/EDS) on the surface film, derived from the release of metal ions into the solution phase; and (3) P sequestration by an amorphous organic resin consisting of a substantial proportion of the surface film, which was deduced by SEM/EDS and XRF.

4.3.3. Fly ash

Fly ash is a major by-product that is produced from the combustion of coal in power stations. It consists of fine and powdery materials (1-100 μm) made up of a mixture of amorphous and crystalline aluminosilicates and several compounds of Si, Al, Fe, Ca, and Mg, (Yunusa et al. 2012) and therefore a good candidate material for phosphate removal from water. The process of sorption and precipitation is the main mechanism for using fly ash to remove phosphate. Ugurlu and Salman (1998) reported that phosphate removal in excess of 99% from a synthetic phosphate solution was achieved using fly ash from Turkey; it contained CaO as the major chemical component (33.8% CaO). They explained this high percentage removal as due to the precipitation of phosphate with Ca dissolved from the fly ash. Hydroxyapatite formation was identified by XRD in fly ash after phosphate removal. However, Oguz (2005) considered that both precipitation and sorption were involved in the removal of phosphate by fly ash containing a medium level of Ca (11.6% CaO).

Lu et al. (2009) studied the mechanisms of phosphate sorption and precipitation separately using acid treatment of three alkaline fly ashes containing predominantly Al and Si oxides and low content of CaO. They compared phosphate removal of treated and untreated fly ashes. Phosphate removal was considerably lower for the acid treated fly ash compared to the untreated fly ash. Because acid treatment reduced the Ca content and pH of the fly ash they assumed there could not be any precipitation of phosphate. Consequently the removal of phosphate involved sorption. They concluded that at pH < 6, phosphate removal was controlled more by sorption and at pH > 8, precipitation predominated. For untreated fly ash, phosphate removal was accompanied by a decrease in Ca concentration and pH in solution, which suggested precipitation of calcium phosphate. They presented XRD data to show that many calcium phosphate minerals were formed on fly ash samples after phosphate removal.

Activation of fly ash containing low content of Ca (2.1-2.7% CaO) by heating (up to 700°C) and acid treatment (0.25 mole/L HCl) was shown to increase phosphate removal (Li et al. 2006). This was due to an increase in surface area or porosity. At temperatures above 700°C and acid strength greater than 0.25 mole/L, phosphate removal declined because of dissolution or decomposition of calcite and other phosphate sorbing minerals. Although acidification increased the surface area of the samples, precipitation of phosphate with Ca is weakened due to the dissolution of calcite. Because the Ca content of the fly ash was low the precipitation mechanism's contribution to phosphate removal was lower than the adsorption mechanism in this fly ash when compared to the fly ash with high Ca content used by Lu et al. (2009).

Fly ash is broadly grouped into acid and alkaline types. The acid type generally has low Ca content (< 20% CaO) and classified as F type ash and the alkaline type has high Ca content (> 20% CaO) and classified as C type ash (Yunusa et al. 2012). Class F ashes are produced mainly from burning anthracite and bituminous coal and Class C ashes from burning lignite and subbituminous coal. Generally, C type ashes remove phosphate by a calcium phosphate precipitation mechanism and the removal efficiency increases with Ca content in the ash (Cheung and Venkitachalam 2000; Lu et al. 2009). Phosphate removal by F type ashes is attributed to sorption or formation of insoluble Al and Fe phosphates at the low to medium values of pH (Grubb et al. 2000).

4.3.4. Other by-products

Because iron oxides are known to have high phosphate sorption capacities, Zeng et al. (2004) conducted sorption studies on phosphate removal capacity of an iron oxide tailing material, an industrial waste derived from a mineral processing industry. They found that the maximum phosphate sorption capacity of the tailing material was 8 mg P/g at pH 3.5 and this decreased to 4.6 mg P/g at pH 9.5. These sorption capacities were reported to be fairly large when considering that the tailings contained only about 30% iron oxides (the majority consisted of magnetite mineral). Literature values for comparative sorption capacities at pH 3.5 for a series of amorphous and crystalline iron oxides were reported to range 5-30 mg P/g. Zeng et al. (2004) also stated that besides iron oxides, Al, Ca and other compounds in the tailing might have contributed to the phosphate removal. The ability to remove phosphate convincingly using the tailing in batch experiments was confirmed by column experiments.

Similar to iron oxide tailing, wollastonite tailing, a by-product from the mining of wollastonite mineral (calcium meta-silicate) was shown in column experiments to be as effective as wollastonite in removing phosphate from secondary wastewater containing an average reactive phosphate concentration of 3.4 mg P/L (Brooks et al. 2000). Greater than 80% removal of phosphate was reported in a majority of column tests and effluent concentration of 0.14-0.50 mg/L. Because the cost of tailings ($3/ton) was 100 times less than pure wollastonite ($308/ton), the tailing was considered to be economical in removing phosphate.

Iron containing humic materials such as iron humate (IH) by-product obtained during the precipitation of wastewaters from alkali humates manufacturing industry with iron salts is able to remove phosphate from water. Janoš et al. (2011) found that an IH material having approximately 11% Fe had a high phosphate sorption capacity of 3.4-11.5 mg P/g. The sorption process proved to be slow in reaching equilibrium (more than three days) and nearly independent of pH in a slightly acidic to neutral range. These results led them to suggest that in addition to the ligand exchange mechanism, other mechanisms such as co-precipitation and surface precipitation played a significant role in the sorption process.

4.4. Biological wastes

The efficiencies of removal of phosphate by various biological wastes, the methods used, and the kinetic and equilibrium models best explained the sorption data are presented in Table 5.

Biological wastes are mostly of agricultural origin and they are commonly used to improve the chemical, physical and biological properties of soils. They can also be used as low-cost sorbents to remove pollutants including phosphate from water. These wastes consist of useful cationic functional groups that have significant potential for sorption of phosphate as discussed earlier. Their sorption capacities can be improved by converting them into activated carbon or chemically modifying the structure of the material to increase the porosity or surface properties. For example, Xu et al. (2010b) produced a wheat straw anion exchanger (WSAE) by grafting compounds having amine groups onto washed and ground raw wheat straw and the product was tested for phosphate removal from water. The maximum sorption capacity of 45.7 mg P/g found for WSAE was higher than the capacities of many commercial anion exchange resins and activated carbon. The high value was due to the presence of abundant amine groups as shown by FTIR and NMR data and high positive zeta potential (-28.2 to +32.4 mV compared to -48.0 to +4.6 mV for unmodified wheat straw in the pH range 2-12).

Similarly, in a more recent study, Xu et al. (2011) determined the phosphate sorption properties of a new kind of sorbent by grafting amine groups onto washed, dried and ground giant reed, a well-known fibre crop cultivated widely in wetlands. The column sorption capacity for phosphate was found to be 55.7 mg/g in comparison with 0.9 mg/g for the raw giant reed material. FTIR spectrum indicated that phosphate was associated with the amine groups in the modified giant reed after sorption. The optimum pH of phosphate sorption was reported to be 5-10 in the pH range 2-12 tested. Yue et al. (2010a) also grafted organic compounds containing amine groups onto giant reeds to increase the phosphate sorptive capacity. The phosphate sorption capacity of 19.89 mg/g obtained for the grafted material was shown to be comparable to many other sorbents. The effective pH range for phosphate removal of 4-9 obtained in their study is consistent with the findings of Xu et al. (2011).

Marshall and Wartelle (2004) developed an anion exchange resin from soybean hulls consisting of lignocellulostic by chemical modification with an organic nitrogen compound and tested the resin for phosphate removal capacity. The positive charge density on the resin surface estimated from the moles of nitrogen added to soybean hulls was 0.71 mmole/g, and the phosphate sorption capacity at pH 7 determined from Langmuir sorption isotherm was 19.5 mg P/g. This sorption capacity was more than that of a commercial cellulose-based resin (14.3 mg P/g) but less than a commercial synthetic resin (Amberlite IRA-400, 32.2 mg P/g).

Increasing the pore volume of sorbents is another means of enhancing the sorptive capacity of materials. Benyoucef and Amrani (2011) reported increased removal of phosphate from a synthetic phosphate solution by a chemically modified saw dust of Aleppo pine (a fibre crop). The chemical modification by hexane-ethanol extraction followed by acid prehydrolysis and urea addition resulted in the development of more pores and increased number of functional groups than those in unmodified saw dust. These changes explained the increased phosphate removal by the chemically modified saw dust.

Iron rich organic wastes have been shown to have good phosphate removal capacities. Rentz et al. (2009) tested samples of biogenic iron oxides produced by iron oxidising bacteria in a freshwater wetland for their phosphate removal capacities. The samples contained 23-34% Fe/g solids and had pH 7.1-7.7. The maximum sorption capacities normalised to iron content (47-165 mg P/g Fe) and total solids (25-40 mg P/g solids) were higher than most of the values reported for iron-rich or iron oxides containing materials of non-biological origin.

Biochar production from organic materials and its application to soils is increasingly important because it can store carbon and reduce or suppress greenhouse gas production, including CO_2, CH_4 and N_2O (Kookana et al. 2011; Lehmann 2007). Biochar is also a good cost-effective sorbent for removing many pollutants, especially organic pollutants from water (Chen et al. 2008). Sorbents prepared by incorporating iron oxides into biochar can serve the twin purposes of removing organic pollutants and phosphate. Recently, Chen et al. (2011) produced such materials by co-precipitation of Fe^3+/Fe^{2+} on orange peel powder and subsequently pyrolysing at different temperatures (250, 400, 700°C) which resulted in magnetite (a form of iron oxide) formation and biochar preparation in one step. The materials indicated hybrid sorption capacities to effectively remove organic pollutants and phosphate simultaneously from water. Phosphate sorption capacity was reported to be lowest at 400°C and highest at 700°C. This was due to the presence of more iron oxides content on the surface of the material produced at 250°C rather than at 400°C, because the higher temperature was more likely to leave the iron oxide encased by the residue of the pyrolysed biomass. At the highest temperature of 700°C there was no biochar remaining and the material was composed only of iron oxide, therefore the phosphate sorption capacity was highest but organic pollutant removal was very low.

Oyster shells (OS) produced as a waste in many shellfish farms have high phosphate removal capacity due to the presence of large amounts of $CaCO_3$ (93-96%, Lee et al. 2009; Park and Polprasert 2008) and high pH (11-12, Lee et al. 2009) when added to water. These conditions favour the precipitation of phosphate as calcium phosphate. Park and Polprasert

(2008) used OS as sorptive media in constructed wetland to remove phosphate from wastewater and found that the removal efficiency during 240 days of operation was 95%, of which 88% was removed by sorption/precipitation and the remaining 7% by plant uptake.

Calcium in OS is present mainly in the form of $CaCO_3$, which is considered to be non-reactive in the short term. Lee et al. (2009) activated the OS by pyrolysis at 750^{o}C to convert $CaCO_3$ in OS into reactive CaO. Using activated OS, they obtained a phosphate removal capacity of 98% from water. They proposed that the key mechanism of phosphate removal was precipitation of phosphate as calcium phosphate, also stating that sorption mechanism did not play a significant role in phosphate removal. This is because when the OS/phosphate suspension was acidified to pH 4.0, less than 4% of the original phosphate was removed. Another advantage of using OS for removing phosphate was reported to be the granular nature of the activated OS which makes it much easier to handle than lime and other powdery sorbents. Yu et al. (2010) heated OS at 700-900^{o}C in the presence of fumed silica and converted $CaCO_3$ in OS into hydrated calcium silicate. This material removed 92% of phosphate from water in 4 hours. The removal occurred due to the phosphate in water reacting with hydrated calcium silicate to form hydroxyapatite precipitate.

5. Sorption thermodynamics

The measures of the strength and spontaneous nature of sorption and whether the sorption process is exothermic or endothermic can be proven by determining thermodynamic parameters such as changes in Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0). These thermodynamic parameters are calculated using the equations,

$$\Delta G^0 = -RT \ln K_d$$

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT$$

where R is the gas constant, T is the absolute temperature, and K_d is the distribution coefficient for the sorption (ratio of the phosphate concentrations on sorbent (mmol/g) and aqueous phase (mmol/mL)). Negative values for ΔG^0 and ΔH^0 indicate spontaneous and exothermic sorption process, respectively. Exothermic reaction means that amount of sorption decreases as temperature increases. Endothermic reaction (positive ΔH^0 value) results from the enlargement of pore sizes and/or activation of the sorbent surface (Masue et al. 2007; Yan et al. 2010). Very low ΔH^0 values are generally associated with physical sorption and very high values with chemical sorption (Faust and Aly 1989). No definite value for distinguishing the two forms of sorption exists. Paleka and Deliyanni (2009) reported ΔH^0 values of -212.2 kJ/mole for goethite and -48.7 kJ/mole for Al oxide. Since these values are higher than the range of ΔH^0 values (8.4–41.8 kJ/mol) for physical sorption, phosphate's sorption mechanism on both goethite and Al oxide was considered to be chemical, probably resulting from ligand exchange.

Positive ΔS^0 values indicate phosphate's good affinity to sorbent and increased randomness at the solid-solution interface associated with structural changes at the sorption sites (Anirudhan and Senan 2011; Benyoucef and Amrani 2011; Faust and Aly 1987; Mezenner and Bensmaili 2009; Yue et al. 2010a).

All studies reported in Table 6 had negative ΔG^0 values indicating good affinity of phosphate for the sorbent and the sorption process was spontaneous. The majority of ΔH^0 values were also negative indicating the exothermic nature of sorption. The ΔS^0 values were mostly positive, again indicating a strong affinity of phosphate towards the sorbents.

6. Phosphate desorption and sorbent regeneration

A suitable sorbent for phosphate removal should not only have high phosphate sorption capacity and cost-effectiveness but should also be amenable to easy desorption of the sorbed phosphate and able to efficiently regenerate and reuse it for a long time. Desorption of phosphate is done by leaching of sorbed phosphate using acids, bases and salts (Table 7).

Simple low-cost salts such as NaCl and KCl have proved to be successful in desorbing phosphate only from sorbents with weak sorption strength where the sorption mechanism is non-specific (ion exchange or outer sphere complexation) (Johir et al. 2011; Xu et al. 2010; Xu et al. 2011). Generally a high concentration of these salts is used for efficient desorption (e.g. 3 and 5 M NaCl, Park et al. 2010) and this can lead to problems if the phosphate in the desorbed solution is to be recovered or used for fertilising and irrigating crops due to the risk of high salinity (Johir et al. 2011). Simple salts are found to be ineffective in desorbing phosphate from sorbents that strongly adsorb phosphate by specific sorption mechanisms (ligand exchange or inner sphere complexation) (Cheng et al. 2009; Zeng et al. 2004).

Acids and bases have been successfully used in removing both specific and non-specific sorbed phosphate (Table 7). This is because phosphate sorption decreases at pH below 3-4 and above 8-10 (Urano et al. 1992a). The reason for the reduction of phosphate sorption below pH 3-4 is that at low pH, phosphate is predominantly present as the un-ionised H_3PO_4 species that has very low sorption capacity. At pH > 8-10, both the sorbent and phosphate species in solution are highly negatively charged (HPO_4^{2-}, PO_4^{3-}), providing an unfavourable condition for sorption to the negatively charged sorbent. Furthermore, the increased number of OH^- ions present at high pH values competes with phosphate for sorption, thereby decreasing phosphate sorption. If the mechanism of phosphate removal at high pH is precipitation, which occurs with Ca, Mg carbonates, phosphate may not be successfully desorbed by bases providing a high pH environment. High concentrations of acids and bases are not suitable for certain sorbents (oxides of Si, Fe, and Al; LDH; carbonates of Ca and Mg) because they can dissolve or corrode parts of the sorbents or cause structural changes, leading to problems in regeneration and reuse of the sorbents (Cheng et al. 2009; Chitrakar et al. 2006a; Delaney et al. 2011).

In some studies, phosphate has been successfully desorbed by using combination of salts and bases (Kuzawa et al. 2006; Urano et al. 1992b.; Table 7). The role of bases is to reduce the sorption capacity of the sorbent and that of salts is to desorb the phosphates by ion exchange process. Salts commonly used are NaCl and KCl, but sometimes special salts are used to regain the lost structure of the sorbent during the desorption process. For example, Urano et al. (1992b) used a sorbent consisting of activated alumina and $Al_2(SO_4)_3$ to remove phosphate from water and the sorbed phosphate was desorbed by NaOH. Some sulphate in the sorbent was desorbed and some Al was also dissolved by the NaOH treatment. Thus the sorbent was not reusable after this desorption process and the sorbent was regenerated by circulating solutions of $Al_2(SO_4)_3$ and acid. Similarly, Kuzawa et al. (2006) used 25% $MgCl_2$ for the regeneration of LDH sorbent after alkaline NaCl treatment to reconstruct the LDH structure and regain the sorption capacity.

Omori et al. (2007) reported that P sorbed onto a metal oxide and polymer (MOP) sorbent was readily desorbed by elution with a 5% NaOH solution at a space velocity of 3/h. After 2 and 6 h of elution (5 and 15 bed volumes) 80 and 90% P, respectively was desorbed. The sorption capacity of the sorbent was regenerated via acid neutralisation. The alkaline (pH 14) and acid (pH 3) treatments did not release any metal ions from the sorbent, indicating the good stability of the sorbent to these reagents. In a pilot plant study the MOP columns, after P removal from wastewaters, were regenerated in situ using 5-8% NaOH (Fitzpatrick et al. 2011).

Genz et al. (2004) cautioned that in most laboratory experiments the volume ratio of desorbing reagent to sorbent was very large compared to that in typical real filtration operation and at these ratios operation costs would be very high. Large volumes of regenerating solution containing high concentrations of desorbing ions create storage and disposal problems unless the desorbing solution is reused as Kuzawa et al. (2006) suggested (Fig. 6). Genz et al. (2004) also pointed out that over long periods of operation, phosphate may be sorbed very strongly and deep inside the sorbent particles producing a significant proportion of non-extractable phosphate fraction. The degree of desorption is, therefore, expected to be less than that observed in laboratory studies.

Low cost sorbents need not be regenerated for reuse. If they have no significant concentration of contaminants, phosphate loaded sorbents can be directly applied to land as fertiliser without further treatment. If organic wastes are used as sorbents they can serve as a soil amendment to increase the organic content of soils. Similarly, calcium and magnesium carbonate sorbents, after the removal of phosphate from water, can be directly applied to land to ameliorate soil acidity.

7. Phosphate recovery

Phosphorus in wastewater represents a significant renewable resource that can be exploited to overcome part of the expected future P resource scarcity. Sludge produced during biological phosphate removal processes, especially by the enhanced biological phosphate removal process (EBPR) are directly applied to land as soil amendments to increase soils' phosphorus fertility (Rittmann et al. 2011). Phosphorus removed by metal salt precipitation produces inorganic sludge that is converted into Ca, Mg and NH_4 phosphates by treating it with appropriate salts (De-Bashan and Bashan 2004; Morse et al. 1998). Phosphate recovery in the form of struvite (magnesium ammonium hexahydrate) is practiced in many countries and is used as high quality phosphate fertiliser (De-Bashan and Bashan 2004; Le Corre et al. 2009; Rittmann et al. 2011).

Recovery of phosphate removed from water using the sorption process has been reported only in laboratory studies. Urano et al. (1992c) showed that phosphate removal by chemically modified activated alumina was desorbed sufficiently (80%) by 1 M NaOH and when $CaCl_2$ was added to the desorbed solution, phosphate was precipitated as Ca hydroxyl phosphate. They added sulphuric acid to convert this precipitate into Ca phosphate that was considered to be a useful phosphate fertiliser. A $CaCl_2$ concentration, 2-3 times that of phosphate in the solution, was vital to precipitate all the P in the solution. A high concentration of $CaCl_2$ was used to make up some of the calcium lost in the reaction with carbonate in the solution.

Kuzawa et al. (2006) proposed a scheme whereby the phosphate desorbed from LDH sorbent by 10% NaCl + 3% NaOH + 25% $MgCl_2$ could be recovered as Ca phosphate precipitate by the addition of $CaCl_2$ and the desorbing solution after every use could be reused by supplementation with additional NaOH (Fig. 6). In their study the exhausted desorption solution in each operation of column leaching ranged from 1700 to 2030 mg P/L. Because of the high P concentration, Ca phosphate compounds were easily precipitated using $CaCl_2$. It was found that a Ca to P mole ratio of 2 was the optimum dosage of $CaCl_2$. At low Ca to P ratios, significant concentration of residual P was present in solution because part of the Ca added was used up in $Ca(OH)_2$ precipitation in the strongly alkaline solution. The alkaline solution after the recovery of P can be reused as desorbing solution saving cost on chemicals and reducing disposal problems. Kuzawa et al. (2006) suggested that this proposed method of recovery needs further research in full scale treatment plants.

Midorikawa et al. (2008) used $Ca(OH)_2$ instead of $CaCl_2$ to recover phosphate desorbed by NaOH from columns containing beads of a mixture of a metal oxide and a polymer. They reported that all P was precipitated as calcium phosphate at a Ca/P mole ratio of 2.0. The XRD and XRF analyses showed that the precipitate was hydroxyapatite with a P content of 16%, which corresponded to a bone phosphate lime value of 80%. This value indicated that the recovered precipitate was a high grade phosphate ore. The metal contents of the recovered precipitate were lower than those in phosphate ore, further indicating the high quality of this precipitate as a P fertiliser (Tsuji et al. 2011). Midorikawa et al. (2008) also proposed a P removal and recovery system with recycling of the alkaline desorbing solution similar to the method reported by Kuzawa et al. (2006). Recently this system was successfully tested in pilot plants in Japan and USA (Fitzpatrick et al. 2011; Tsuji et al. 2011).

8. Summary and conclusions

Excessive P released into water bodies by mining, industrial and agricultural activities and municipal discharge causes eutrophication. To control it, many countries' regulations and guidelines set limits on the concentration of P entering receiving waters. To comply with these regulations and guidelines, wastewaters are treated with physical, chemical, and biological processes. Sorption is generally considered an effective and attractive treatment process because of its ease of operation, simplicity of design, ability to remove phosphorus at very low concentrations and minimal waste production. However, in most waste treatment plants, chemical and biological removal of phosphate is the method used, but with the emphasis on recovery of removed phosphate, sorption is becoming attractive.

Several sorbents are used as filter media in filter-based systems and as bed media in constructed wetlands. A sorbent is considered suitable if it has high phosphate sorption capacity, cost-effectiveness, is able to regenerate for reuse, and good hydrological conductivity without filter clogging. The sorbents tested for phosphate removal can be classified as multivalent metal oxides and hydroxides, silicates, Ca and Mg carbonates, layer double hydroxides (LDHs), natural and synthetic organic compounds, industrial by-products, and organic wastes. Most studies reported were conducted in laboratories where using the batch method was prevalent while others mainly using the dynamic column.

Of the sorbents, Fe, Al, and Zr metal oxides and hydroxides, LDHs, and highly porous metal oxide/polymer composites generally had the highest phosphate sorption capacities. Activation by heat and acid treatments enhanced the sorption capacities of some sorbents (e.g. LDHs, Fe and Al oxides and hydroxides, red mud). Surface modification of sorbents by grafting metals and organic functional groups also enhanced sorption capacities. However, activation and surface modification of sorbents increase the cost of sorbents and therefore a cost-benefit analysis is required. These sorbents, because of their high sorption capacities, are promising materials if extremely low P concentration is required in the treated water.

Though many industrial by-products and organic wastes have low sorption capacities they are attractive because they have low costs (mainly transport) and money can be saved on disposal costs. These materials' low sorption capacity can be overcome by using large volumes of sorbents. These materials are recommended for use in areas where they are locally available to reduce transport costs.

Sorption capacities of sorbents are difficult to compare because of many inconsistencies in data presentation such as methodology and environmental conditions used (e.g. pH, temperature, phosphate concentration range, presence of competing ions). In some studies, different sorption capacities were reported for the same material because of variations in the materials' chemical and physical characteristics (e.g. mineralogy, chemical composition, porosity, surface area).

Many anions co-exist with phosphate in wastewater. In general, nitrate and chloride do not interfere with phosphate sorption, because they are non-specifically sorbed, whereas phosphate is specifically sorbed in many sorbents. Sulphate, carbonate, and bicarbonate are specifically sorbed in certain sorbents, and therefore they can compete with phosphate for sorption depending on their relative concentrations.

The mechanisms of phosphate removal are ion exchange (non-specific sorption), ligand exchange (specific sorption), precipitation, and diffusion. All studies reporting on sorption thermodynamics showed negative ΔG^0 values indicating spontaneous sorption process. Many studies reported exothermic sorption reaction (negative ΔH^0). Equilibrium sorption data generally fitted to the Langmuir or Freundlich sorption isotherm models or both. Much of the kinetic data fitted to the pseudo-second order model. Phosphate removal for most of the sorbents was lower at $pH < 2$-3 and $pH > 7$-8. For some sorbents the removal decreased when pH rose from pH 4 onwards. For sorbents which remove phosphate by precipitation at high pH (e.g. Ca and Mg carbonates) the removal was highest at $pH > 7$-8.

Sorbents can be regenerated for reuse by regaining 80% or more of the sorption capacity using acids, bases, and salts to desorb the sorbed phosphate. Phosphate in the desorbed solution can be recovered as Ca phosphate compounds by the addition of $CaCl_2$ or $Ca(OH)_2$. Schemes have been proposed for this recovery, which requires testing in real treatment plants. If phosphate can be economically recovered, it can be used as a fertiliser.

This technology can help overcome part of the perceived future shortage of phosphate reserves. Low-cost sorbents containing minimum contaminants, after phosphate removal, can be directly applied to lands to supply phosphate to plants. Some can produce additional benefits such as increase in organic carbon content and acid-ameliorated soils.

Future research must explore highly efficient, low cost sorbents that can be easily regenerated over several cycles of operations without significant loss of sorptive capacity and have good hydraulic conductivity to prevent filters clogging during a fixed-bed treatment process. Reuse of the regenerating solution will alleviate the problems of storage and discharge of the solution. Most studies reported have been conducted in batch trials on synthetic waters. These trials need to be extended using continuous mode column trials which are more relevant to real operating systems on natural waters containing other ions as well. Recovery of the phosphate removed by sorption and production of fertilisers need to be researched in full scale plants.

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List of Tables

List of figures

Table 1 . Comparison between non-specific and specific anion sorption processes (Bolan et al. 1999)

Non-specific sorption	Specific sorption
Electrostatic attraction between the negatively charged anions and the positive sites on the sorbent.	Chemical bond formation between the anions and the ions on the sorbent surface.
Balances the positive charges on the surface and hence no new charges are added to the surface.	Adds negative charge to the surface and the number of negative charges added is generally less than the anion charge.
Significant sorption occurs only when the sorbent is net positively charged.	Sorption occurs even when the surface is net negatively charged.
Sorption depends on the number of positive charges (anion exchange capacity) on the surface.	Sorption exceeds the anion exchange capacity of the sorbent.
In variable charge sorbent, the sorption is high at low pH and decreases with an increase in pH.	Sorption occurs over a wide range of pH values.
Sorption is weak and reversible.	Sorption is strong and less reversible.

Table 2. Characteristics of sorptive removal of phosphate from water by inorganic sorbents

Sorbent	Sorption method: batch (B), column (C); Water type: synthetic (S), wastewater (W)	pH; Temperature (°C)	Initial (I), Equilibrium (E) concentration (mg/L); Sorbent concentration (g/L);column ht, height; d, diameter; FL, flow rate	Sorption capacity (mg/g) and other results	Best kinetic model to fit data	Best equilibrium model to fit data	Reference
				Metal oxides and hydroxides			
Goethite	B; S	5.0, 6.7; 25, 45, 65	I, 10; 0.1-1.0	Langmuir sorption max: 25°C, 144; 45°C, 57; 65°C, 19	Pseudo-first, second and third order	Langmuir, Freundlich	Peleka and Deliyanni (2009)
Iron oxide/gypsum	B; S, W	4-10; 20	I, 0.01-10; 0.002-0.2	Phosphate removal 4-20 mg P/g; Phosphate removal not altered between pH 4 to 8, above 8 it increased	-	-	Bastin et al. (1999)
Goethite	B; S, sea water	2-9; room temp.	I, 0.33, 50; 0.05, 0.1	Synthetic water: sorption decreased from pH 2 to 10. Max sorp. 24; Sea water: increased from pH 2 to 7 and then decreased up to 10. Max sorp. 11	-	Freundlich	Chitrakar et al. (2006a)
Akaganeite	B; S, sea water	2-9; room temp.	I, 0.33, 50; 0.05, 0.1	Synthetic water: sorp. decreased from pH 2 to 10. Max sorp 28; Sea water: increased from pH 2 to 7 and then decreased up to 10. Max sorp. 9	-	Freundlich	Chitrakar et al. (2006a)

Table 2 contd.

Akaganeite	B; S	7; 25, 45, 65	E, 0-250; 0.5	Langmuir sorp. max: 25^0C, 60; 45^oC, 45; 65^oC, 27	Pseudo-second order	Langmuir, Freundlich	Deliyanni et al. (2007)
Akaganeite + surfactant	B; S	7; 25, 45, 65	E, 0-250; 0.5	Langmuir sorp. max.: 25^0C, 451; 45^oC, 401; 65^oC, 354	Pseudo-second order	Langmuir, Freundlich	Deliyanni et al. (2007)
Akaganeite (granulated)	B, C; Membrane bioreactor effluent	B, 5.5; 20 C, 8.2; 18-25	B, E, 0-3.5; 0.04-4. C, I, 0.3;2.5 cm d, 20 cm ht, 1.6-17 BV/h	B, Langmuir sorp. max, pH 5.5 = 23, pH 8.2 = 17 C, complete breakthrough 31, 500 BV	-	Langmuir	Genz et al. (2004)
Alumina (activated)	B, C; Membrane bioreactor effluent	B, 5.5; 20 C, 8.2; 18-25	B, E, 0-3.5; 0.04-4. C, I, 0.3; 2.5 cm d, 20 cm ht, 1.6-17 BV/h	B, Langmuir sorp. max, pH 5.5 = 14, pH 8.2 = 12. C, complete breakthrough 21, 000 BV	-	Langmuir	Genz et al. (2004)
Alumina (activated)	B; S	6.9-7.1;	I, 0.5-10; 5	Langmuir sorp. max, 3.3	-	Langmuir	Wang et al. (2009)
Magnetite impregnated into (GAC)34 mg/mixture	B; S	6.3; 25	I, 500; 5-40	Langmuir sorp. max, 145 mg P/g Fe or 4.9 mg P/ g mixture	Pseudo-second order, diffusion	Langmuir	Zach-Maor et al. (2011)
Zirconium hydroxide (amorphous)	B; S, sea water	2-10; room temp.	Sea water 1-10; 0.05 S 0.3; 0.006-0.2	Freundlich: synthetic water (pH 5.0) 30; max sorp. at pH 2, then decreased up to pH 10. Sea water (pH 7.7) 10. Sorp. increased from pH 2 to 6 and then decreased to pH 10	.-	Freundlich	Chitrakar et al. (2006b)

Table 2 contd.

Iron/zirconium binary oxide	B; S	3-11; 25	I, 0-100; 1	Langmuir sorp. max 13.65 (at pH 4). Max sorp. at pH 3, then decreased continuously to pH 10	Pseudo-second order	Langmuir	Long et al. (2011)
Iron, aluminium, zirconium oxides	B; S	4-10; 20	I, 0.01-10; 0.002-0.2	Max sorp. between pH 3 and 5; At pH 4 it was 40	Pseudo-second order	Langmuir	Chubar et al. (2005)
Iron/manganese binary oxide (molar ratio 6:1)	B; S	3-10; 25	I, 2-40; 667	Langmuir sorp. max 33, Freundlich sorp. max 27; Max sor.p at pH 3-4 then continue to decrease to pH 10	Pseudo-second order	Freundlich	Zhang et al. (2009)
Metal oxide/polymer mixture	C; S, W	7; 25	S: I, 9; W: I, 1.7-2.4 20 BV/h	S: breakthrough sorp. Capacity 12 W: breakthrough sorp. Cap. 8.4	-	-	Omori et al. (2007)
				Calcium, magnesium carbonates			
Limestone (+ or – GAC)	B; S	2-13; 25	I, 6-25;	94% P removal from 20 mg P/L at pH range 2-13; Langmuir sorp. max for 25:15 limestone: GAC 3 mg/g	Pseudo-second order	Langmuir, Freundlich	Hussain et al. (2011)
Limestone (mean diameter 0.9 mm)	B; S	8.5; room temp.	I, 5-25; 20	Increased % P removal (30 to 90%) with increase P conc. From 10 to 25 mg/L. Sorp. capacity at 25 mg/L was 0.3 mg P/g (pH 8.5)	-	-	Johansson (1999b)
Opoka (50% $CaCO_3$, mean diam. 0.9mm)	B; S	8.5; room temp.	I, 5-25; 20	P removal % constant (10%) with increase P conc. Sorp. capacity at 8 mg P/L was 0.1 mg P/g (pH 8.5)	-	-	Johansson (1999b)
Dolomite and calcined dolomite	B; S	1-11; 20	I, 3.3-33; 2	Increased conc. 10 to 100 mg P/L, increased sorp. 1 to 15 mg P/g. Increased pH, increase sorp. Calcination to 350^0C decreased sorp.	-	Freundlich	Karaca et al. (2006)

Table 2 contd.

Dolomite (calcined at 650-750^{0}C	C; S	8.5-10.5; 25	I, 100; 5-100, 13 cm ht, 15 cm d	Freundlich sorp. max 10 mg P/g (pH 8.5)	-	Freundlich	Roques et al. (1991)
				Layered double hydroxides (LDH)			
MgAl-LDH (granular)	B; S	6.9; 25	E, 0-150;	Modified Langmuir sorp. max 47.3	-	Modified Langmuir	Kuzawa et al. (2006)
Divalent/trivalent metals LDH	B; W	6.8; Room temp.	I, 1-6; 0-4	Sorp. capacity: Zn-Al » Mg-Fe, Zn-Fe » Cu, Ni, Co combinations	Pseudo-second order	Langmuir	Cheng et al. (2009)
ZnAl-LDH (raw and calcined)	B; W	6.8; Room temp.	I, 20; 0.4	Raw 27 increased with calcining temp. up to 300^{0}C with a value of 41 and then decreased with temp. of 400^{o}C, 500^{0}C and lowest of 27 at 600^{o}C	Pseudo-second order	Langmuir	Cheng et al. (2009)
CO_3^{2-}, Cl^-, NO_3^- ZnAl-LDH	B; S	5.1;	I, 5; 124	Distribution coefficient (K_d) was highest for ZnAl-NO_3^- (>10^6 ml/g) and calcined ZnAlCO_3^{2-}LDHs (>10^4 ml/g)			He et al. (2010)
MgFe and CaFe-OH, CO_3^{2-}LDH	B; S C; W	6.9; 8.4 7.4	I, 1-1500; 5 I, 0.2; 0.2g, 1mm ht, 20 ml/h FL	B: pH 8.4 Langmuir sorp. max, MgFe 15.5, CaFe 28.8. pH 6.9, > 50-70 C: > 80% removal for 3000 times feed volume than the sorbent volume	-	Langmuir	Seida and Nakano (2002)
MgCaFe-Cl^- LDH	B; S Triphosphate removal	8; 25	I, 0-45; 0.2	Maximum sorp. capacity MgFeCl LDH 10.5 CaFeCl LDH 56.4	Pseudo-second order	-	Zhou et al. (2011)

Table 2 contd.

ZrMgFe-CO_3^{2-} LDH	B; S, sea water	4-10; -	I, 1-30; 1	S: pH 4 sorp. capacity 77, at pH 10 it was 20. Sea water, 26-30 at pH 3.5-6, and 4 at pH > 7. Sorp. capacity > than MgAlLDH and ZrO_2	-	Freundlich	Chitrakar et al. (2010)
ZnAl and ZnAlZrCO_3^{2-} LDH	B; S	2-12; 30	I, 200; 1	Sorp. capacity at pH 5.5, ZnAl LDH 9, ZnAlZr LDH 99. Max sorp. of 110 at pH 2.3 decreased to 80 at pH 7 and further to 10 at pH 10-12 for ZnAlZr LDH	-	Langmuir	Koilraj and Kannan (2010)
				Silicates			
Wollastonite	C; S	-; 18-21	I, 5-12; 15cm d, 1.5 m ht	Max. average removal 96% over 83d. Effluent 0.14-0.5 mg/L for residence time(RT) >40 h. For <40h 39% removal	-	-	Brooks et al. (2000)
Zeolite	B; S	-; 20	I, 0-17; 8	Langmuir sorp. max. 0.04	-	Langmuir	Ma et al. (2011)
	C; S	7; 20	I, 0.5; FL, 43 L/m^2.min	Sorp. capacity < 0.004 (empty bed contact time 2.6 min)			
Tephra (volcanic ash)	C; S	-; Room temp.	I, 12; 120 cm ht 4.5 cm d Residence time 35 min	After 214 h, 0.25-1mm Tephra Removed 2.6 (8.6) 0.1-2 mm, 1.6 (58%)	-	-	Hanly et al. (2008)
Tephra (volcanic ash)	C; S	-; Room temp.	I, 20.5; 5cm d, 20 cm ht, FL, 1.2 mL/min	After 54 d, Tephra 1 adsorbed 8 (97% removal) Tephra 2 sorbed 4 (52%)	-	-	Liesh (2010)

Table 3. Characteristics of sorptive removal of phosphate from water by organic sorbents

Sorbent	Sorption method: batch (B), column (C); Water type: synthetic (S), wastewater (W)	pH; Temperature (^oC)	Initial (I), Equilibrium (E) concentration (mg/L); Sorbent concentration (g/L); Column d, diameter; ht, height; FL, flow rate	Sorp. capacity (mg/g) and other results	Best kinetic model to fit data	Best equilibrium model to fit data	Reference
Activated carbon (AC)	B; S	4; -	I, 3-31; 2	Langmuir sorp. max 3.2	-	Langmuir	Mahmudov and Huang (2011)
Granular AC	B; S	-; 20	I, 0-17; 8	Langmuir sorp. max. 0.4	-	Langmuir	Ma et al. (2011)
	C; S	7; 20	I, 0.5; FL 43 L/m^2.min	Sorp. capacity 0.11 (empty bed contact time 2.6 min)			
Activated carbon (AC) with and without Fe oxides)	B; S	2-12; -	I, 70-400; 0.8	Langmuir sorp. max at pH 3.0, AC, 2.5, AC + Fe, 3.2. AC + Fe sorp. abruptly decreased from pH 2 to 5 and then slowly to pH 12. Sorp. optimum at 15 mg Fe/g AC	Pseudo-second order	Freundlich	Shi et al. (2011)
Purolite anion exchange resins	C; W (MBR effluent)	-; -	I, 3.1; 12 cm ht, 2.5 m/h FL	For 1950 bed volumes, 50-90% P removal by Purolite A500P and 10-30% by Purolite A520E	-	-	Johir et al. (2011)

Table 3 contd.

Anion exchange fibres (FVA-c, FVA-f)	B (FVA-c); S C (FVA-f); S	3-9; 30 7; 30	I, 310; I, 2.2-55.6; 0.5; FL 150-2000/h	B:sorp. capacity, pH 3 (201); decreased continuously to pH 9 (100). In the presence of sulphate, sorp. at pH 5 (5); pH 7 (60); pH 9 (10). .C: Breakthrough capacity 26-44.	-	-	Awual et al. (2011)
Aminated wheat straw anion exchanger	B; S C; S	- ; 20 - ; 20	I, 17-170; 2 I: 20, 25; 1; FL, 5 ml/min	Langmuir sorp. max 15 Column sorp. capacity 13-14	-	Langmuir	Xu et al. (2010b)
Iron/amine grafted cellulose	B; S	2-9; 30	I, 50; 0.4-4	Max sorp. at pH 6 Langmuir sorp. max at pH 6: 20^0C 21, 30^oC 19	Two-step pseudo-first order	Sips, Langmuir	Anirudhan and Senan (2011)
Amine group grafted giant reed	B; S	2-12; 20	I, 50; 0.5-16	Maximum sorp. at pH 4-9 Langmuir sorp. max 11	Pseudo-second order	Langmuir	Yue et al. (2010a)
Anion exchange resin from soybean hulls	B; S	7; 25	I, 0-620; -	Langmuir sorp. max 20	-	Langmuir	Marshell and Wartelle (2004)
Ammonium functionalised silica	B; S	2-10; 5-40	I, 100-700; 1-10	Maximumsorp. at pH 4-6 Langmuir sorp. capacity 15	-	Langmuir-Freundlich, Redlich-Peterson	Hamoudi et al. (2007)

Table 4. Characteristics of sorptive removal of phosphate from water by industrial by-products

Sorbent	Sorp. method: batch (B), column (C); Water type: synthetic (S), wastewater (W)	pH; Temperature (^{o}C)	Initial (I), Equilibrium (E) concentration (mg/L); Sorbent concentration (g/L);Column d, diameter; ht, height	Sorp. capacity (mg/g) and other results	Best kinetic model to fit data	Best equilibrium model to fit data	Reference
Red mud (activated by acid treat.)	B; S	3.5-6; -	E, 0-6.2; 2	Percentage removal decreased with pH Langmuir sorp. capacity at pH 5.2 was 22.5	-	Langmuir	Pradhan et al. (1998)
Red mud (raw and activated by acid and heat)	B; S	1-11; 25	I, 0.31-3100; 5	Maximum sorp. at pH 7 Langmuir sorp. capacity: raw red mud, 38; 700^{o}C heated red mud, 113; acidified red mud, 54	-	Langmuir	Li et al. (2006)
Red mud (granulated: starch/bentonite)	B; S	3; 17, 27, 37	I, 50; 4	Maximum sorp. capacity of 2-6 at granule cintering temperatures of 980-1080^{o}C	-	-	Yue et al. (2010b)
Bauxsol (sea water treated red mud)	B; S	5.2-9; 23	I, 0.05-63; 2-5	Maximum sorp. at pH 5-6 Langmuir sorp. capacity at pH 5.2, 15; at pH 6.2, 14; pH 9, 6	Pseudo first order	Langmuir	Akhurst et al. (2006)
Blast furnace slag	B; S	- ; 25	E, 0-300; 100	Langmuir sorp. max 44.2	-	Freundlich	Sakadevan and Bavor (1998)
Blast furnace slag	B; S	8.5-9.5; Room temp.	I, 5-25; 60	At E = 10, sorp. capacity 0.1-0.8 depending on amorphous or crystalline slag and fineness of slag	-	-	Johansson (1999a)

Table 4 contd.

Blast furnace slag(BFS), BFS+lime (L)	B; S	7-8; 30	E, 0-270; 0.8	Langmuir sorp. max BFS 29, BFS/L (slurry temp 70°C) 45	Pseudo second order	Langmuir	Gong et al. (2009)
Basic oxygen steel slag	B; S C; S	2-12; -	I, 0-1000; - I, 100-300; -	Sorp. increased with pH (pH 2, 5; pH 5-12, 8) Maximum effective removal 8.4 after 306 days	-	Langmuir	Bowden et al. (2009)
Basic oxygen furnace slag	B; S	2-13; 20	I, 3-170; 10	Langmuir sorp. max (pH 7-7.2): slag milled 20, acidified 14, original 11. Sorp. decreased with pH. Sorp. selectivity: $Cl<NO_3<SO_4<PO_4$	-	Langmuir, Freundlich	Xue et al. (2009)
Fly ash (pH 11;34% CaO)	B; S	11; 26	I, 7, 17, 33; -	Amount of P sorbed for 7, 17, and 33 mg P/L solutions were 4.3, 11.9 and 6.6 respectively	-	-	Ugurlu and Salman (1998)
Fly ash (alkaline, 11.6% CaO)	B; S	11.5; 20	I, 27, 33, 43; 1.6	Maximum sorp. capacity 24	-	-	Oguz (2005)
Fly ash (pH 7.7, 12.4; 2.6, 5.0% Ca)	B; S	-; 25	-; 200	Langmuir sorp. max. Fly ash pH 7.7, 3.1; Fly ash pH 12.4, 13.8	-	Langmuir, Freundlich	Cheung and Venkitachalam (2000)
Fly ash (pH 11-12)	B; S	9.4-11.5; Room temp.	I, 17-667; 20	Langmuir sorp. max. 30-36	-	Freundlich	Lu et al. (2009)
Fly ash (Type F, pH 4.5, 1% CaO)	B; S	4-6; -	I, 17. 33; -	Phosphate removal of 100% and 70% for 17 and 33 mg P/L, respectively	-	-	Grubb et al. (2000)
Fly ash (pH 9.4, 2.7% CaO)	B; S	7; 25	I, 0.31-3100; 5	Langmuir sorp. max.: raw fly ash, 21; fly ash heated to 700°C, 20; Fly ash acidified, 26	-	Langmuir	Li et al. (2006)

Table 4 contd.

Alum sludge (water trea. tment plant)	B; S	4, 7, 8; -	I, 0-300; 10	Langmuir sorp. max: pH 4 = 32; pH 7 = 23; pH 9 = 10	Pseudo 1st/ 2nd order, diffusion	Langmuir	Babatunde and Zhao (2010)
Iron oxide tailings (23% Fe)	B; S	3-10; 20-21	I, 5-150; 0.8	Langmuir sorp. max. (pH 6.6-6.8) 8; Sorp. 8.3(pH3) decreased to 5 at pH 10.	Power function and Elovich	Langmuir-Freundlich	Zeng et al. (2004)
	C; S	7.2-8.3; 20-21	I, 20-22, 40-50; 2.5 cm d, 25 cm ht	Effluent concentration of total and dissolved P was < 2 mg/L			

Table 5. Characteristics of sorptive removal of phosphate from water by biological wastes

Sorbent	Sorp. method: batch (B), column (C); Water type: synthetic (S), wastewater (W)	pH; Temperature (°C)	Initial (I), Equilibrium (E) concentration (mg/L); Sorbent concentration (g/L); Column d, diameter; ht, height; FL, flow rate	Sorp. capacity (mg/g) and other results	Best kinetic model to fit data	Best equilibrium model to fit data	Reference
Water hyacinth plants/straw	B; S	-; 15-20	I, 17.5; 20	Initial P conc. Dropped by 12% on 3rd day, by 17th day by 36%. Sorp. capacity 0.32	-	-	Chen et al. (2010)
Date palm (trunk) fibers	B; S	2-11; 18	I, 10-110; 1	Sorp. capacity decreased from 8 to 3 with increased pH	-	-	Riahi et al. (2009)
Aleppo pine saw dust (modified)	B; S	3.5-10.6; 25	I, 80-400; -	Optimum pH for sorp. 7.5 but not much change between pH 3.5 and 10.6. Freundlich sorp. capacity 0.9	Pseudo second order	Freundlich	Benyoucef and Amrani (2011)
Iron humate (waste by product)	B; S	1-4.5; 22	I, 3-124; 10-40	Sorption did not change between pH 2 and 4.5, but decreased below pH 2. Langmuir sorp. max. (pH 3-4) 3-5	Pseudo second order	Langmuir-Freundlich	Janoš et al. (2011)
Microbial mat (biogenic Fe oxides)	B; S	6.2-6.4; 20	E, 0-20; -	Langmuir sorp. max. 11-40	Pseudo first order	Langmuir	Rentz et al. (2009)

Table 5 contd.

Eggshell waste/iron hydroxide	B; S	7; 25	I, 2-47; 7.5	Langmuir sorp. max. 3.5	Pseudo second order, diffusion	Freundlich	Mezenner and Bensmaili (2009)
Oyster shell (pyrolised 700^{0}C)	B; S, W	7-11; -	I, 11.9; 6	98% P removed in 30 min. Final P conc. < 0.2 mg/L. Initial pH 7.2, final pH 11.6	-	-	Lee et al. (2009)
Giant reed (GR), chemically modified GR	C; S	2-12; -	I, 200; 1.2cm d, 20cm ht, 1 g, 5ml/min FL	Column sorp. capacity: GR, 0.3; modified GR, 18. Maximum sorp. capacity at pH 4-8.	-	-	Xu et al. (2011)

Table 6. Thermodynamic parameters for phosphate sorption by different sorbents

Sorbent	ΔG^0 (kJ/mol) ----------------------- Temperature (^oC)				ΔH^0 (kJ/mol)	ΔS^0 (J/mol/^{0}C)	Reference
Amine grafted cellulose	-26.5	-23.6	-21.9	-20.0	-89.5	-120	Anirudhan and Senan (2011)
	20	30	40	50			
Chemically modified Aleppo pine saw dust	-0.77	-1.35	-1.93	-3.09	16.2	32	Benyoucef and Amrani (2011)
	20	30	40	60			
Iron oxide loaded activated carbon	-3.8	-5.3	-10.6		66.6	132	Zhong-liang et al. (2011)
	18	30	50				
Al-bentonite	-3.7	-4.4	-4.8		13.5	32	Yan et al. (2010)
	30	40	50				
Fe-bentonite	-4.2	-4.7	-4.9		6.9	20	
	30	40	50				
Fe-Al-bentonite	-3.6	-3.9	-4.4		9.4	24	
	30	40	50				
Chemically modified giant reed	-13.4	-14.3	-15.1		-0.91	24	Yue et al. (2010a)
	20	40	60				
Iron hydroxide-eggshell waste	-0.27	-2.66	-5.75	-7.19	82	157	Mezenner and Bensmaili (2009)
	20	25	35	45			
Goethite					-212		Peleka and Deliyanni (2009)
	25	45	65				
Aluminum oxide	25	45	65		-49		
Layered double hydroxide	25	45	65		124		
Tricarboxylic acid coated alumina	-15.6	-16.8					Saha et al. (2009)
	25	50					
Akaganéite	-2.3	-1.6	-1.0		-12.2	18	Deliyanni et al. (2007)
	25	45	65				
Surfactant-akaganéite	-7.1	-6.0	-5.6		-18.3	21	
	25	45	65				
Ammonium functionalised mesoporous silica					-51	-112	Hamoudi et al. (2007)

Table 7. Phosphate desorption and sorbent regeneration

Sorbent (batch (B), column (C) method used)	Desorption/regeneration reagent (BV, bed volume; d and ht, column diameter and height; FL, flow rate	Results	Reference
FVA anion exchange fibres (C)	BV 2.4 ml (0.5 g). 1.3 cm d. 1 M HCl. FL 10/h.	At 20 BV FVA-f and 50 BV FVA-c 98-102% desorp.	Awual et al. (2011)
Ti-oxide/meso-porous silica(B)	P- loaded sorbent washed with 0.02M NaOH (20 min)	100% desorbed. Repeated use reduced ads. capacity to 75%	Delaney et al. (2011)
Purolite anion exchange resin (C)	2 cm d, 6 cm ht, vol., NaCl, 2.5 m/h FL.	1% NaCl (20 BV) / 2-3% NaCl (4 BV) desorp. 95-97%	Johir et al. (2011)
Fe/amine grafted cellulose (B)	0.1 g/50 ml 0.001-0.1 M NaOH, 2 h shaking	60 to 99% desorp. with increase NaOH conc.	Anirudhan and Senan (2011)
Amine grafted giant reed (C)	1.2 cm d, 20 cm ht (I g). 0.001-0.1 M NaCl, HCl, NaOH	HCl (100%),NaCl (83-92%),NaOH (47-65%) 0.1>0.01>0.001M;	Xu et al. (2011)
Amine grafted wheat straw (B)	0.25 g in 50 ml 0.1 M HCl or 0.1 M NaCl shaken 2 h	4 adsorp./desorp. cycles: HCl, 87-98% desorp.NaCl 87-95%	Xu et al. (2010b)
Zr oxide loaded MgFe LDH (C)	0.5 g sorbent; 200 ml 0.05 M NaOH. FL 0.5 cm^3/min	Cycle 1: 90% desorp.; Cycles 2-10, 92-94% desorp.	Chitrakar et al. (2010)
ZnAl LDH (B)	0.1 g + 20 ml 0.1 M NaOH + 4 M NaCl. 3 d shaking	5 sorp./desorp. cycles: ~ 100% every cycle	He et al. (2010)
MgAl LDH (B)	NaCl conc.: 1 M, 3 M, and 5 M	100% 5M, 80% 3M, 40% 1M for 3 successive desorp.	Park et al. (2010)
ZnAl LDH (calcined) (B)	5% NaOH, NaCl, Na$_2$CO$_3$ 24 h interaction	desorp:8% NaCl, 88% NaOH, NaCO$_3$ 40%. Regeneration (R): 60% after 6 cycles of sorp., desorp./R by NaOH	Cheng et al. (2009)
MgAl LDH (powdered, granular) (B), (C)	Desorp. (B): 1 g + 50 ml NaCl, NaOH, NaCl+ NaOH Regeneration (R) (B): 15-25% MgCl$_2$ contact for 24 h R + reuse (C): 2 cm d, 19 cm ht, FL 1.0/h. 10% NaCl + 3% NaOH + 25% MgCl$_2$	Desorp. (B): 30% NaCl, 14%; 3% NaOH, 40%; 10% NaCl + 3% NaOH, 70% Regeneration (B): 25% MgCl$_2$, 101%. Reuse (C): after 3 cycles, sorp. capacity 75% of initial value, after 10 cycles 60%	Kuzawa et al. (2006)
La doped vesuvianite (B)	0.3 g soaked in 25 ml 5% HNO$_3$ for 24 h.	Sorp. capacity maintained at least for one recycling	Li et al. (2009)

Tricarboxylic acid coated alumina (B)	1 g shaken with 50 ml of 0.1-0.5 M NaOH for 30 min	desorp. increased from 80 to 100% for 0.1 to 0.5 M NaOH	Saha et al. (2009)
Fe-Mn binary oxide (B)	0.05 g shaken with 50 ml 0.01-0.5 M NaOH for 24 h	Desorp. 60% for 0.01 M, 93% for both 0.1 M & 0.5 M	Zhang et al. (2009)
Ammonium-doped mesoporous silica (B)	5 g shaken with a litre 0.01 M NaOH for 1 h. Acidified with HCl/repeated 4 cycles	Desorp. complete in 10 min. No loss of sorp. capacity during the 5 cycles	Hamoudi et al. (2007)
Goethite (G), akaganeite (A) (B)	0.5 g soaked in 200 ml 0.1 M NaOH for 1 d	After 1 cycle, G sorp. 33%. After 10 cycles, 'A' desorp. 90%, regeneration 100%	Chitrakar et al. (2006a)
Zr hydroxide (amorphous) (B)	0.5 g soaked in 200 ml 0.1 M NaOH for 1 d	For 5 cycles, desorption rate 82%, regeneration rate 90%	Chitrakar et al. (2006b)
Ferric hydroxide (granulated) (FH), aluminium oxide (activated)(AA)(C)	0.25 or 0.5 g on glass beads bed. 0.6 M NaOH, 2.8 M NaOH or 3% H_2O_2 passed through for 17 or 68 h	Regeneration most effective with 0.6 M NaOH for 3 reloadings with phosphate	Genz et al. (2004)
Iron oxide tailings (B)	0.2 g shaken with 100 ml 0.01 M KCl for 24 h	13-14% desorbed	Zeng et al. (2004)
Alumina (activated) + Aluminum sulphate (C)	180 mL BV. 0.1-2.0 M NaOH , FL 15-90 mL/min (5-30/h space velocity) Regeneration: 1 BV 0.05 M H_2SO_4 + 0.5 M $Al_2(SO_4)_3$ circulated at FL 90 mL/min	1 M NaOH at 90 mL/min most suitable, 80% desorp. Maintained sorp. capacity of > 80% for 20 reuse cycles	Urano et al. (1992b,c)

Chemical precipitation

- Most widely used
- Low effectiveness, especially at low P concentration
- Large amounts of chemicals required
- Costs of chemicals, chemical storage and feeding system
- Large volumes of waste sludge
- Acid or alkali neutralisation of effluent required
- Chemicals used may affect subsequent biological treatment

Biological methods

- Low effectiveness, especially at low P concentration
- Low operational cost but infrastructural investment required
- Low volumes of wastes
- No chemicals usage
- Simultaneous removal of both excess P and N
- Highly skilled operation (strict anaerobic and aerobic conditions required)
- Uncontrolled microbial growth

Constructed wetlands

- Low maintenance cost
- Low-tech process
- Practical in any location
- Need land availability

Electrodialysis

- Excellent removal when P is in ionic form
- High capital cost
- No waste production
- No ion selectively

Sorption/Ion Exchange

- Effective even at low P concentration
- Flexible
- Simplicity of design
- Ease of operation
- No waste production

- Can be costly, needs pretreatment, sorbent regeneration; can use low-cost sorbent (including certain waste materials)
- Low selectivity against competing ions

Reverse osmosis

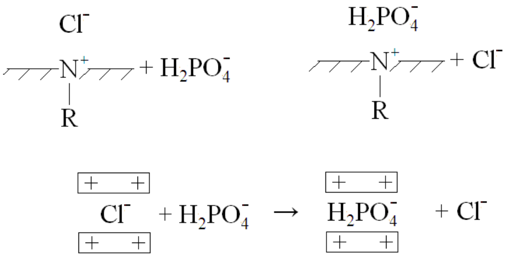
- Excellent removal
- High capital cost
- No waste production
- No ion selectively
- Very high energy cost
- Some membranes pH sensitive

Nano filtration

- Excellent removal
- High Capital cost
- No waste production
- No ion selectively
- High to moderate energy cost

Fig. 1. Key characteristics of common technologies for phosphate removal from wastewater sources.

Ion Exchange

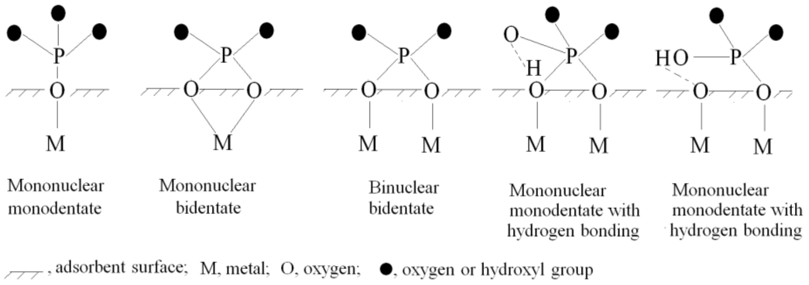


- Physical sorption (Electrostatic attraction)
- Weak sorption
- Outer-sphere complex
- Very fast process
- Water molecules between phosphate and sorbent surface
- Reversible

Ligand Exchange

$$\equiv M - OH + H_2PO_4^- \rightarrow \equiv M - H_2PO_4^- + OH^-$$

$$2 \equiv M - OH + H_2PO_4^- \rightarrow (\equiv M)_2HPO_4 + H_2O + OH^-$$



- Chemical sorption
- Strong sorption
- Inner-sphere complex
- Fast process
- ZPC reduced (Fig. 5)
- Not always reversible

Hydrogen Bonding

- Weak bonding between oxygen of adsorbent and hydrogen of sorbate and vice versa
- Stronger than ion-exchange but weaker than ligand exchange
- Inner-sphere complex formation
- Fast process
- Not always reversible

Surface precipitation

$$Zn\,Al\,Zr - LDH + H_2PO_4^- \rightarrow$$

$$ZnAl\,Zr - LDH - Zn_3(PO_4)_2 \cdot 4H_2O$$

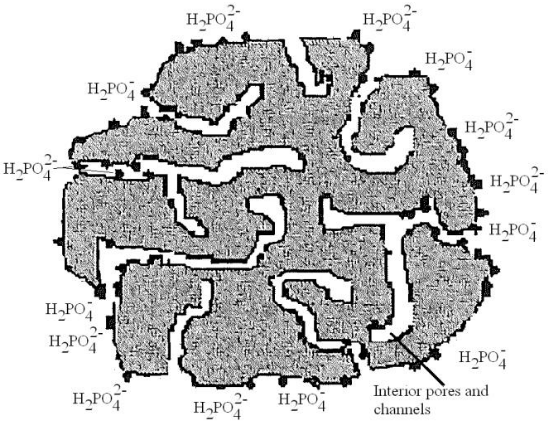
(LDH - layered double hydroxide)

Ca based sorbent (bentonite, calcium hydroxide, coal)

$+ H_2PO_4^-$ →hydroxyapatite on sorbent surface

- Precipitation of phosphate with metallic atoms on sorbent surface
- Fast process
- Not easily reversible

Diffusion



- Physical sorption inside pores and cavities of sorbent
- Extremely slow process
- Irreversible

Fig. 2. Schematic illustration of different phosphate sorption mechanisms

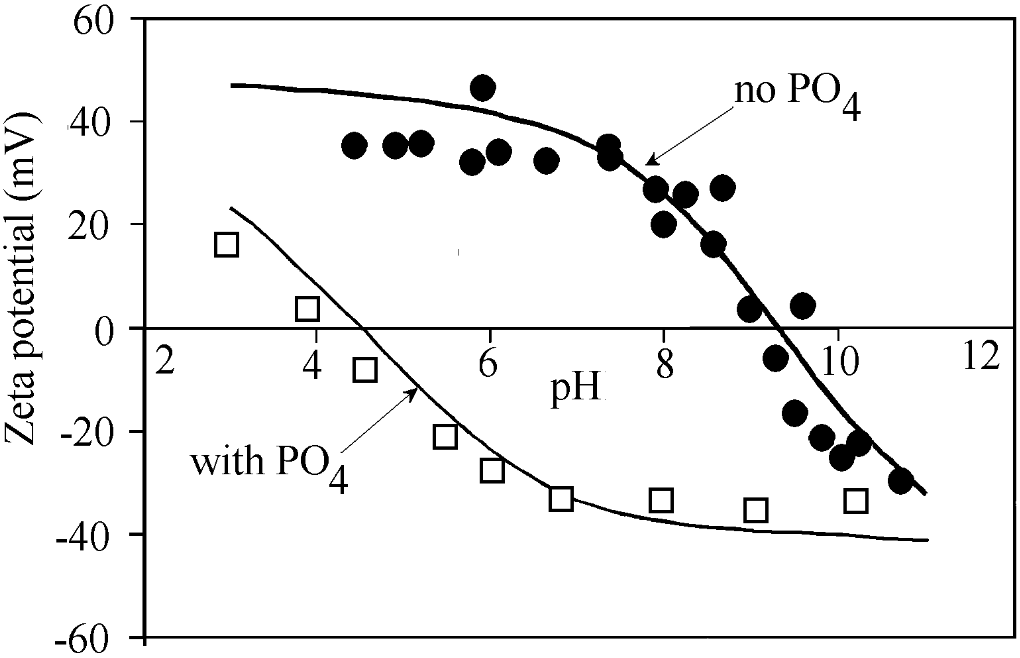


Fig. 3. Electrophoretic mobility of goethite in the absence and presence of phosphate in 0.01 M KNO_3 solutions indicating the shift in ZPC/IEP of goethite with phosphate sorption (redrawn from Antelo et al. (2005)).

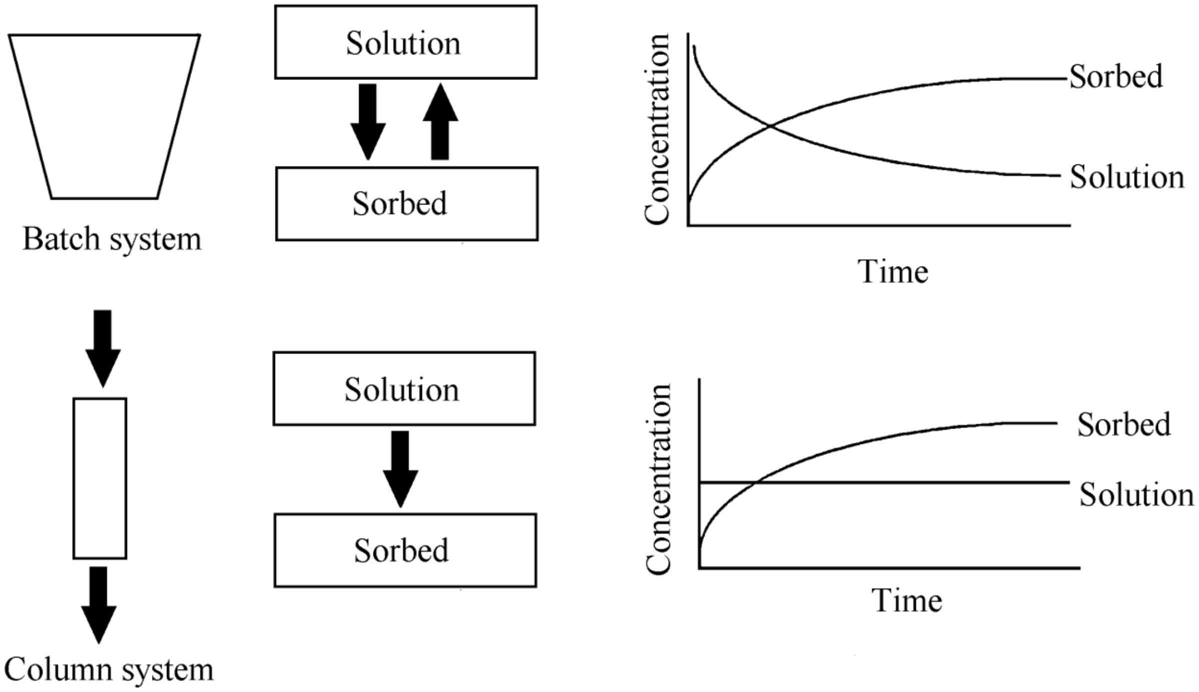
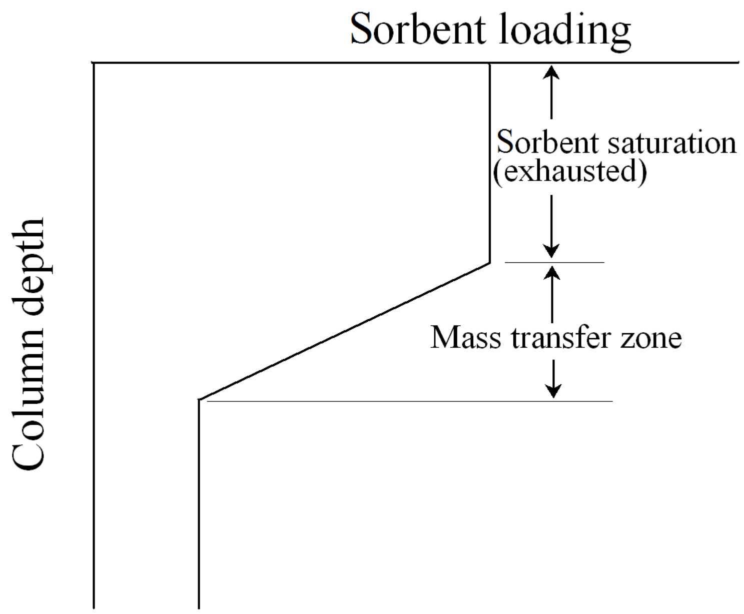
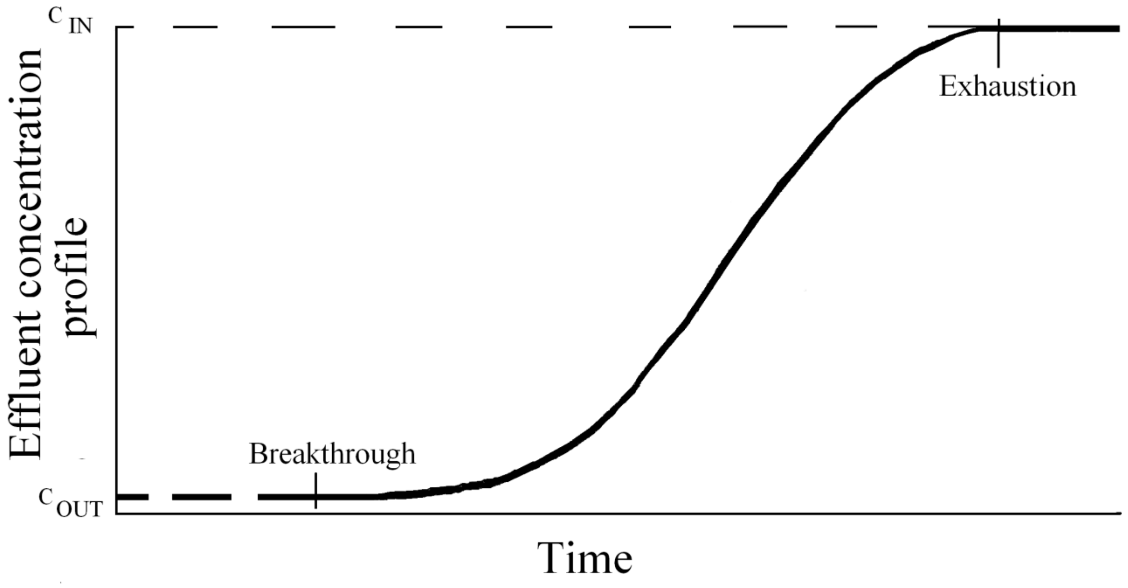


Fig. 4. A schematic representation of concentrations in sorbed and solution phases with time in batch and column sorption systems (redrawn from Kookana et al. (1999)).



(a)



(b)

Fig. 5. Schematic illustration of (a) mass transfer zone and (b) breakthrough curve in column sorption systems (redrawn from Faust and Aly (1987)).

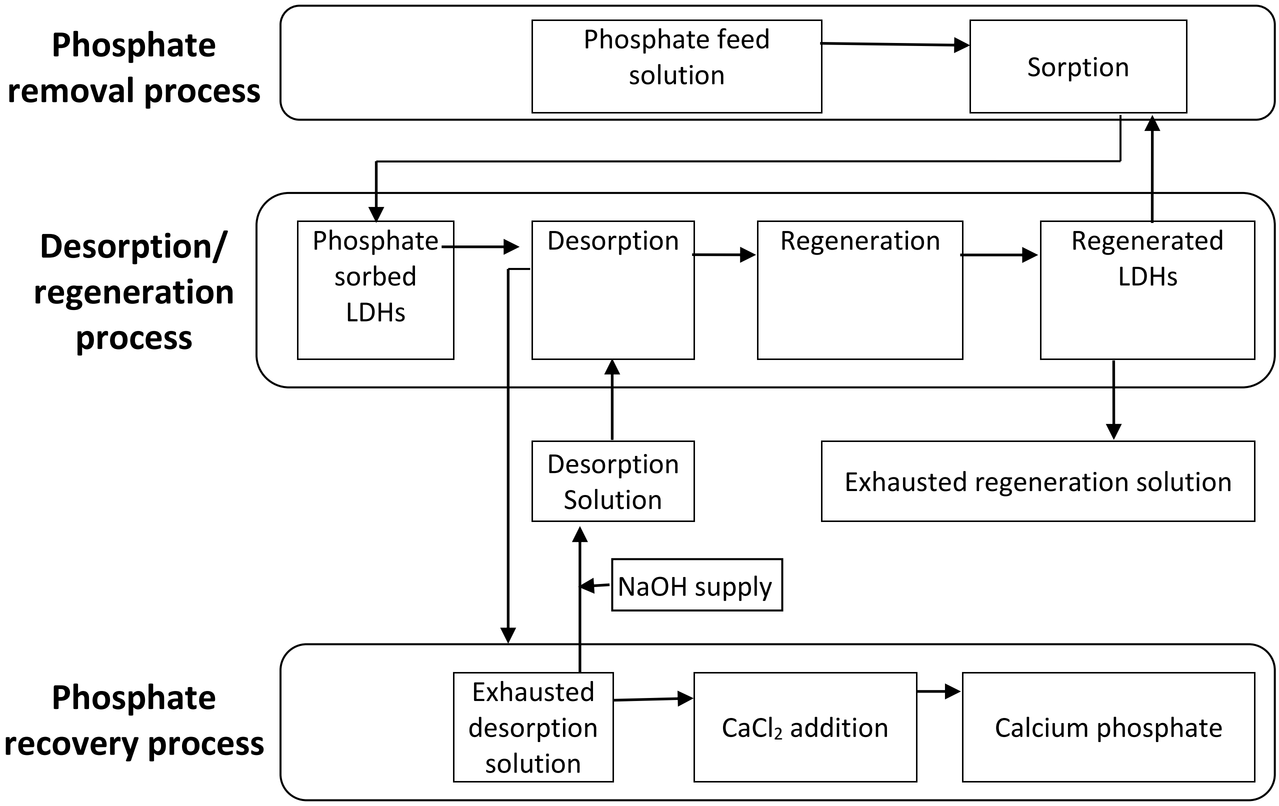


Fig. 6 Schematic illustration of the system for phosphate removal/recovery, regeneration of Layered double hydroxide, and regeneration of desorption solution (redrawn from Kuzawa et al. (2006)).