CHAPTER 14

Agricultural By−Products for Phosphorous Removal and Recovery from Water and Wastewater: A Green Technology

Huu Hao Ngo, Wenshan Guo, Thi An Hang Nguyen, Rao Surampalli and Tian Zhang

14.1 Introduction

Phosphorus (P) is a critical nutrient for the plant growth (Mezenner and Bensmaili 2009). In addition, as a component of DNA, RNA, ATP, phospholipids, P plays an important role in animal lives (Karachalios 2012). Furthermore, P is one of the principal materials for many industries, such as fertilizer, pesticide, steel production, etc. (Choi et al. 2012). The excessive amount of P in aquatic medium may originate from natural sources (e.g. precipitation, soil erosion, decomposition of organic matters) and/or artificial sources (e.g. mining, fertilizers, detergents, human and animal excreta). Karachalios (2012) claims that the agricultural runoffs contribute more than 50% to the freshwater eutrophication. The level of PO_4-P in municipal wastewater is in the range of 4−15 mg/L, while it may exceed 10 mg/L in industrial wastewater (Peleka and Deliyanni 2009). According to Biswas (2008), each person discharges 2−3 g P into domestic wastewater via feces and urine per day. The concentration of P in receiving water bodies greater than 0.02 mg/L may induce eutrophication (Ismail 2012; Mallampati and Valiyaveetttil 2013). This phenomenon leads to the depletion of oxygen in aquatic medium, thus threatening the aquatic lives (Jyothi et al. 2012). To prevent aquatic medium from eutrophication, United States Environmental Protection Agency recommended that the PO_4^{3-} levels should not be higher than 0.05 mg/L if streams discharge into lakes or reservoirs (Benyoucef and Amrani 2011; Ismail 2012). To meet more stringent environmental regulations, the removal of P from water and wastewater is necessary (Kalmykova and Fedje 2013). Also, there was a warning that the global existing rock P reserves could be depleted in 50−100 years (Ogata et al. 2012; Eljamal et al. 2013). Due to increasing scarcity of natural P ores, the P recovery from water and wastewater has recently become a matter of urgent (Anirudhan et al. 2006; Zhang et al. 2012).

Understanding different forms of P in aqueous solutions enables an appropriate selection of treatment technologies (Neethling 2011). Though, in natural water bodies, P can exist in different forms (Figure 14.1), only orthophosphate can accelerate the algae growth, inducing the eutrophication (Bhojappa 2009). Depending on pH values of the aquatic medium, orthophosphate may exist in various species. In strongly alkaline conditions, PO_4^{3-} is the main form, whilst in weakly alkaline conditions, HPO_4^{2-} is dominant. In weekly acidic conditions, $H_2PO_4^-$ prevails, whereas H_3PO_4 is most common in strong acidic conditions (Karachalios 2012).

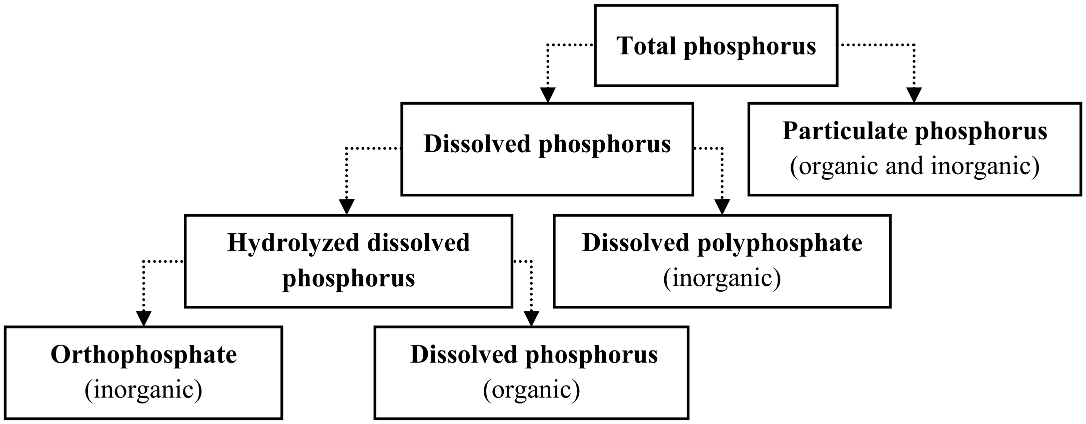


Figure 14.1. Different forms of phosphorus in aqueous solutions

Until now, various technologies are available for controlling PO_4^{3-} pollution. These processes can be classified as chemical methods (precipitation, crystallization, anion exchanger, and adsorption), biological methods (assimilation, enhanced biological phosphorus removal, land treatment system, constructed wetlands), and physical methods (microfiltration, reverse osmosis, electrodialysis, and magnetic separation) (Hu et al., 2005; Zhang et al. 2007; Bhojappa 2009; Benyoucef and Amrani 2011). Of these methods, chemical precipitation and biological processes are most commonly used. However, each method represents its own demerits (Table 14.1). The chemical precipitation is often prone to high chemical expense, effluent neutralization requirement, inadequate efficiency for dilute P solutions, etc. (Kumar et al. 2010; Zhang et al. 2011; Mallampati and Valiyaveetttil 2013). Similarly, the biological process associated with activated sludge systems suffers from drawbacks, such as low removal efficiency (≤ 30%), complicated operation, high energy consumption and footprint (Ning et al. 2008; Peleka and Deliyanni 2009). On the other hand, adsorption is proven to be affordable, effective and best suited for low levels of PO_4^{3-} (Li et al. 2009; Zhang et al. 2011). Notably, this method is believed to have an advantage when used for P recovery, owing to the selective P adsorption capability (Loganathan et al. 2014). Previously, activated carbon or anion exchanger resins are commonly used for P decontamination. However, the problems associated with high cost, no renewability and disposal after use hinder their widespread application in developing countries (Karthikeyan et al. 2004). Hence, increasing attention has been paid to agricultural by-products (AWBs) in an attempt to search for a viable alternative option (Jyothi et al. 2012). It is desirable to develop AWBs that have low cost, high effectiveness, good selectivity, potential renewability, and high adaptability to various process parameters (Ning et al. 2008).

Table 14.1. Comparison of different technologies for phosphorous removal[a]

Methods	**Effluent features**	**Advantages**	**Disadvantages**
Chemical precipitation	EPC: 0.005−0.04	• Easy to install • Flexible • High P removal efficiency • Less space	• Inappropriate for wastewater with low P concentrations • High cost for chemicals • Chemical sludge generation • Neutralization of effluent • Do not recycle P • Cannot meet strict regulations
Crystallization	EPC: 0.3−1.0	• Final product can be used as a fertilizer without further processing	• Chemicals and operation skills are necessary • Complex process • Increased salinity
Biological P removal	EPC: 0.1−0.3 RE < 30	• Avoiding chemical use • Potential P recovery	• More complex technology • Low removal efficiency (10−30%) • Biological sludge handling • External carbon source may be required • Sensitive to changes in temperature and P load (min. ~0.02 mgP/L is required) • Inefficient P recovery • Cannot meet strict regulations
Enhanced biological P removal	0.02 ≤ EPC < 0.1, depending on duration RE: 100	• Can remove P to very low levels • Modest cost • Minimal sludge production	• More energy consumption • More space
Constructed wetlands	EPC: 0.02; RE: 39−99, depending on plant type	• Low cost • Low technology	• Sediments
Magnetic separation	EPC: 0.1−0.5	• High P removal • Low power input	• Chemicals required • Technology is complex

Note: EPC = Effluent phosphorous concentration (mgP/L); RE = Removal efficiency (%).
[a]References: Biswas (2008); Everglades hub (2013); Kumar et al. (2010); Li et al. (2009); Loganathan et al. (2014); Mallampati and Valiyaveetttil (2013); Nguyen et al. (2012); Ning et al. (2008); Peleka and Deliyanni (2009); Zhang et al. (2011).

Table 14.1. Continued

Methods	Effluent features	Advantages	Disadvantages
Membrane technology	EPC: 0.04 (MBRs, Tertiary membrane filtration); 0.008 (RO); < 0.005 (Electro dialysis)	–	• High capital & operation cost
Ion exchange		• Simple operation • Adaptability to various solution compositions and flow rates • High P removal • Struvite produced can be used in agriculture	• High capital & operation cost • Complex technology • Chemicals required • Low selectivity • Materials originated from nonrenewable resources
Adsorption	EPC: 0.005−0.01 RE > 80	• Simple operation • Cost-effectiveness • Recommended for low P concentration wastewater • Few chemicals involved • Without additional sludge • Potential P recovery • Multiple regeneration of adsorbents	• Experimental technology • High cost • Disposal problems after use

Note: EPC = Effluent phosphorous concentration (mgP/L); RE = Removal efficiency (%).

There is growing interest in the use of AWBs for P removal/recovery. There are many reasons accounting for this (Figure 14.2). Firstly, this practice can prevent surface water from eutrophication, owing to the production of cleaner effluents, reduction of P pollution caused by mining activities, and mitigation of P leaching and runoff. Secondly, huge amounts of agricultural wastes generated worldwide represent an environmental burden. The recycling wastes to control PO_4^{3-} pollution provides a viable option to reduce wastes in a low cost and green way (Tshabalala et al. 2004; Ismail 2012; Eljamal et al. 2013). This also fits well with one of the 12 principles of Green Chemistry, i.e. “use of renewable resources” (Srivastava and Goyal 2010). In addition, the successful exploitation of P from wastewater will diminish the use of mineral P, and thus saving exhausting P rock reserves. Moreover, a large amount of anion exchanger resins created from abundant, cheap and renewable materials may help to fill a need for innovative, inexpensive and efficient method for PO_4^{3-} removal. Consequently, the cost of water treatment will be reduced (Liu et al. 2012). Eventually, by converting waste into fertilizers and useful materials for water treatment, this practice may create revenues (Huang et al. 2010; Peng et al. 2012). Apparently it may provide a sustainable, efficient and profit regenerating solution for

P management (Kuzma 2011). For these reasons, this practice should be considered as a promising green technology.

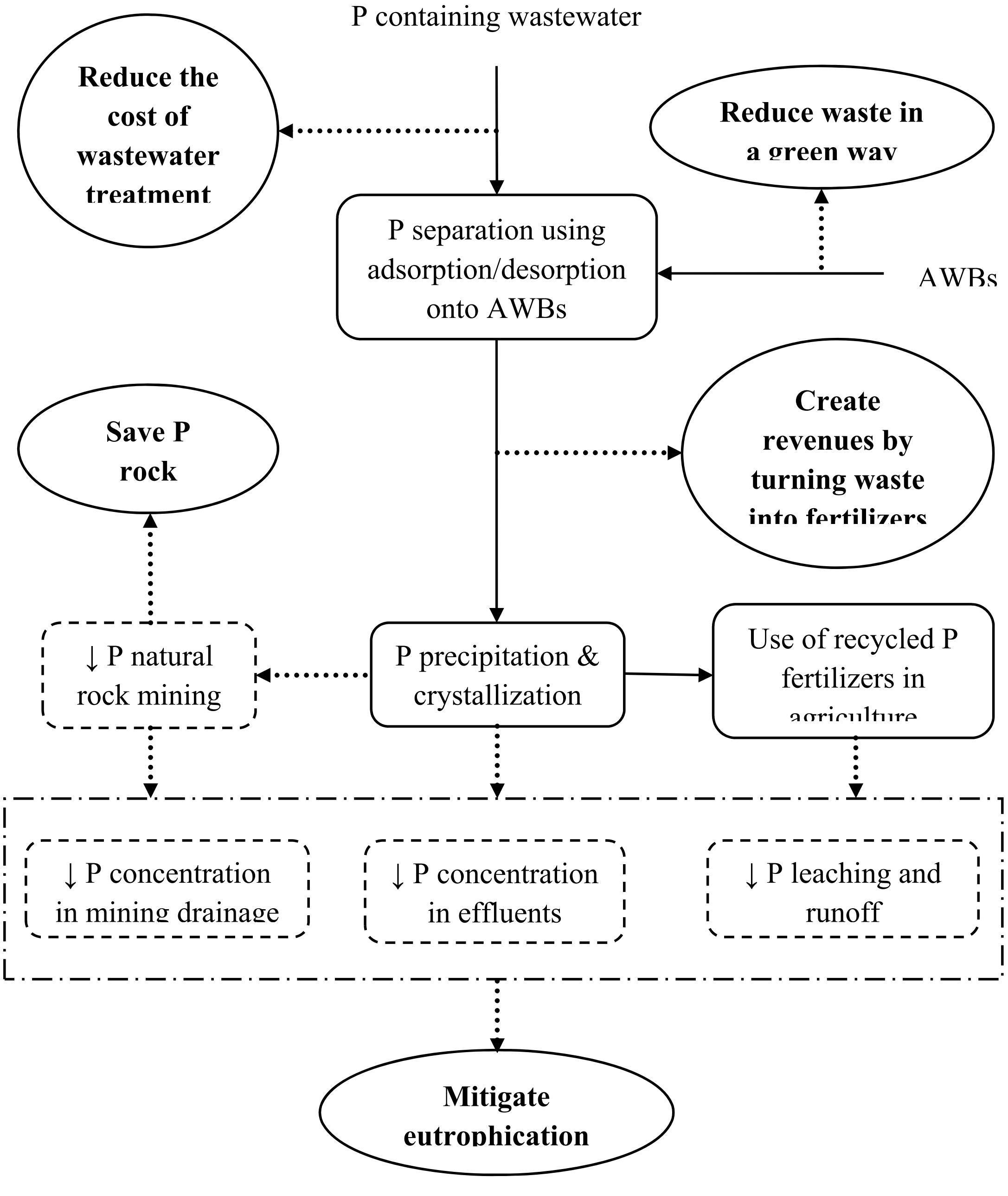


Figure 14.2. The benefits of using AWBs for P removal/recovery from wastewater

This chapter focuses on the fundamental and applied aspects of the removal/recovery of PO_4^{3-} from water and wastewater using AWBs. Part I (Section 14.2) provides new insights into adsorption and desorption mechanisms. In addition, it refers to the effect of process parameters. Part II (Section 14.3) evaluates the adsorption performance of AWBs in both natural and modified forms. Also, this section mentions the recovery process of PO_4^{3-} using AWBs in terms of drivers, technologies, and barriers. Part III (Sections 14.4 and 14.5) summarizes the recent developments and proposes the future work.

14.2 Process Fundamentals

14.2.1 Mechanistic Aspects of Phosphorus Sorption Process

Insights in sorption mechanisms are necessary for optimizing the sorption process. Due to the complexity of these processes, various information (pH profile, desorption, kinetic, activation energy, etc.) and techniques (FTIR, XRD, TEM, etc.) have been used. The reported types of adsorption of PO_4^{3-} by AWBs include ion exchange, ligand exchange, surface precipitation, and diffusion.

14.2.1.1 Ion Exchange

This mechanism is considered as physical adsorption (electrostatic attraction). It is associated with very fast, weak and reversible adsorption, which occurs through the outer-sphere complex. This replaces any ion on the surface of an ion exchanger by a chemically equal number of another ion while preserving the electroneutrality of the ion exchanger (Loganathan et al. 2014). The ion exchange mechanism can be found in many studies removing P by AWBs, such as banana stem (Anirudhan et al. 2006); wood residues (Karachalios 2012); giant reed (Xu et al. 2011a); etc. A typical method to predict the type of adsorption is based on the activation energy (E) magnitude. While E values in the range of 8−16 kJ/mol represents the chemical adsorption, E values lower than 8 kJ/mol stand for physical adsorption. The E values for the sorption of P onto modified wheat residue, modified sawdust and calcined waste eggshell were found to be 3.39 3.088, 0.4 kJ/mol, respectively. This implies that physical adsorption might be dominant sorption mechanism in these cases (Xu et al. 2009; Benyoucef and Amrani 2011; Kose and Kivanc 2011). Based on the effect of pH, Anirudhan et al. (2006) concluded that in the pH range of 5.0−7.0, the removal of P by quaternized banana stem could mainly be attributed to ion exchange between Cl^- of quaternary mine group and HPO_4^{2-}/ $H_2PO_4^-$ in the solution as follows:

$$2BS{-}CH_2{-}N^+H(CH_3)_2Cl^- + HPO_4^{2-} \rightarrow [BS - CH_2 - N^+H(CH_3)_2]_2HPO_4^{2-} + 2Cl^-$$

$$BS{-}CH_2{-}N{+}H(CH_3)_2Cl^- + H_2PO_4^- \rightarrow BS{-}CH_2{-}N{+}H(CH_3)_2\ H_2PO_4^- + Cl^-$$

Similarly, Xu et al. (2011a) proposed that the ion exchange could be an important pathway for the remediating P by modified giant reed. The replacement of chloride ions in the amine groups of quaternized giant reed by phosphate ions in the solution could occur as follows:

$$R'{-}N + (CH_2CH_3)_3 \ldots Cl^- + H_2PO_4^- \rightarrow R'{-}N + (CH_2CH_3)_3 \ldots H_2PO_4^- + Cl^-$$

From FTIR results, De Lima et al. (2012) suggested that the modification of coconut shell fibers with ammonium quaternary salt led to the integration of −NH_2 groups into the material. Consequently, the removal of P by quaternized coconut shell fibers occurred mainly via electrostatic interactions between −NH_2 groups and PO_4^{3-} anions.

14.2.1.2 Ligand Exchange

This is considered as chemical sorption, which is characterized by fast, strong and less reversible adsorption with reduced zero point charges. It may happen through the inner sphere complex, when PO_4^{3-} anions create a covalent chemical bond with a metallic cation on the surface of AWBs, leading to the liberation of other anions, which formerly attached to the metallic cation (Loganathan et al. 2014). This mechanism was reported for the case of decontaminating P by natural and iron impregnated coir pith (Krishnan and Haridas 2008). The authors suggested that in the pH range of 2.0−3.5, the ligand exchange occurred between $H_2PO_4^-$ ions and surface OH^- groups to form inner-sphere complexation as follows:

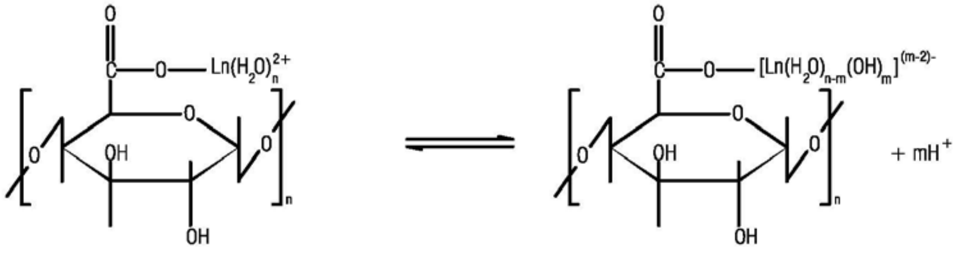
$$\mathrm{CP{-}OH} + H_2PO_4^- \xrightarrow{H^+} \mathrm{CP{-}}\,(H_2PO_4) + H_2O$$

$$\mathrm{CP{-}Fe(OH)} + H_2PO_4^- \xrightarrow{H^+} \mathrm{CP{-}Fe}(H_2PO_4) + H_2O$$

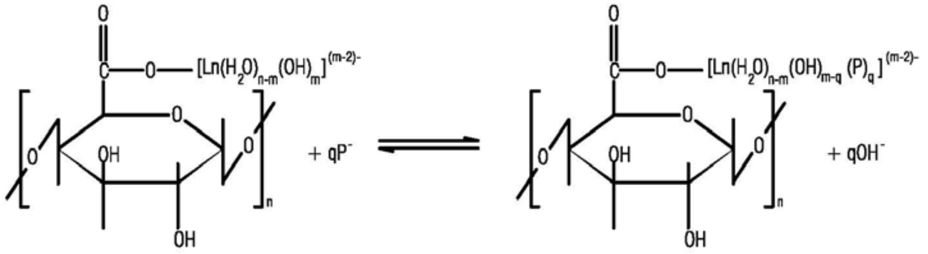
Likewise, based on the effect of pH, Biswas (2007) concluded that the adsorption of P by metal loaded orange waste (SOW) gels was possibly due to ligand exchange mechanism between PO_4^{3-} ions and OH^- ions coordinated on the metal ions impregnated on the orange waste gels (Schemes 14.1 &14.2). The authors suggested that loaded metal ions could be readily converted into hydrated forms e.g. $[Ln(H_2O)_n]^{3+}$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, and $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species with the abundant amount of OH^- ions and H_2O molecules. The H_2O molecules were deprotonated by releasing H^+ ions to form OH^- ions, which could be replaced by PO_4^{3-} ions via the ligand exchange mechanism.

14.2.1.3 Surface Precipitation

When the concentration of components of the precipitate surpasses the solubility product of the precipitate, the precipitation of P with metallic ions may take place on the surface of AWBs. This mechanism is described as fast and hardly reversible adsorption. Using the X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) results, Shin et al. (2005) verified the contribution of surface precipitation to the PO_4^{3-} binding onto La(III) loaded bark fiber. Based on kinetic studies, Namasivayam et al. (2005) concluded that the removal of P by oyster shell powder (OSP) was probably through precipitation of P as calcium phosphate and then turned into hydroxyapatite on the surface of OSP.



Scheme 14.1. Formation of exchangeable hydroxyl ions during hydrolysis, where m =1 or 2; Ln stands for La(III), Ce(III), Fe(III) (Biswas et al. 2007)



Scheme 14.2. Ligand exchange reaction, where q = 1 or 2 and P represents phosphate anion (Biswas et al. 2007)

14.2.1.4 Intraparticle Diffusion

This process is known as physical sorption, which takes place inside pores and cavities of AWBs. It is characterized by irreversible and very slow adsorption, which may last for days to months (Loganathan et al. 2014). If intraparticle diffusion mechanism prevails, a plot between the PO_4^{3-} adsorption capacity and the square root of the contact time should be a straight line passing through the origin. The relationship attained in a study by Karachalios (2012) was non-linear. That clearly indicated that intra-particle diffusion could not play a major role in the sorption of PO_4^{3-} onto quarternized wood residues. Based on Transmission electron microscopy (TEM) results, Riahi et al. (2009) suggested that intra-particle diffusion led to the accumulation of PO_4^{3-} into internal cells of date palm fibers.

14.2.1.5 Co-existing Mechanisms

Due to the complex nature of the sorption process using AWBs, it is quite common that the process can be attributed to several mechanisms. Based on the effect of pH and desorption results, Anirudhan et al. (2006) and Namasivayan and Sangeetha (2004) concluded that ion exchange and chemisorption mechanisms could be important pathways for the removal of P by quaternized banana stem and $ZnCl_2$ activated carbon, respectively. Tshabalala et al. (2004) observed a reduction in PO_4^{3-} uptake with increasing ionic strength and presence of SO_4^{2-}, NO_3^- anions. For that reason, they suggested that ion exchange and Lewis acid-base interactions might be responsible for retention of PO_4^{3-} ions onto cationized milled wood residues. From P surface loading and spectroscopic analysis results, Shin et al. (2005) claimed that ion exchange and surface precipitation could contribute to the elimination of P by La(III) treated juniper bark fiber. Similary, physisorption and chemisorption mechanisms are found to co-exist in the studies conducted by Mezenner and Bensmaili (2009); Huang et al. (2010); Benyoucef and Amrani (2011). In a more recent study, Karachalios (2012) explored that the adsorption process of PO_4^{3-} onto quaternized pine bark residues resulted from both boundary layer and intra-particle diffusion mechanisms.

14.2.2 Mechanistic Aspects of Phosphorus Desorption Process

Desorption plays an important role in enabling the reusability of AWBs and recovery of P. The P can be efficiently eluted from spent AWBs by distilled water, salts, acids, and bases (Table 14.2).

In an attempt to reduce the cost of chemicals used for desorption and mitigate adverse impacts on the environment, some researchers have used distilled water as an eluent. Namasivayam and Sangeetha (2004) investigated desorption of P from spent $ZnCl_2$ activated coir pith carbon using distilled water at various pH values (2−11). Desorption was shown to be favored at pH 2 (30%) and pH 11 (50%), while suppressed in pH range of 3−11 (< 10%). The high desorbability at pH values 2&11 was explained by the dissociation constants of phosphate and the dominant phosphate species at different pH values. At pH 2, unionized H_3PO_4 species are dominant. These P species have low affinity toward the biosorbent, and thus providing favorable conditions for P desorption. At pH 11, more OH^- ions are available in the solution, leading to a stronger competition with HPO_4^{2-} and PO_4^{3-} for binding sites. That was the reason why the efficient desorption was obtained at pH 11. Nevertheless, the maximum desorption efficiency was the relatively low (50%). This was probably due to the fact that PO_4^{3-} ions were removed by both ion exchange and chemisorptions mechanisms, whereas only PO_4^{3-} ions removed by ion exchanged was desorbed. On the other hand, Mallampati and Valiyaveettil (2013) observed a relatively high desorption capacity (90%) in very short time (10 min.), when distilled water pH 12 was employed in case of desorbing P from Zr(IV) loaded apple peels. The successful desorption of P at high pH value was explained by the replacement of PO_4^{3-} on apple peel surface by OH^- anions in the solution.

Another means of desorption of P from AWBs is using neutral salts, e.g. NaCl, KCl. In some studies, the use of these salts at different concentrations resulted in particularly high desorption efficiencies, e.g. 99.8% for NaCl 0.2 M from quaternized wood residues (Karachalios 2012); 95.4% for NaCl 0.1 M from wheat straw anion exchanger (WS-AE) (Xu et al. 2010); 100% for NaCl 0.1 M from modified giant reed (Xu et al. 2011a). Conversely, very poor desorption capacities could be found in other studies, e.g. 0.7% for NaCl 0.5 M from calcined waste eggshell (Kose and Kivanc 2011); 11.2% and 13% for KCl 0.01 M from granular date stones and palm surface fibers, respectively (Ismail 2012). Loganathan et al. (2014) suggested that neutral salts were efficient eluents for weak and reversible sorption, where ion exchange could be an important pathway for the removal of P (e.g. Xu et al. 2010, 2011; Karachalios 2012). In contrast, for strong and less reversible sorption, which was controlled by such mechanisms as ligand exchange, surface precipitation, or chemisorptions, the efficacy of these salts was usually low (e.g. Kose and Kivanc 2011; Ismail 2012). The higher concentrations of neutral salts seem to favor desorption. A rise in the concentration of NaCl as an eluent from 0.001 to 0.1 M led to a significant improvement (48.7%) in P desorption efficiency of modified giant reed (Xu et al. 2011a). However, it should be emphasized that the use of neutral salts as desorbents at high concentrations may increase the salinity in arable lands once P desorbed by this method was recovered and applied as fertilizers (Loganathan et al. 2014). One advantage of desorbing by this method is a minor loss in the adsorption capacity and weight of AWBs after several cycles of operation. For example, the adsorption capacity of was found to decrease by 5.59% after 5 operation cycles for NaCl 0.2 M (Karachalios 2012); 9.58% after 4 operation cycles for NaCl 0.1 M (Xu et al. 2010). The slight weight loss (1−3%) was reported when NaCl 0.1 M was used for desorption of P from modified giant reed (Xu et al. 2011a). This property facilitates the reusability of AWBs.

In some cases, to improve desorption efficiency of P, distilled water and neutral salts have been replaced by acids or bases. Among these, NaOH and HCl are widely used. NaOH and HCl normally demonstrated remarkable desorption capacities. For example, the desorption efficiency was found to be 97.1% for NaOH 0.1M (Anirudhan et al. 2006); 85% for HCl 0.4 M and 95% for NaOH 0.2 M (Biswas 2008); 97.5% for HCl 0.1 M (Xu et al. 2010); 100% for HCl 0.1 M and NaOH 0.1 M (Xu et al. 2011a); 95.6% for NaOH 0.05 M (Zhang et al. 2012). High efficacy of acids or bases could be explained by the low affinity of dominant P species, such as H_3PO_4 (in acidic medium), HPO_4^{2-} and PO_4^{3-} (in alkaline medium), toward binding sites on AWBs surface. Another reason for that was the stronger competition in alkaline medium between OH^- ions and PO_4^{3-} for binding sites on AWBs. It is worth mentioning studies conducted by Ismail (2012) and Zhang (2012), where the adsorption was controlled by chemisoprtion mechanism. While KCl 0.01 M demonstrated very poor desorption capacities (11.2−13%), the satisfactory elution was observed for NaOH 0.05 M (95.6%). This provides strong evidence that, bases are superior to neutral salts in desorbing P in case of strong sorption. Both Xu et al. (2011a) and Zhang et al. (2012) found that, higher concentration of NaOH enabled desorption of P from spent AWBs. This was probably due to a stronger competition between OH^- ions and PO_4^{3-} for binding sites. Though HCl and NaOH were proven to be effective eluents, their application could result in some side effects. The loss in the adsorption capacity was shown to be 12% for NaOH 0.1 M (Anirudhan et al. 2006) or 10.53% for HCl 0.1 M (Xu et al. 2010). Particularly, the complete loss of the adsorption capacity of modified coconut shell fibers was recorded after the second cycle of reuse. This could be ascribed to the physical ruin of the biosorbent (De Lima et al. 2012). Xu et al. (2011c) revealed a weight loss of 12−18% as a result of using HCl 1 M as a desorbent. They attributed this to the corrosion of cellulose/hemicellulose structure. In addition, Biswas (2008) reported the release of La(III) during desorption when HCl 0.4 M was used as an eluent. In view of practical application, these effects are undesirable as they may reduce the stability and thus restricting reusability of AWBs. Hence, these factors need to be taken into consideration in exploring for appropriate desorbents. The appropriate desorbents should meet the following criteria: high desorption efficiency, satisfactory reusability of the biosorbent (e.g. negligible reduction in adsorption capacities after many cycles of reuse, marginal weight loss, etc.), and minimal detrimental impacts on the environment.

In some cases, desorption efficiency was found extremely poor e.g. 11.2−13% (Ismail 2012); 0.7−37.6% (Kose and Kivanc 2011); 11−13% (Riahi et al. 2009). It is recommended to use phosphorous bearing AWBs as fertilizers or soil conditioners in acid soils, due to their high contents of nutrients (P, Ca, Mg, etc.) (Loganathan et al. 2014). However, from the recovery of P point of view, with a desire to use recycled P to replace mineral P in many industries, appropriate AWBs should be easily regenerated and reused. This property needs to be taken into consideration when the selection of potential AWBs is made.

14.2.3 Factors Influencing Phosphorus Biosorption

14.2.3.1 Effect of pH

The pH value of the solution influences the dissociation, P species abundance, the chemical state of binding sites, and affinity of P species towards binding sites. The pH profiles are useful for elucidating sorption mechanisms, optimizing process, and selecting appropriate eluents. Thus, efforts have been directed toward identifying optimum pH values in various AWBs-PO_4^{3-} adsorption systems.

Generally, AWBs tend to effectively sequester PO_4^{3-} anions in a specific pH range, while extremely acidic or alkaline medium is found to suppress the process. Yue et al. (2010) found that pH range of 4−9 favored the adsorption of PO_4^{3-} onto modified giant reed (MGR), whereas pH < 4 or pH > 9 was found to be disadvantageous to the process. The authors explained this by dissociation constants of phosphate, dominant phosphate species in the solution, and affinity of phosphate ions towards binding sites. The dissociation constants of H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} are 2.12, 7.21 and 12.67, respectively (Biswas 2008). Consequently, the dominant P species can vary, depending on pH value of the aquatic medium.

Table 14.2. Comparison of PO_4^{3-} desorption capability of different elution solutions

Biosorbent	**Elution solution**	**Desorption efficiency (%)**	**Remark**	**References**
Modified banana stem	NaOH 0.1 M	First cycle 97.1 Fourth cycle 90.7	No weight loss	Anirudhan et al. (2006)
Zr(IV)-loaded SOW gel	NaCl HCl NaOH 0.2 M	NaCl 0 HCl < 40 NaOH 95	NaOH exhibited anextremely high desorption ability without any remarkable release of loaded Zr	Biswas (2008)
La(III)-loaded SOW gel	HCl 0.4 M	85	Lathanum was leaked	Biswas et al. (2007)
Modified coconut shell fibers	HCl	C1−50; C2−40; C3−40 RC1− 35; RC2−7	Significant loss of P adsorption capacity and remarkable reduction in P removal efficiency	De Lima et al. (2012)
Granular date stones (GDS) Palm surface fibers (PSF)	KCl 0.01 M	GDS 10−11.2; PSF 12.1−13	Low desorbability	Ismail (2012)
Quarternized pine bark residues	NaCl 0.2 M	99.8	Minor loss (5.59%) in PO_4^{3-} sorption capacity after 5 uninterrupted sorption−desorption cycles	Karachalios (2012)
Calcined waste eggshell	NaOH 0.5 M and NaCl 0.5 M	NaOH 37.6 NaCl 0.7	–	Kose and Kivanc (2011)
Apple peel	Distilled water at different pH values (2−12)	Acidic pH: minimum desorption pH 12: 90 (10min.)	Zr was not detached at various pH values	Mallampati and Valiyaveettil (2013)
$ZnCl_2$ activated coir pith carbon	Distilled water at different pH values (2−11)	pH 2: ~ 30; pH 11: 50; pH 3−11: < 10	Low desorbability	Namasivayam and Sangeetha (2004)
Zr(IV) loaded saponified orange waste	NaOH 0.2 M	93	Zr was not leaked during elution process	Ohura et al. (2011)
Iron(III) loaded carboxylatedpolyacrylamide grafted sawdust	Different extractants were tested, including $NaNO_3$, NaCl, Na_2SO_4, HCl, HNO_3, NaCl-HCl, H_2SO_4, NH_4NO_3-HNO_3 and NaOH	NaOH 96.8 Na_2SO_4 73.6 NH_4NO_3-HNO_3 50.8 HCl 36.8 NaCl 34.5	Adsorption capacity reduced by 8.9% after 3 cycles, recovery of phosphate decreased from 98.2% in the 1st cycle to 92.8% in the 3rd cycle, 3% sorbent weight loss after treatment with NaOH 0.1M	Unnithan et al. (2002)

Table 14.2. Continued

Biosorbent	**Elution solution**	**Desorption efficiency (%)**	**Remark**	**References**
Giant reed	HCl 0.1 M NaCl 0.1 M NaOH 0.1 M	HCl 100 NaCl 100 NaOH 100	Weight loss (1−3%)	Xu et al. (2011a)
Wheat straw anion exchanger	NaCl 0.1 M HCl 0.1 M	NaCl 86.6−95.4 HCl 87.4−97.5	Marginal reductions in their initial adsorption capacities	Xu et al. (2010)
Cotton stalk (CS) and wheat stalk (WS)	NaCl 0.1 M HCl 0.1 M	HCl CS 93.1−98.4; WS 93.7−98.9 NaCl CS 92.3−97.1; WS 95.0−98.2	5% weight loss with HCl 0.1M	Xu et al. (2011b)
Wheat straw (WS)	HCl 1 M	Medium cost resin: 98−100	12−18% weight loss	Xu et al. (2011c)
Sugarcane bagasse	NaOH 0.05 M	95.6		Zhang et al. (2012)

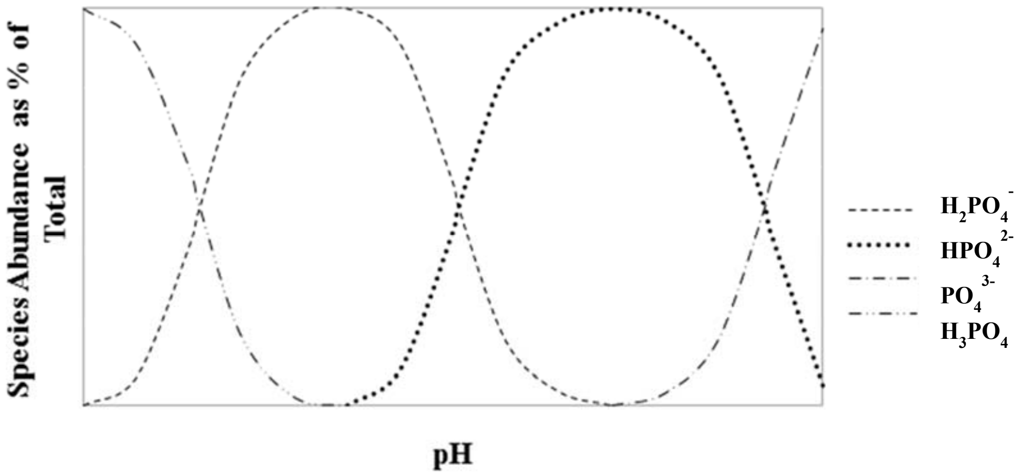


Figure 14.3. Orthophosphate species as a proportion of the total orthophosphate concentration (Hanrahan et al. 2005)

As can be seen from Figure 14.3, in the pH range of 4-9, $H_2PO_4^-$ and HPO_4^{2-} species were dominant. Due to their strong affinity toward binding sites, the sorption of P was enhanced. In contrast, at pH < 4, the H_3PO_4 and HPO_4^{2-} species were most common. Their inferior affinities toward binding sites led to the poor removal of P. In the same way, at pH > 9, HPO_4^{2-} and PO_4^{3-} species were prevalent. The weak affinity of these species for active site combined with strong competition between OH^- ions and PO_4^{3-} ions for adsorption sites hampered the process. Similarly, the effective pH range was found to be 5−7 for modified banana stem (Anirudhan et al. 2006); 7−10 for metal loaded orange waste gel (Biswas 2008); 3.5−6.0 for quaternized pine bark residues (Karachalios 2012); 3−10 for $ZnCl_2$ activated coir pith carbon (Namasivayam and Sangeetha 2004); 3−11 for calcined waste eggshell and modified sugarcane bagasse (Xu et al. 2011a; Zhang et al. 2012); 4−9 for modified giant reed (Yue et al. 2010), etc. This trend more or less agrees with the findings reported by Riahi et al. (2009) and Ismail (2012). They both found that an increase in the pH value led to a decrease in the P uptake. The authors explained this phenomenon by stronger repulsion force in the alkaline medium. The optimum pH values were found to be low (e.g. 2, 3) by Krishnan and Haridas (2008); Jeon and Yeom (2009); Mallampati and Valiyaveetttil (2013). On the other hand, high optimum pH values (e.g. 7.5, 10) were reported by Biswas (2008); Benyoucef and Amrani (2011); Jyothi et al. (2012). The former was explained by the dominance of $H_2PO_4^-$ species and their affinity toward binding sites in acidic medium (Mallampati and Valiyaveetttil 2013). In contrast, the latter was attributed to the possible existence of natural compounds and metal ions (e.g. Ca, Mg, Fe, Al, Cu, Zn) inside these AWBs, which had strong affinity toward HPO_4^{2-} in alkaline medium (Jyothi et al. 2012). It is worth pointing out that, in some studies, a wide pH range was found to have a marginal effect on the sorption of PO_4^{3-}, e.g. 4-10 for crab shells (Jeon and Yeom 2009); 5.0−10.5 for oyster shell powder (Namasivayam et al. 2005); 2−7.5 for scallop shells (Yeom and Jung 2009). Especially, De Lima et al. (2012) claimed that pH could hardly affect the sorption of PO_4^{3-} onto coconut fiber. It seems that many AWBs are highly effective in a wide pH range. This property represents an appreciable advantage of AWBs over conventional adsorbents for PO_4^{3-} removal.

14.2.3.2 Effect of Temperature

Normally, the adsorptive removal of PO_4^{3-} by AWBs is temperature sensitive. Some adsorption processes are endothermic, whilst others have exothermic nature. Mezenner and Bensmaili (2009) found that the retention of PO_4^{3-} by iron hydroxide eggshell was enhanced with a rise in the temperature from 20 to 45 °C. From the positive ΔH° (81.84 kJ/mol), they concluded that the adsorption was endothermic. It was assumed that, higher temperature led to the better solubility of iron hydroxide eggshell compound, and thus producing more iron and calcium hydrolysis complexes. Consequently, the phosphate precipitation was enhanced. Similar observations were noticed by Boujelben et al. (2008), Yeom and Yung (2009), Kumar et al. (2010), Benyoucef and Amrani (2011), Chen et al. (2012), and Peng et al. (2012). Benyoucef and Amrani (2011) explained this phenomenon by the enlargement of pore sizes, whereas Kumar et al. (2010) ascribed this to the better dissolution of PO_4^{3-} ions and higher rate of intra-particle diffusion at higher temperature. On the contrary, Yue et al. (2010) explored that the P uptake by modified giant reed declined from 19.89 to 17.79 mg/g as the temperature increased from 20 to 60°C, indicating the exothermic nature of the adsorption process. From negative values of ΔG° and ΔH°, Karachalios (2012) concluded that the adsorption of PO_4^{3-} by quaternized pine bark residues was exothermic. These results were in harmony with those reported by Kose and Kivanc (2011) and Xu et al. (2009). They explained that higher temperature resulted in stronger leakage of PO_4^{3-} ions from AWBs surface into the solution (Xu et al. 2009). Particularly, the change in the temperature from 15 to 45 °C could hardly affect the sorption of PO_4^{3-} onto crab shell (Jeon and Yeom 2009).

14.2.3.3 Effect of Initial Phosphorus Concentration

Typically, the uptake capacity of PO_4^{3-} increased, whilst the PO_4^{3-} removal efficiency decreased with a rise in the initial concentration of PO_4^{3-} ions. On the one hand, Mezenner and Bensmaili (2009) claimed that the extent of PO_4^{3-} removal by iron hydroxide eggshell waste decreased from 95 to 64% with increasing initial concentration of phosphate from 2.8 to 110 mg/L. Similar tendency has been reported for sugarcane bagasse by Zhang et al. (2012). The authors explained this by higher ratio of PO_4^{3-} moles to the active binding sites at higher PO_4^{3-} initial concentrations. For a specific dose of AWBs, the amount of binding sites is unchanged. Therefore, an increase in initial concentration of PO_4^{3-} led to the decrease in its percentage removal accordingly. On the other hand, Riahi et al. (2009) reported that the PO_4^{3-} adsorption capacity of date palm fibers increased from 1.45 to 5.85 mg/g as the initial phosphate concentration increased from 10 to 110 mg/L. These results were in consistent with those reported by Anirudhan et al. (2006); Mezenner and Bensmaili (2009); Xu et al. (2009); Kumar et al. (2010); Yue et al. (2010) and Zhang et al. (2012). Both Kumar et al. (2010) and Yue et al. (2010) attributed this to the stronger driving force to convey PO_4^{3-} ions from solution to the surface of AWBs at higher PO_4^{3-} initial concentrations. Mezenner and Bensmaili (2009) and Riahi et al. (2009) ascribed this to increasing interaction between binding sties and PO_4^{3-} ions, which resulted from the increase of PO_4^{3-} ions provided by higher PO_4^{3-} initial concentrations.

14.2.3.4 Effect of AWBs Dosage

The general trend is that PO_4^{3-} removal efficiency increases with a rise in the AWBs dose to a certain level then remains constant or reduces slightly with further increase in the AWBs dose. The better PO_4^{3-} removal efficiency at higher AWBs dose was explained by more binding sites for PO_4^{3-}adsorption and larger surface area available at higher dose of AWBs (Xu et al. 2009; Kose and Kivanc 2011; Zhang et al. 2012). The reduction in the PO_4^{3-} removal efficiency when the AWBs dose exceeded the optimum dose could be attributed to the resistance to mass transfer, particle aggregates and repulsive forces between binding sites at higher dose (Mezenner and Bensmaili 2009; Riahi et al. 2009; Ismail 2012). On the contrary, an increase in the dose of AWBs results in a reduction in P uptake capability. Karachalios (2012) found that the PO_4^{3-} uptake by modified pine bark residues decreased from 55 to 25 mg/g as the dose increased from 0.5 to 5 g/L. These results are in harmony with those reported by Yue et al. (2010) and Zhang et al. (2012). This could be ascribed to the lower PO_4^{3-} concentration gradient between solution and sorbent surface (Zhang et al. 2012). Conversely, Riahi et al. (2009) explored that the PO_4^{3-} uptake increased from 3.75 to 4.69 mg/g as date palm fiber dose increased from 2 to 6 g/L. However, further increase in biosorbent dose suppressed the sorption process. This can be explained by poor interaction between PO_4^{3-} ions and the biosorbent as a result of the roll up of fibers at excessive doses. In view of practical application, for the same removal efficiency, the lower the AWBs dose, the better the efficacy of AWBs is. For the referring purpose, PO_4^{3-} removal efficiency and the corresponding dose of AWBs in various adsorption systems were introduced as follows: 79.8% for 1 g/L of MSBG (Zhang et al. 2012); 92.5% for 2 g/L of modified wheat residue (Xu et al. 2009); 85−87% for 5 g/L of date palm wastes (Ismail 2012); 99.6% for 10 g/L of calcined waste eggshell (Kose and Kivanc 2011); and 98% for 16 g/L of modified giant reed (Yue et al. 2010).

14.2.3.5 Effect of Interfering Anions

Examining the effect of co-existing ions on the adsorption of PO_4^{3-} by AWBs is necessary to enhance the practical application of these biosorbents. Namasivayam and Sangeetha (2004) reported that Cl^-, NO_3^-, MoO_4^{2-}, VO_3^- scarcely affected the PO_4^{3-} removal by $ZnCl_2$ activated coir pith carbon. Equally, Biswas et al. (2007) revealed that the adsorption of PO_4^{3-} onto La(III) loaded SOW gel was not substantially influenced by the addition of Cl^-, CO_3^{2-}, SO_4^{2-}. In a later study, Biswas (2008) revealed that Cl^- (0.56 mM), CO_3^{2-} (0.33 mM), SO_4^{2-}(0.42 mM) could hardly affect the sorption of PO_4^{3-} (0.20 mM). Kose and Kivanc (2011) claimed that the addition of SO_4^{2-}, NO_3^- and NH_4^+ with the concentrations ranging from 10 to 50 mg/L had minor influences on the retention of PO_4^{3-} by calcined waste eggshell. Jyothi et al. (2012) discovered that such foreign anions as Cl^-, SO_4^{2-}, NO_3^-, F^- and CO_3^{2-} with the same concentration had minimum interference on the sorption of PO_4^{3-} by thermally activated barks/stems and their ashes of *Ficus religiosa,Cassia auriculata, Punica granatum* and *Calotropis gigantean.* The adsorption of PO_4^{3-} by AWBs was not affected by the presence of co-anions, implying the potential for employing these AWBs to the real wastewater. On the other hand, Namasivayam and Sangeetha (2004) explored that the presence of ClO_4^-, SeO_3^{2-} and SO_4^{2-} with the same concentrations as PO_4^{3-} hampered the removal of PO_4^{3-} ions. Likewise, Karachalios (2012) claimed that SO_4^{2-} was superior to NO_3^- in competing with PO_4^{3-} for binding sites. The higher Cl^- concentrations resulted in the lower PO_4^{3-} uptake. It is interesting to note that presence of divalent cations (i.g. Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+}) with the concentration 10 times greater than that of PO_4^{3-}, boosted the PO_4^{3-} extraction by thermally activated barks/ stems and their ashes of *Ficus religiosa,Cassia auriculata, Punica granatum* and *Calotropis gigantean* (Jyothi et al. 2012). The positive effect of divalent cations on the adsorption process suggests a way further to improve the PO_4^{3-} adsorption capacity of these biosorbents.

14.2.3.6 Effect of Contact Time

The contact time is an indicator of the speed of the adsorption process. Therefore, it is a critical factor in evaluating the efficacy of AWBs (Eljamal et al. 2013). In many cases, the adsorption was found to be rapid, reaching the equilibrium in approximately 1 h. The equilibrium time was found to be 20 min. for quaternized wood residues (Karachalios 2012); 25 min. for modified giant reed (Yue et al. 2010); 40 min. for modified sawdust (Benyoucef and Amrani 2011); and 60 min. for natural date palm wastes (Ismail 2012) and sugarcane bagasse (Zhang et al. 2011). In contrast, the longer contact time was necessary for the equilibrium to be reached by other AWBs. It was shown to be 15 h for La(III), Ce(III) and Zr(IV) loaded SOW gels (Biswas 2008); 12 h for iron impregnated coir pith (Krishnan and Haridas 2008); and 6 h for Zr(IV) loaded apple peels (Mallampati and Valiyaveettil 2013). The short contact time means that AWBs do not have to be kept in reactors for a long time, and thus the space can be saved. This can be considered as an advantageous property of potential AWBs, from a practical application point of view.

14.2.3.7 Effect of Particle Sizes of AWBs

Chen et al. (2012) found that PO_4^{3-} uptake capacity increased with a decrease in oyster shell diameter from 590 to 180 µm. Similarly, Yeom and Jung (2009) revealed that 100 mg PO_4^{3-}/L could be removed entirely by 1 g of scallop shells of 0.045 mm diameter in 3 h, whereas it was scarcely eliminated by that of 3 mm in 80 h. In the same way, Jeon and Yeom (2009) found that crab shells particles <1 mm in diameter showed a removal percentage >85%, whereas particles 3.35 mm could remove only 50%. These proved that smaller size of AWBs had an advantage when used for the adsorption of P. However, for prevention of a clogging problem in a packed-bed reactor, the optimum particles sizes need to be identified.

Table 14.3. Phosphate adsorption capacity and processing parameters of diverse phosphate - AWBs adsorption systems

Biosorbent	**Ads. cap. (mg PO_4^{3-}/g AWBs)**	**pH**	**Tem. (°K)**	**Initial P con. (mg /L)**	**Bios. dose (g/L)**	**Cont. time (min.)**	**Shaking speed (rpm)**	**References**
Natural AWBs								
Giant reed	0.836 column	5−10 (opt)	–	–	–	–	–	Xu et al. (2011a)
Sugarcane bagasse	1.10	4−11 (opt)	293	50 PO_4^{3-}	1	180	120	Zhang et al. (2012)
Coir pith	4.35	3		50 PO_4^{3-}	2	960		Krishnan and Haridas (2008)
Date palm fibers	13.33	6.8	291±2	50 PO_4^{3-}	6	120	200	Riahi et al. (2009)
Scallop shells	23.00	–	–	–	–	–	–	Yeom and Jung (2009)
Palm surface fibers	26.05	7−7.5	298	5, 10, 25, 50 P	5	120	200	Ismail (2012)
Granular date stones	26.66	7−7.5	298	5, 10, 25, 50 P	5	120	200	Ismail (2012)
Crab shells	108.9	2.0 (opt)	–	–	–	–	250	Jeon and Yeom (2009)
Modified AWBs								
Coir pith	5.10	3−10	308	10−40 PO_4^{3-}	6	–	200	Namasivayam and Sangeetha (2004)
Juniper fibre	7.08	–	298	10 P	2−20	1440	150	Han et al. (2005)
Coir pith	7.74	6 (opt)	308	40 P	4	180	150	Kumar et al. (2010)
Bark	12.65	–	298±1	0.1÷500 P	2.5	1440	7	Tshabalala et al. (2004)
Eggshell	14.49	–	293−318	2.8−110 PO_4^{3-}	2.5−20	–	–	Mezenner and Bensmaili (2009)
Biomass char	15.11	–	298±0.5	30 PO_4^{3-}	1	300	100	Peng et al. (2012)
Wood particles (modified by 2 methods)	2.05 & 17.38	–	298	100 PO_4^{3-}	4	1440	150	Eberhardt and Min (2008)
Soybean hulls	19.84	7	298	620 P	10	1440	300	Marshall and Wartelle (2004)
Apple peel	20.35	2 (opt)	303	5-200 PO_4^{3-}	10	360	200	Mallampati and Valiyaveettil (2013)

Note: Ads. cap. = Adsorption capacity; Tem. = Temperature; Con. = concentration; Bios. = Biosorbent; Cont. = Contact

Table 14.3. Continued

Biosorbent	Ads. cap. (mg PO_4^{3-} /g AWBs)	pH	Tem. (°K)	Initial P con. (mg /L)	Bios. dose (g/L)	Cont. time (min.)	Shaking speed (rpm)	References
Modified AWBs								
Sugarcane bagasse	21.30	4–11	293	50 PO_4^{3-}	1	180	120	Zhang et al. (2012)
Coir pith	22.05	3		50 PO_4^{3-}	2	960		Krishnan and Haridas (2008)
Eggshell	23.02	2-10	298	100 PO_4^{3-}	2 (opt)	60	140	Kose and Kivanc (2011)
Wood	26.03	–	298±1	0.1–200 P	1.67	1200	7	Karthikeyan et al. (2004)
Juniper bark fibre	33.35	6 (opt)	298	1–450 P	1	720		Shin et al. (2005)
La(III) loaded orange waste gel	42.72	7.5 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)
Ce(III) loaded orange waste gel	42.72	7.5 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)
Fe(III) loaded orange waste gel	42.72	3.0 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)
Bark	44.65	–	298±1	0.1-200 P	1.67	1200	7	Karthikeyan et al. (2004)
Wheat residue	45.70	–	–	50-500 PO_4^{3-}	–	–	–	Xu et al. (2010)
Giant reed	54.67 column	5–10 (opt)	–	–	–	–	–	Xu et al. (2011a)
Giant reed	60.95	4−9 (opt)	293	10−200 P	1	60	200	Yue et al. (2010)
Corn stover	62.70	7	298		10	1440	300	Wartelle and Marshall (2006)
Skin split waste (loaded with 2 types of metals)	21.65 & 72.00	7	303	47.5−285 PO_4^{3-}	1	1440	–	Huang et al. (2009)
Banana stem	72.46	2-10	303	10−300 PO_4^{3-}	2		200	Anirudhan et al. (2006)
Sawdust of Aleppo pine	116.25	7.5 (opt)	298	300 PO_4^{3-}	2	40	120	Benyoucef and Amrani (2011)
Pine bark residues	205.63	3.5–6 (opt)	293	200 P	1.25 (opt)	1440	200	Karachalios (2012)

Note: Ads. cap. = Adsorption capacity; Tem. = Temperature; con. = concentration; Bios. = Biosorbent; Cont. = Contact

14.3 Applications

14.3.1 Phosphorus Adsorption Performance by Unmodified AWBs

Unmodified AWBs have received far less attention for being used as adsorbents for the removal of PO_4^{3-} than their modified counterparts. Up to date, only a few reports exist on the use of raw AWBs for eliminating PO_4^{3-} e.g. Krishnan and Haridas (2008), Jeon and Yeom (2009), Riahi et al. (2009), Yeom and Yung (2009), Xu et al. (2011a), Ismail (2012), and Zhang et al. (2012). Table 14.3 introduces some natural AWBs and their reported adsorption capacities for PO_4^{3-}. For comparison purpose, the levels of PO_4^{3-} retention by typical conventional adsorbents are shown in Table 14.4.

Table 14.4. Maximum adsorption capacity of various conventional adsorbents

Adsorbent	**q_{max} (mg PO_4^{3-}/g)**	**References**
Natural adsorbents		
Zeolite	0.92	Jiang et al. (2013)
Pb-Zn tailings	1.07	Wang et al. (2013)
Pyrrhotite	1.15	Li et al. (2013)
Granular boehmite	8.40	Ogata et al. (2012)
Fe-Mn binary oxide	22.99	Zhang et al. (2009)
Composite metal oxides synthesized from Mn ore tailings	26.30	Liu et al. (2012)
Pumice	36.40	Karimaian et al. (2013)
Hydrous zirconium oxide	61.00−66.00 (298−338 K)	Rodrigues et al. (2012)
Fe-Zr binary oxide	76.31 (pH 8.5)	Ren et al. (2012)
Tantalum hydroxide	78.50−97.00 (298−338 K)	Yu et al. (2012)
AMD (Acid mine drainage sludge)	98.00	Bhojappa (2009)
Fe-Zr binary oxide	102.35 (pH 5.5)	Ren et al. (2012)
Goethite	144.00	Peleka and Deliyanni (2009)
Titanium	151.02	Choi et al. (2011)
Modified adsorbents		
Naturally iron oxide coated sand	0.88	Boujelben et al. (2008)
Synthetic iron oxide coated	1.50	Boujelben et al. (2008)
Iron oxide coated crushed brick	1.80	Boujelben et al. (2008)
Sponge iron	3.37	Jiang et al. (2013)
Vesuvianite doped with La(III)	4.05	Li et al. (2009)
Activated carbon fiber loaded with La(III) oxide	5.85	Zhang et al. (2011)
Zeolite modified with La/Al	7.44	Meng et al. (2013)
Activated carbon fibre doped with La(III)	6.34−7.92 (NaCl 0.001 to 0.1 M)	Liu et al. (2011)

Table 14.4. Continued

Adsorbent	**q_{max} (mg PO_4^{3-}/g)**	**References**
Modified adsorbents		
Activated carbon doped with Fe(III)	8.13	Wang et al. (2012)
Activated alumina	9.90	Li et al. (2009)
Montmorillonite pillared with Al/ La−Al	10.31/13.02	Tian et al. (2009)
Bentonite modified with Al/Fe/Fe-Al	12.7/ 11.20 /10.50	Yan et al. (2010)
Activated carbon doped with Fe(II)	14.12	Wang et al. (2012)
Zeolite modified with lanthanide	24.60	Ning et al. (2008)
Silica sulphate	46.32	Jutidamrongphan et al. (2012)
Pumice modified with $MgCl_2$	54.27	Karimaian et al. (2013)
Hydrotalcite coated with sulphate	68.09	Choi et al. (2012)
Fe(III)-AM-PGMACell	70.11	Anirudhan and Senan (2011)
Activated alumina coated with sulphate	152.21	Choi et al. (2012)
Zeolite coated with sulphate	341.66	Choi et al. (2012)
Commerical adsorbents		
Zr-MCM 41	3.36	Jutidamrongphan et al. (2012)
Whatman QA-52	14.26	Marshall and Wartelle (2004)
Zirconium ferrite	27.73	Jutidamrongphan et al. (2012)
Duolite A-7	31.74	Anirudhan et al. (2006)
Amberlite IRA-400	32.24	Marshall and Wartelle (2004)
Aluminium oxide	34.57	Peleka and Deliyanni (2009)
Zirconium ferrite	39.84	Biswas (2008)
Dowex	40.23	Anirudhan and Senan (2011)
Hydrotalcite	60.00	Peleka and Deliyanni (2009)
Zirconium loaded MUROMAC	131.77	Biswas (2008)

Among existing raw AWBs, crab shell displayed the highest PO_4^{3-} adsorption capacity (108.9 mg/g) (Jeon and Yeom 2009). This value is higher than those obtained with the majority of the commercial adsorbents (3.36−60 mg/g). This was assumed that not only calcium carbonate but also proteins and cellulose-like backbone of the crab shells played significant roles in the PO_4^{3-} retention. The extremely good adsorption capacity places crab shell among the best AWBs currently available for PO_4^{3-} removal, in term of the adsorption capacity. In contrast, other unmodified AWBs displayed the adsorption capacity in the range of 1.10−26.66 mg/g. These values are significantly lower when compared with many well-known commercial adsorbents (31.74−131.77 mg/g). Obviously, with very few exceptions, the removal of PO_4^{3-} by unmodified AWBs was not efficient enough for practical implications. This can be explained by the fact that as the lignocellulosic materials, unmodified AWBs contain a large amount of negatively charged functional groups

(−OH, −COOH) on their surface. Consequently, raw AWBs are supposed to be less effective in decontaminating anionic contaminants than cationic ones (Mallampati and Valiyaveetttil 2013). Because of the lack of efficacy, the widespread use of unmodified AWBs for decontaminating PO_4^{3-} from wastewater is still limited.

14.3.2 Phosphorus Adsorption Performance by Modified AWBs

Most of unmodified AWBs are inefficient in decontamination of P from water and wastewater. The reason is supposed to be the lack of anion binding sites on the AWBs surface. Thus, to improve the affinity of AWBs towards P, AWBs need to be cationized (Nguyen et al. 2012; Mallampati and Valiyaveettil 2013). This could be done via metal loading, hybridizing with inorganic chemicals, and grafting with ammonium type chemicals (Han et al. 2005).

Among these methods, metal loading appears to be preferred, because of its simplicity and effectiveness. It was found that metal oxides (e.g. Fe, Al, Mn, etc.) in some low-cost materials played important roles in their PO_4^{3-} retention capability (Penn et al. 2007; Liu et al. 2012). These may suggest a solution for the enhancement of P uptake in AWBs, which is metal impregnation. It was assumed that metals can be deposited on the surface of AWBs via chemical interactions e.g. substitution for Ca(II) or binding onto active sites (Han et al. 2005). It is expected that metal treated AWBs with high positive charges can sequester effectively PO_4^{3-} anions (Cheng et al. 2013). The common metals used for cationization of AWBs include Zn(II), Fe(II, III), La(III), Ce(III), Zr(IV). These metals can be used alone or in combination (Eljamal et al. 2013). Each metal has its own merits and demerits when used as modifiers of AWBs. While La(III) has a high affinity toward PO_4^{3-} anions and non toxicity, it suffers from drawbacks associated with the limited reusability (Zhang et al. 2011). Zr(IV) possesses favorable characteristics, such as high affinity and selectivity, large surface area, and chemical stability. Nevertheless, high cost is a critical factor, limiting its commercial application in PO_4^{3-} removal (Mallampati et al. 2013). Similarly, though the properties of cheapness, easy acquiring and non-hazardousness enable the use of Fe(II, III) for this purpose, their week point is less sorption efficiency. Based on this, it seems to be a good idea to use loading metals collectively to make use of their advantages while mitigating their drawbacks (Ren et al. 2012). Some researchers have treated raw AWBs directly with metal solutions, e.g. Han et al. (2005); Krishnan and Haridas (2008); Huang et al. (2009); Kose and Kivanc (2011); Mallampati and Valiyaveettil (2013). Krishnan and Haridas (2008) found that, the maximum PO_4^{3-} adsorption capacity of Fe impregnated coir pith (CP-Fe-I) was improved 5-6 times as compared to natural coir pith (CP), owing to iron impregnation. The adsorption capacity of AWBs directly loaded with metals was in the range of 7.08−23.02 mg/g (Table 14.5). These values were found to be in the same order of magnitude as those achieved for modified conventional adsorbents (0.88−14.12 mg/g), but still far lower when compared with many commercial adsorbents (27.73−131.77 mg/g) (Table 14.4). To further improve the P uptake capacity of modified AWBs, efforts have been directed toward strengthening the anchor of metals on the surface of AWBs via reactions with carboxylation or bases. Eberhardt and Min (2008) explored that the PO_4^{3-} adsorption capacity by wood particles modified by carboxymethylation and Fe(II) was 8.47 times higher than that of wood particles pretreated with Fe(II) alone. Similar observation was noticed by Carvalho et al. (2011). They reported that due to carboxymethylation, the adsorption capacity of Fe(II) by sugarcane bagasse fibers was boosted 371.25%.

This was supposed to be responsible for a rise in the PO_4^{3-} removal efficiency, from 94 to 97%. In their 2007 and 2008 studies, Biswas (2008) used $Ca(OH)_2$ and NaOH to enhance the incorporation of La(III), Ce(III), Fe(III) and Zr(IV) into orange waste. The modified orange waste gels displayed satisfactory sorption behaviors. The PO_4^{3-} uptake capacity reached as high as 42.72 mg/g for gels loaded with La(III), Ce(III) and Fe(III) and 174.68 mg/g for gels loaded with Zr(IV). The former can be in competition with some modified adsorbents while the latter is superior to all commercial adsorbents given in Table 14.4. The effectiveness of metal loaded AWBs is found to rely on the type and concentration of metal solutions as well as method of metal loading onto the AWBs surface. Wang et al. (2012) reported that AC/N-Fe(II) exhibited better adsorption capacity for PO_4^{3-} than AC/N-Fe(III). The authors ascribed this to higher intra-particle diffusion and binding energy of AC/N-Fe(II) in comparison with AC/N-Fe(III). Shin et al. (2005) found that the level of PO_4^{3-} capture by La(III) loaded juniper bark fiber was improved from 20.05 to 33.35 mg/g as the concentration of $La(NO_3)_3{\cdot}6H_2O$ increased from 0.01 M to 0.1 M. Nada and Hassan (2006) revealed that etherification was more efficient than oxidation and esterification in deposition of all four investigated heavy metals (i.e., Cu, Fe, Ni, Cr) onto carboxymethyl cellulose.

Another way to cationize AWBs is quarternization. This can be done via reactions between hydroxyl (OH^-) groups in AWBs with amines ($-NH_2$) groups in quaternary ammonium compounds (Nada and Hassan 2006; Karachalios 2012; Karachalios 2012). This process includes two steps, namely cross-linking and quaternizing (Marshall and Wartelle 2004). Quartenization improves the PO_4^{3-} adsorption capacity of raw AWBs, possibly owing to better anion exchange capacity (Wang et al. 2010), larger surface area and higher number of amine groups (Xu et al. 2010). Various quaternizing reagents have been tested for this purpose, e.g. dimethylamine (Anirudhan et al. 2006); urea (Benyoucef and Amrani 2011; Karachalios 2012); 2-hidroxypropyltrimethyl ammonium chloride (De Lima et al. 2012); polyallylamine hydrochloride (Karthikeyan et al. 2004); trimethylammoniumchloride (Marshall and Wartelle 2004; Wartelle and Marshall 2006); ethylenediamine & triethylamine (Wang et al. 2010; Yue et al. 2010; Xu et al. 2011a), etc. In most cases, quaternized AWBs exhibited the enhanced adsorption capacities for PO_4^{3-} as compared to raw AWBs. Zhang et al. (2012) revealed that the PO_4^{3-} uptake capacity of quarternized sugarcane bagasse (MSBG) and raw sugarcane bagasse (SBG) was 21.30 and 1.1 mg/g, respectively. They explained this by the difference in the zeta potential between MSBG (32 mV) and SBG (-22 mV) after quarternization. Due to electrostatic interactions, the former favored the retention of

PO_4^{3-}, whilst the latter hinder the adsorption process. Similarly, Xu et al. (2009) found that modified wheat residue showed greatly higher PO_4^{3-} removal efficiency (92.5%) than raw wheat residue (4.8%). In a more recent study, Xu et al. (2011a) reported that amine grafted giant reed showed an extremely high PO_4^{3-} adsorption capacity (54.67 mg/g) as compared with raw giant reed (0.863 mg/g). It is interesting to note that quaternization of banana stem not only improved PO_4^{3-} removal efficiency by 25.8%, but also reduced COD by 83.40% as compared to raw materials (Anirudhan et al. 2006). Compared to some well-known commercial adsorbents (3.36−131.77 mg/g), comparable and higher adsorption capacities could be obtained with quaternized AWBs (45.7−205.63 mg/g) (Tables 14.4, 14.5). The extremely good adsorption capacity for PO_4^{3-} makes quaternized AWBs attractive for practical application. In view of searching potential AWBs for quaternization, Wartelle and Marshall (2006) recommended to use AWBs with low lignin-to-cellulose ratios, because of their strong affinity toward quarternizing reagents. These results highlight the potential of improvement of PO_4^{3-} uptake capacity of AWBs using quaternization.

In addition to metal loading and quaternization, thermal activation is shown to be efficient in boosting the P removal. Huang et al. (2010) found that preheating oyster shell in the temperature range of significantly 100−400 °C improved its adsorption capacity for PO_4^{3-} ions. While untreated oyster shells could hardly remove PO_4^{3-} from 80 mL wastewater with PO_4^{3-} concentration of 20 g/L, the removal efficiency of preheated oyster shells reached up to 100% after 3 or 4 days. This is attributed to the increase in the pore size and surface area. The temperature range of 500−700 °C resulted in the decrease in the P removal efficiency, owing to the collapse of pore structure while lack of $CaCO_3$ decomposition. The P removal percent increased again as temperature increased from 750 to 900 °C. This can be explained by the dominant presence of CaO, which plays an important role in the adsorption of PO_4^{3-}. Peng et al. (2012) found that better PO_4^{3-} uptake was achieved for pine sawdust char (BC) produced at the higher pyrolysis temperature. The maximum adsorption capacity of BC is comparable to Whatman QA−52 and higher−when compared with Zr-MCM 41.

Table 14.5. A summary on modification methods for developing better AWBs

Biosorbent	Modifying reagents	Maximum adsorption capacity (mg PO_4^{3-}/g)	References
Metal impregnation			
Wood particles	Fe(II) salt	2.05	Eberhardt and Min (2008)
Coir pith carbon	Zn(II) salt	5.10	Namasivayam and Sangeetha (2004)
Juniper fiber	Acid mine drainage (AMD)	7.08	Han et al. (2005)
Wood particles	Carboxymethylation + $FeCl_2$	17.38	Eberhardt and Min (2008)
Juniper bark fiber	$La(NO_3)_3.6H_2O$ 0.01M	20.05	Shin et al. (2005)
Apple peel	$ZrO_2Cl.8H_2O$	20.35	Mallampati and Valiyaveettil (2013)
Skin split waste	Al(III) salt	21.65	Huang et al. (2009)
Coir pith	$Fe(NO_3)_3.9H_2O$	22.05	Krishnan and Haridas (2008)
Eggshell	Calcination	23.02	Kose and Kivanc (2011)
Juniper bark fiber	$La(NO_3)_3.6H_2O$ 0.1M	33.35	Shin et al. (2005)
Orange waste	$Ca(OH)_2$ + La(III)/ Ce(III)/ Fe(III) salts	42.72 for 3 types of gels	Biswas et al. (2007)
Sugarcane baggage fibers	Carboxymethylation	67.50	Carvalho et al. (2011)
Skin split waste	Fe(III) salt	72.00	Huang et al. (2009)
Sugarcane baggage fibers	Carboxymethylation + $FeCl_2$	152.00	Carvalho et al. (2011)
Orange waste gel	$Ca(OH)_2$ + NaOH + Zr(IV) salt	174.68	Biswas (2008)
Quarternization			
Milled pine bark	Poly-allylamine hydrochloride (PAA HCl) + Epichlorohydrin	12.65	Tshabalala et al. (2004)
Wheat residue (Low/ medium/ high cost resins)	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	16.50/ 32.05/ 52.40	Xu et al. (2011c)
Soybean hulls	N-(3-chloro-2-hydroxypropyl) + Trimethylammonium chloride	19.84	Marshall and Wartelle (2004)

Table 14.5. Continued

Biosorbent	**Modifying reagents**	**Maximum adsorption capacity (mg PO_4^{3-}/g)**	**References**
Quarternization			
Sugarcane bagasse	Epichlorohydrin + N,N-Dimethylformamide + Dimethylamine + Pyridine	21.30	Zhang et al. (2012)
Milled woods/ bark	Poly-allylamine hydrochloride (PAA HCl) + Epichlorohydrin	26.03/ 44.65	Karthikeyan et al. (2004)
Yellow pine (wood/ bark)	Poly-allylamine hydrochloride (PAA-HCl) or 3 chloro -2- hydroxypropyltrimethylammonium chloride	22.83/36.65	Karthikeyan et al. (2002)
Wheat straw	Epichlorohydrin + Triethylamine + Pyridine	45.70	Xu et al. (2010)
Cotton stalk/ wheat stalk	Epichlorohydrin + N,N-Dimethylformamide + Diethylenetriamine + Trimethylamine	51.54/ 60.61	Xu et al. (2011b)
Giant reed	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	54.67	Xu et al. (2011a)
Giant reed	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	60.95	Yue et al. (2010)
Corn stover	N-(3-chloro-2-hydroxypropyl) + Trimethylammonium chloride	62.70	Watelle and Marshall (2006)
Banana stem	Epichlorohydrin + N,N-Dimethylformamide + Dimethylamine + Pyridine	72.46	Anirudhan e al. (2006)
Sawdust of Aleppo pine	Surface activation, acid prehydrolysis, urea treatment	116.25	Benyoucef and Amrani (2011)
Green coconut shell fibers	Ammonium quaternary salt (2-hidroxypropyltrimethyl ammonium chloride)	200.00	De Lima et al. (2012)
Wood residues	Choline chloride derivative + Urea + Imidazole	205.63	Karachalios (2012)
Thermal activation			
Pine sawdust char	Fast pyrolysis	15.11	Peng et al. 2012

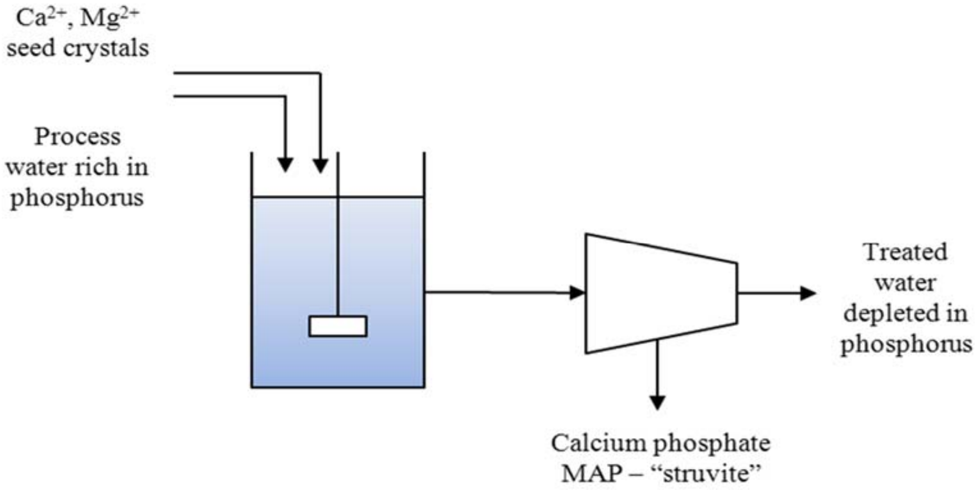
14.3.3 Phosphorus Recovery

14.3.3.1 Drivers for Phosphorus Recovery

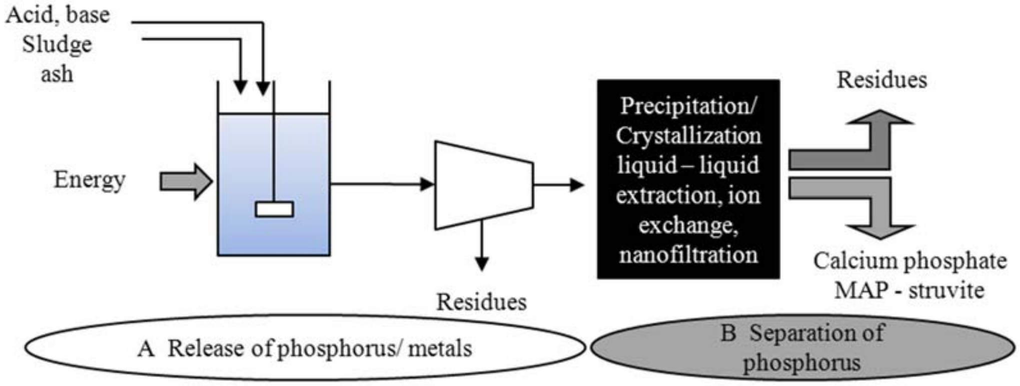
The P recovery is becoming a matter of interest in recent years. There are several drives for this. Firstly, the P recovery can contribute to conserving the global P rock reserves, which will be depleted within 150 years (Tyagi and Lo 2013; Loganathan et al. 2014). As the recycled P can replace the mineral P used in agriculture and phosphate industry, the P recovery is expected to diminish the amount of P rock mined annually, which is estimated at 160 million tons (Cornel and Schaum 2009; Kuzma 2011; Kalmykova and Fedje 2013). Secondly, the P recovery can protect the water environment from eutrophication by reducing P concentration in effluents. The increasing use of recycled P products as slow release fertilizers in the agriculture reduces the risk of P leaching and loss, and thus indirectly mitigating the eutrophication (Garcia-Belinchon et al. 2013). Moreover, the P recovery can create revenues by converting waste into commercial products. It is estimated that the P recovery from sewage sludge can produce a profit of about US$ 2.1 per capita and year (Tyagi and Lo 2013). Finally, this process may prevent struvite scale, which is a threat to most of the engineered systems (Kuzma 2011).

14.3.3.2 Phosphorus Recovery Technologies

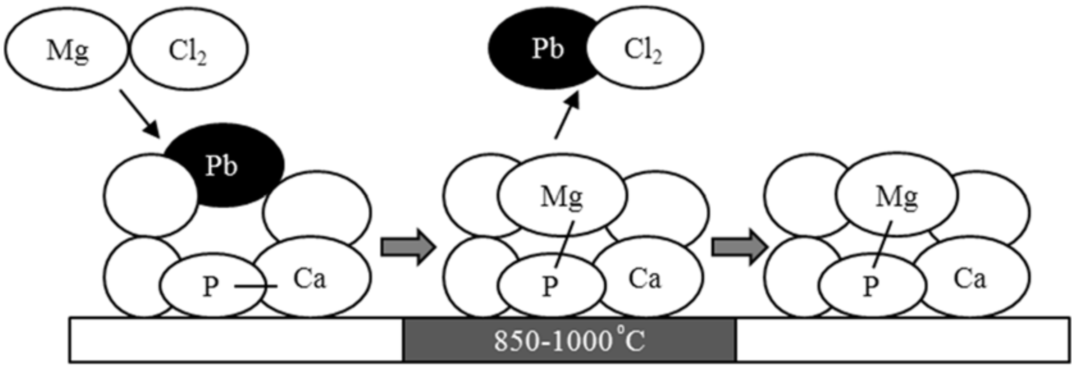
Till date, various technologies are available for P recovery. Depending on the WWTPs products (water, sludge or ash) utilized for P recovery, the P recovery technology can be precipitation/crystallization, wet-chemical or thermo-chemical, respectively (Figure 14.4). Due to very low P concentration (≤ 5 mg/L), effluents of WWTPs cannot be a good source, as high volume needs to be treated. On the contrary, the higher P concentration (20−100 mg/L) in the sludge liquor reduces the volume to be treated, and thus this product is widely used (Schick et al. 2009). As P in the sludge and ash is biologically/chemically bonded to other substances, it needs to be extracted by acids or bases before being separated by means of precipitation, ion exchange, nanofiltration, etc. This is the principle of wet-chemical technology. By using chlorine compounds (e.g. KCl, $MgCl_2$) and high temperature (>1000 °C), thermo-chemical technology is expected to remove heavy metals in the form of vaporized heavy metals chlorides, and thus enabling P separation. The P recovery potential may vary, depending on the utilized WWTPs products. While the recovery rate from the water phase is limited to 55%, the values from sewage sludge and ash can reach 90% (Cornel and Schaum 2009; Nieminen 2010). Among influential factors, pH and molar ratios of Mg^{2+}, NH_4^+, and PO_4^{3-} are found to play the critical roles in the P recovery process (Liu et al. 2012). The most common products of this process are magnesium ammonium phosphate (MAP, struvite) and calcium phosphate (Cornel and Schaum 2009).



(a) The principle of precipitation/crystallization technologies (Cornel at al. 2011)



(b) The principle of wet-chemical technology (Cornel et al. 2011)



(c) The principle of thermo-chemical technology (adapted from Adam 2011)

Figure 14.4. Phosphorus recovery technologies

14.3.3.3 Phosphorus Recovery by Means of Adsorption

P recovery is defined as the utilization of any process for precipitating or crystallizing P from wastewater, sewage sludge, and ash into a pure product for recycling purposes (Green et al. 2004). Although P recovery as struvite or calcium phosphate is widely known, only a few reports exist on the use of adsorption for this purpose. Ebie et al. (2008) investigated the P recovery in decentralized advanced Johkasou by means of adsorption onto Zr(IV). The spent adsorbent was immersed in the NaOH 7% solution to elute P. Because of the two-step desorption process, the desorption efficiency was enhanced from 80 to 95%. The maximum recovery efficiency (95.6%) was achieved by crystallization using low-temperature concentrator in vacuo. The recovered P product ($Na_{3.25}(OH)_{0.25}PO_4.12H_2O$) had the purity of > 95% with the permissible levels of hazardous elements (e.g. As, Hg, Pb, Cd, and Ni). The tests on germination rate and fertilizer response showed that recovered P was as good as Na_2HPO_4, a chemical fertilizer. As the elution solution after crystallization was recycled as a desorbent, the chemical costs and the disposal problems could be mitigated. Similarly, Midorikawa et al. (2008) utilized a high-speed adsorbent for P recovery from municipal wastewater secondary effluent. Due to the particularly high removal percentage (99.5%) and desorption efficiency (97%) of this adsorbent, P was successfully separated. $Ca(OH)_2$ was added to precipitate eluted P as calcium phosphate. With 16% P and very low levels of toxic substances, the recovered product could be used as a replacement for P ore and fertilizer. The works on P recovery via a combination of biosorption onto AWBs and precipitation/crystallization are rare. Most of the studies are limited to desorption of P and reusability of AWBs. It was found that some AWBs possessed very high desorption efficiencies with good reusability, e.g. modified banana stem (Anirudhan et al. 2006); Zr(IV) loaded orange waste gel (Biswas 2008); Zr(IV) loaded apple peels (Mallampati et al. 2013); modified sugarcane bagasse (Zhang et al. 2012), etc. Unfortunately, these AWBs have not been used in combination with precipitation/crystallization for P recovery.

Biswas (2008) claimed that P could be efficiently extracted from incinerated sewage sludge ash (ISSA) using 0.05 M H_2SO_4 or 0.1M HCl. Due to the selective adsorption onto Zr(IV) loaded orange waste gel, the extracted P was separated from other contaminants, e.g. Ca, Fe, Al, etc. The adsorbed P could be easily eluted using NaOH 0.2M. That paves the way to the recovery of P from ISSA. Kose and Kivanc (2011) proposed a procedure whereby the P eluted from calcined waste eggshell by NaOH 0.5 M could be recovered as calcium phosphate by the addition of solid CaO. Desorption and recovery efficiencies of P were 37.6% and 37.72%, respectively. It is inferred from the obtained results that, adsorption may hold a promise for P recovery from wastewater, but it has not been fully exploited. Based on published results, a diagram of P removal/recovery from wastewater by means of adsorption onto AWBs is proposed (Figure 14.5).

14.3.3.4 Barriers for Phosphorus Recovery

Until now, P recovery is still an un-established process. The reason for this remains in the quality of recycled P fertilizers (Sartorius et al. 2012). The excessive level of heavy metals in P fertilizers recovered from municipal solid waste incineration fly ash prevents them from being used in arable lands (Kalmykova and Fedje 2013). In addition, recycled P seems to be more expensive than mineral P (Cornel and Schaum 2009). The cost for P recovered from sludge liquor by ion exchange was 8.2 €/kg while that for mined P was only 0.652 €/kg (Bottini and Rizzo 2012). These findings are in harmony with those reported by Tyagi and Lo (2013), who claimed that recovered P was 22 times more costly than mined P. Molinos-Senante et al. (2011) suggested that the P recovery would not be a financially viable option, unless the environmental benefits were considered. These constraints are expected to be addressed in the next 20 years in developed countries (Sartorius et al. 2012).

14.3.4 Selection of Potential AWBs for P Removal and Recovery

The selection of proper AWBs for PO_4^{3-} removal/recovery plays an important role as it may affect the whole process. However, up to date, little work has been done on building the guideline for this. Consequently, while one AWB can be successfully tested in the lab, unexpected results can be obtained from its practical application. Thus, this section briefly discusses key criteria for screening potential AWBs in PO_4^{3-} removal/recovery.

It is well recognized that the main advantage of biosorbents as compared to other methods is their “cost-effectiveness” (Srivastava and Goyal 2010; Everglades hub 2013). Hence, this should be considered as a fundamental principle in selecting potential adsorbing materials. As mentioned above, the removal and recovery of PO_4^{3-} from wastewater using AWBs includes two steps: the separation of PO_4^{3-} followed by the precipitation/crystallization of PO_4^{3-}. While the first step can be done via selective adsorption with AWBs, the second step can be accomplished by using $Ca(OH)_2$, $CaCl_2$, etc. For that reason, ideal AWBs should have high affinity toward PO_4^{3-} anions to ensure their efficient removal. As raw AWBs are often prone to less adsorption efficiency, modification methods are required to improve PO_4^{3-} uptake capacity of raw AWBs. In addition, high selectivity is needed for separation of PO_4^{3-} anions from other pollutants. Moreover, easy desorption property may be necessary as it paves the way to P recovery. It should be noted that, these properties are necessary but not adequate for successful removal/recovery of PO_4^{3-}. Penn et al. (2007) suggested that while the cost and availability should be considered, in view of large scale application, the particle size or hydraulic properties may be significant if AWBs are used in the column mode. Similarly, Srivastava and Goyal (2010) highlighted reusability property as an efficient way to make the process cost-saving. Accordingly, ideal AWBs should have no physical damage, minor diminished P uptake, marginal weight loss, trivial loaded metal leakage, etc. after many cycles of adsorption and desorption. In the same way, Loganathan et al. (2014) suggested that suitable adsorbents for P removal/recovery should have a high sorption capacity, good hydrological conductivity and easy regeneration and proper reuse. Besides these things, from our own experience, we highly recommend that appropriate AWBs should not cause any significant detrimental effects on the quality of aqueous solutions (e.g. color, turbidity, DO, COD, BOD, heavy metals, etc.).

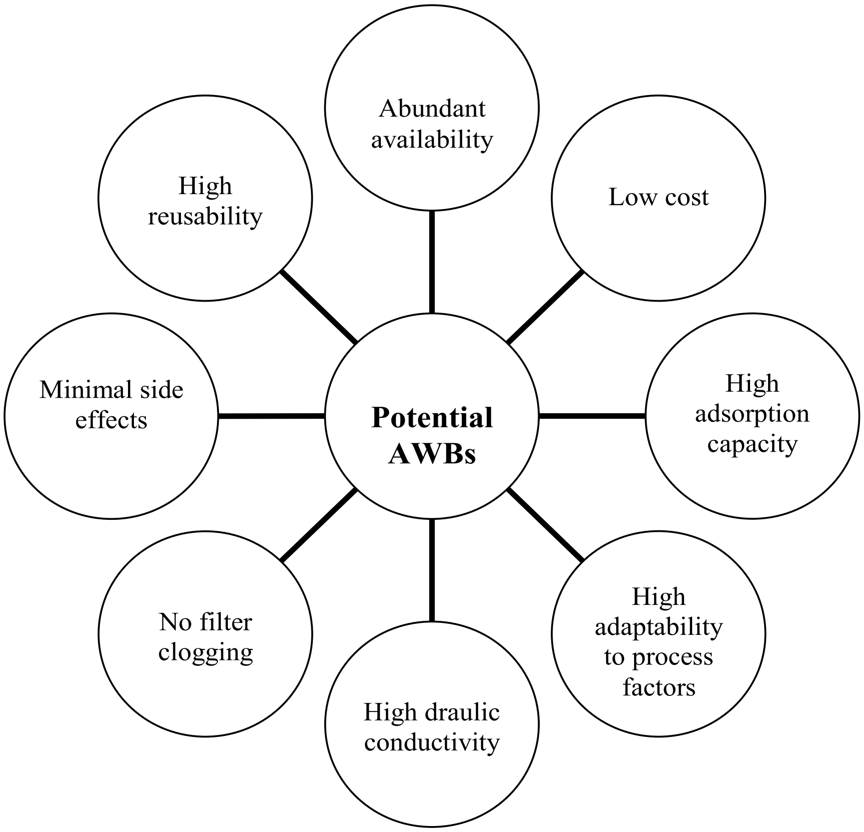


Figure 14.6. Selection criteria of potential AWBs used for P removal/recovery

Regarding the availability characteristic of AWBs, we suggest using wastes or by-products from food processing industries (e.g. orange peel, sugarcane bagasse, soybean milk residues, etc.) for developing potential AWBs, due to their stable quality and supply source. Keeping the above views in mind, appropriate AWBs for P removal/recovery should own the following properties:

- Abundant availability;
- Low cost;
- High affinity toward PO_4^{3-};
- High adaptability toward process parameters;
- High reusability;
- High hydraulic conductivity;
- No filter clogging; and
- Minimal side effects to the water environment.

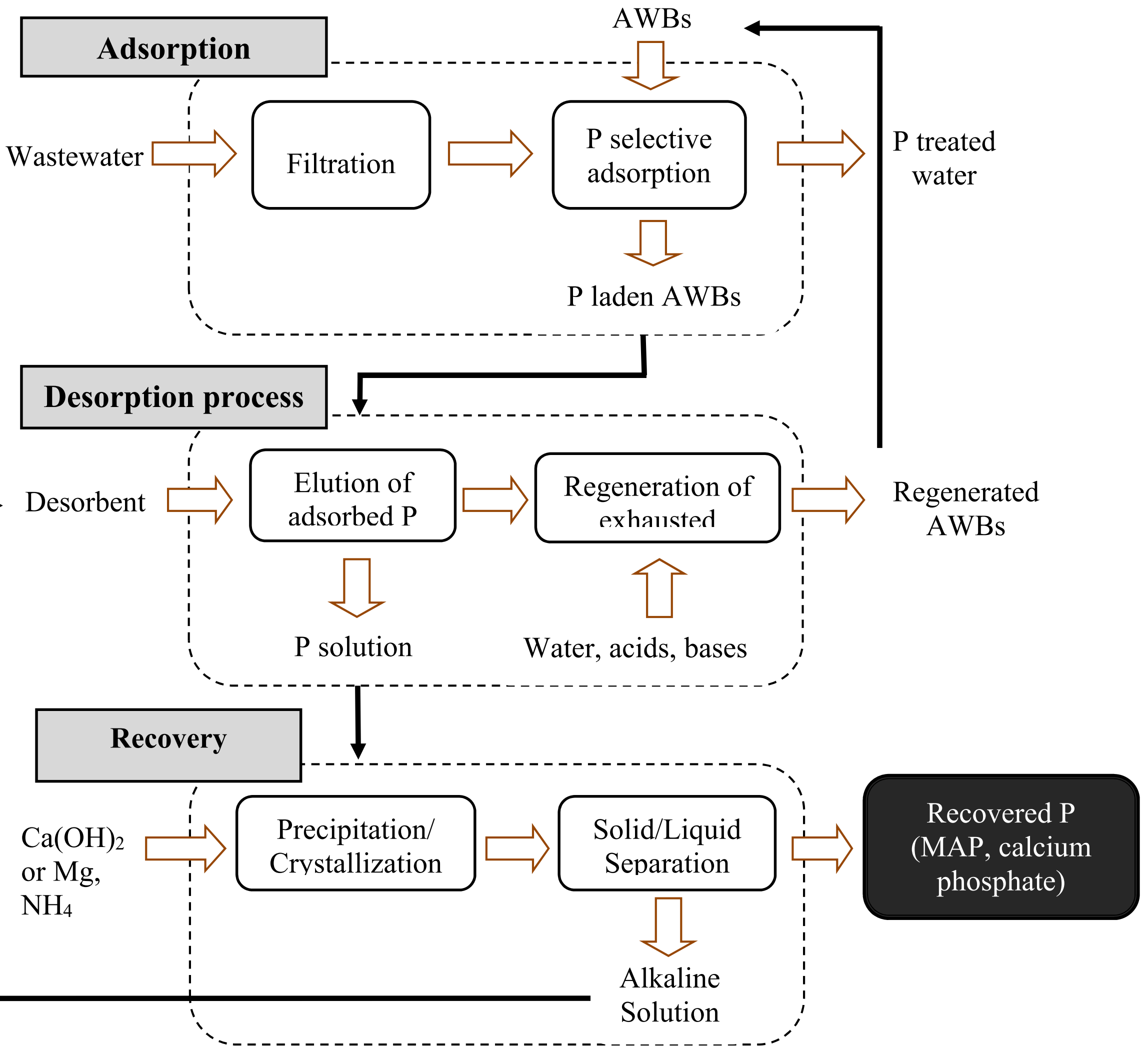


Figure 14.5. Diagram of P removal/recovery from water and wastewater via adsorption onto AWBs

14.4 Recent Advances

The adsorptive removal and recovery of PO^{3-} from water and wastewater using AWBs is a relatively new process. In the initial stage of its development, the results obtained mainly focus on basic knowledge. Understanding the operation principles is expected to enable the application of AWBs in the future. The recent developments drawn from studies on removal and recovery of PO^{3-} from water and wastewater using AWBs include:

- Confirming that raw AWBs are frequently inefficient in P removal and thus satisfactory decontamination of P requires appropriate modifications. The common methods are found to be metal loading and quaternization of AWBs. Side effects of modifying AWBs are also identified;
- Some potential AWBs have been found, mainly based on the maximum adsorption capacity;
- The mechanisms of the adsorption/desorption processes have been initially elucidated. This provides useful information for process optimization and selection of appropriate desorption solutions;
- The effects of process parameters have been investigated in an attempt to comprehend and optimize the process. For example, understanding the effect of pH can help to explain the desorption mechanism and choose the appropriate desorption solutions, whereas identification of the effect of particle sizes, contact time, interfering anions, etc. on the adsorption of P onto AWBs is necessary for their practical application; and
- The recovery of P based on the combination of adsorption onto AWBs and precipitation/ crystallization is initially investigated in the labs.

14.5 Conclusion and Future Work

Due to increasing concerns relevant to water quality deterioration and depletion of global P rock reserves, the P removal/recovery has recently become a matter of interest. Even though various technologies are presently available, adsorption seems to have advantages when used for P recovery. Due to selective adsorption property of AWBs, P can be separated from other contaminants and thus enabling P recovery in the next stage. Though AWBs in both natural and modified forms can be used for P removal, the low P uptake capacity of raw AWBs hinders their widespread application. In contrast, satisfactory adsorption behaviors can be obtained with AWBs modified by metal loading, $-NH_2$ groups grafting, and thermal activation. However, this should be applied with caution, due to possible side effects. While several mechanisms are reported for the sorption of PO_4^{3-} onto AWBs (e.g. ion exchange, ligand exchange, chemisorption, surface precipitation, and diffusion), it is found that desorption of PO_4^{3-} from spent AWBs can be largely attributed to anion-exchange mechanism. Of influential factors, pH appears to play the most important role. In many cases, AWBs demonstrated the ability to remove PO_4^{3-} efficiently in a short time (< 1 h), in the presence of interfering anions, over a wide pH range (4−9). These properties provide favorable conditions for their practical applications. The adsorbed P could be desorbed by distilled water, salts, acids, bases. Distilled water and neutral salts are proven to be effective as long as ion exchange mechanism dominates. Conversely, when other mechanisms can be important pathways, acids or bases should be used alternatively. The P recovery process is in its initial stage of development. It can be done via a combination of P separation using AWBs and P precipitation/crystallization using $Ca(OH)_2/CaCl_2$. Off these, the first step can be successfully accomplished through adsorption onto AWBs.

Although significant efforts had been contributed to make progress in the removal and recovery of PO_4^{3-} by AWBs, there are still many points for future research as follows:

1. Further improve modification methods that currently exist in the directions of cost saving, effectiveness, and environmental friendliness. This can be done via examining various quaternizing reagents and combined loading metals;
2. Keep searching for novel potential AWBs in view of practical application, which should have favorable physical properties, less harmful effects, low cost, abundant availability in addition to high affinity and selectivity towards PO_4^{3-}anions;
3. Developing a systematic and comprehensive method with essential tools to better understand mechanisms of adsorption and desorption;
4. Examining potential AWBs in the column mode on the real wastewater to promote large-scale application of these biosorbents; and
5. Employing potential AWBs in the PO_4^{3-} recovery process at the pilot and full scales. Further work in this matter includes process optimization, product quality improvement, simultaneous recovery of other resources, cost-benefit analysis, field trials, etc.

As a final remark, the adsorptive removal and recovery of PO_4^{3-} from water and wastewater using AWBs can provide a sustainable, efficient, beneficial solution for P management. Thus, it should be considered as a promising green technology. However, the above challenges need to be addressed before ready-to-use recycled P products can be achieved.

14.6 References

Adam, C. (2011). "Case study: Phosphorus recovery from sewage sludge – Results of the European FP6- and FP7-projects SUSAN and SUSYPHOS." *International Conference on Environmental (Bio)Technologies and EU–FP7 Environment Brokerage Event*, 5−8 September, Gdańsk, Pomeranian, Poland.

Anirudhan, T. S., Noelin, B. F., and Manohar, D. M. (2006). "Phosphate removal from wastewaters using a weak anion exchanger prepared from a lignocellulosic residue." *Environmental Science & Technology*, 40, 2740−2745.

Anirudhan, T. S., and Senan, P. (2011). “Adsorption of phosphate ions from water using a novel cellulose based adsorbent.” *Journal of Chemical Ecology*, 27(2), 147−164.

Benyoucef, S., and Amrani, M. (2011). “Adsorption of phosphate ions onto low cost Aleppo pine adsorbent.” *Desalination*, 275, 231−236.

Bhojappa, S. (2009). *Removal of phosphorus/ selenium from aqueous solution by adsorption processes*, Master Thesis, West Virginia University, Morgantown, West Virginia.

Biswas, B. K., Inoue, K., Ghimire, K. N., Ohta, S., Harada, H., Ohto, K., and Kawakita, H. (2007). “The adsorption of phosphate from an aquatic environment using metal loaded orange waste.” *Journal of Colloid and Interface Science,* 312, 214−223.

Biswas, B. K. (2008).*Removal and recovery of arsenic and phosphorus by means of adsorption onto orange waste, an available agricultural by−product*, Doctoral Dissertation, Saga University, Japan.

Bottini, A., and Rizzo, L. (2012). “Phosphorus recovery from urban wastewater treatment plant sludge liquor by ion exchange.” *Separation Science and Technology*, 47, 613−620.

Boujelben, N., Bouzid, J., Elouear, Z., Feki, M., Jamoussi, F., and Montiel, A. (2008). “Phosphorous removal from aqueous solution using iron coated natural and engineered sorbents.” *Journal of Hazardous Materials*, 151, 103−110.

Carvalho, W. S., Martins, D. F., Gomes, F. R., Leite, I. R., Silva, L. G., Ruggiero, R., and Richter, E. M. (2011). “Phosphate adsorption on chemically modified sugarcane bagasse fibres.” *Biomass Bioenergy*, 35, 3913−3919.

Chen, W. T., Lin, C. W., Shih, P. K., and Chang, W. L. (2012). “Adsorption of phosphate into waste oyster shell: Thermodynamic parameters and reaction kinetics.” *Desalination Water Treatment,* 47(1-3), 86−95.

Cheng, X., Wang, Y., Sun, Z., Sun, D., and Wang, A. (2013). “Pathways of phosphate uptake from aqueous solution by ZnAl layered double hydroxides.” *Water Science and Technology*, 67(8), 1757−1763.

Choi, J., Lee, S., Park, K., Lee, K., Kim, D., and Lee, S. (2011). “Investigation of phosphorus removal from wastewater through ion exchange of mesostructure based on inorganic material.” *Desalination*, 266, 281−285.

Choi, J., Lee, S., Lee, S., Kim, J., Park, K., Kim, D., and Hong, S. (2012). “Comparison of surface modified adsorbents for phosphate removal in water.” *Water Air & Soil Pollution*, 223, 2881−2890.

Cornel, P., and Schaum, C. (2009). “Phosphorus recovery from wastewater: needs, technologies and costs.” *Water Science and Technology*, 59(6), 1069−1076.

Cornel, P., Meda, A., and Bieker, S. (2011). *Chapter 4.12 Wastewater as a source of energy, nutrients, and service water*, Treatise on Water Science, Vol. 4, Elsevier, Oxford, UK.

De Lima, A. C. A., Nascimento, R. F., de Sousa, F. F., Filho, J. M., and Oliveira, A. C. (2012). “Modified coconut shell fibers: A green and economical sorbent for the removal anions from aqueous solutions.” *Chemical Engineering Journal*, 185-186, 274−284.

Eberhardt, T. L., and Min, S. H. (2008). “Biosorbents prepared from wood particles treated withanionic polymer and iron salt: Effect of particle size on phosphate adsorption.” *Bioresource Technology*, 99, 626−630.

Ebie, Y., Kondo, T., Kadoya, N., Mouri, M., Maruyama, O., Noritake, S., Inamori, Y., and Xu, K. (2008). “Recovery oriented phosphorus adsorption process in decentralized advanced Johkasou.” *Water Science and Technology*, 57(12), 1977−1981.

Eljamal, O., Okawauchi, J., Hiramatsu, K., and Harada, M. (2013). “Phosphorus sorption from aqueous solution using natural materials.” *Environmental Earth Sciences*, 68, 859−863.

Everglades hub (2013). *Phosphorous removal technologies*, available at http://www.evergladeshub.com/okeechobee/P.htm. (Accessed on January 14, 2013).

Garcia-Belinchon, C., Rieck, T., Bouchy, L., Gali, A., Rouge, P., and Fabregas, C. (2013). “Struvite recovery: pilot scale results and economic assessment of different scenarios.” *Water Practice & Technology*, 8(1), 119−130.

Green, C. J., Johnson, P., Allen, V. G., and Crossland, S. L. (2004). *Treatment technologies for phosphorus removal from water derived from cattle feedyards*, available at http://www.tcfa.org/Research/92_treatment_technologies_green.pdf. (Accessed on September 25, 2013).

Han, J. S., Min, S., and Kim, Y. (2005). “Removal of phosphorous using AMD−treated lignocellulosic material.” *Forest Products Journal,* 55(11), 48−53.

Hanrahan, G., Salmassi, T. M., Khachikian, C. S., and Foster, K. L. (2005). “Reduced inorganic phosphorus in the natural environment: significance, speciation and determination.” *Talanta*, 66(2), 435−444.

Hu, C., Zhang, T. C., Huang, Y. H., Dahab, M. F., and Surampalli, R. Y. (2005). “Effects of long-term wastewater application on chemical properties and phosphorus adsorption capacity in soils of a wastewater land treatment system.” *Environ. Sci. Technol.,* 39(18), 7240−7245.

Huang, M., Yu, Y., and Wu, R. (2010). “Researches on the treatment of phosphorous wastewater with oyster shells.” *Chinese Journal of Structural Chemistry*, 29(12), 1886−1892.

Huang, X., Liao, X., and Shi, B. (2009). “Adsorption removal of phosphate in industrial wastewater by using metal loaded skin split waste.” *Journal of Hazardous Materials*, 166, 1261−1265.

Ismail, Z. Z. (2012). “Kinetic study for phosphate removal from water by recycled date−palm wastes as agricultural by-products.” *International Journal of Environmental Studies*, 69(1), 135−149.

Jeon, D. J., and Yeom, S. H. (2009). “Recycling wasted biomaterial, crab shells, as an adsorbent for the removal of high concentration of phosphate.” *Bioresource Technology*, 100, 2646−2649.

Jiang, C., Jia, L., He, Y., Zhang, B., Kirumba, G., and Xie, J. (2013). “Adsorptive removal of phosphorous from aqueous solution using sponge iron and zeolite.” *Journal of Colloid and Interface Science,* 402, 246−252.

Jutidamrongphan, W., Park, K. Y., Dockko, S., Choi, J. W., and Lee, S. H. (2012). “High removal of phosphate from wastewater using silica sulphate.” *Environmental Chemistry Letters*, 10, 21−28.

Jyothi, M. D., Kiran, K. R., and Ravindhranath, K. (2012). “Phosphate pollution control in waste waters using new biosorbents.” *International Journal of Water Resources and Environmental Engineering*, 4(4), 73−85.

Kalmykova, Y., and Fedje, K. (2013). “Phosphorus recovery from municipal solid waste incineration fly ash.” *Waste Management*, 33, 1403−1410.

Karachalios, A. P. (2012). *Nutrient removal from water by various quaternized wood agricultural residues using a choline based ionic liquid analogue*, Doctoral Dissertation, Stevens Institute of Technology, Hoboken, New Jersey.

Karimaian, K. A., Amrane, A., Kazemian, H., and Panahi, R. (2013). “Retention of phosphorous ions on natural and engineered waste pumice: Characterization, equilibrium, competing ions, regeneration, kinetic, equilibrium and thermodynamic study.” *Applied Surface Science*, 284, 419−431.

Karthikeyan, K. G., Tshabalala, M. A., Wang, D., and Kalbasi, M. (2004). “Solution chemistry effects on orthophosphate adsorption by cationized solid wood residues.” *Environmental Science & Technology*, 38(3), 904−911.

Karthikeyan, K. G., Tshabalala, M. A., and Grad, D. W. (2002). “Use of lignocelluloses materials for sorption media for phosphorus removal.” *ASAE Annual International Meeting*, July 28−31, Chicago, Illinois.

Kose, T. E., and Kivanc, B. (2011). “Adsorption of phosphate from aqueous solutions using calcined waste eggshell.” *Chemical Engineering Journal*, 178, 34−39.

Krishnan, K. A., and Haridas, A. (2008). “Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith.” *Journal of Hazardous Materials*, 152, 527−535.

Kumar, P., Sudha, S., Chand, S., and Srivastava, V. C. (2010). “Phosphate removal from aqueous solution using coir pith activated carbon.” *Separation Science and Technology*, 45, 1463−1470.

Kuzma, M. (2011). *Phosphorus removal and recovery in wastewater: How far can we go?* Available at http://www.azwater.org/common/files/committees/e8fbf236-e225-4d3b-8e17-d94ae7beb19d/Matt%20Kuzma%20-%20Phosphorus%20Removal%20and%20Reocvery%20from%20Wastewater%20Oct%202nd%202011.pdf. (Accessed on September 19, 2013).

Li, H., Ru, J., Yin, W., Liu, X., Wang, J., and Zhang, W. (2009). “Removal of phosphate from polluted water by lanthanum doped vesuvianite.” *Journal of Hazardous Materials*, 168, 326−330.

Li, R., Kelly, C., Keegan, R., Xiao, L., and Morrison, L. (2013). “Phosphorous removal from wastewater using natural pyrrhotite.” *Colloids and Surfaces A,* 427, 13−18.

Li, Y. J., Wang, L. H., and Lan, Y. Z. (2009). “Experimental study on phosphorous removal by activated alumina adsorbents.” *Journal Kunming Metallurgy College*, 25, 59−65.

Liu, J., Wan, L., Zhang, L., and Zhou, Q. (2011). "Effect of pH, ionic strength, and temperature on the phosphate adsorption onto lanthanum doped activated carbon fiber." *Journal of Colloid and Interface Science*, 364, 490−496.

Liu, T., Wu, K., and Zeng, L. (2012). "Removal of phosphorus by a composite metal oxide adsorbent derived from manganese ore tailings." *Journal of Hazardous Materials*, 217-218, 29−35.

Loganathan, P., Vigneswaran, S., Kandasamy, J., and Bolan, N. S. (2014). "Removal and recovery of phosphate from water using sorption." *Critical Reviews in Environmental Science and Technology*, 44(8), 847-907.

Mallampati, R., and Valiyaveettil, S. (2013). "Apple peel−a versatile biomass for water purification." *ACS Applied Materials and Interfaces*, 5, 4443−4449.

Molinos−Senante, M., Hernandez-Sancho, F., Sala-Garrido, R., Garrido-Baserba, M. (2011). "Economic feasibility study for phosphorus recovery processes." *Ambio*, 40, 408−416.

Marshall, W. E., and Wartelle, L. H. (2004). "An anion exchange resin from soybean hulls." *Journal of Chemical Technology and Biotechnology*, 79, 1286−1292.

Meng, S., Li, Y., Zhang, T., Chen, J., Xu, P., Song, C., Fan, L., and Qiu, L. (2013). "Influences of environmental factors on lanthanum/aluminium modified zeolite adsorbent for phosphorous adsorption from wastewater." *Water, Air, & Soil Pollution*, 224, 1556−1564.

Mezenner, N. Y., and Bensmaili, A. (2009). "Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide eggshell waste." *Chemical Engineering Journal*, 147, 87−96.

Midorikawa, I., Aoki, H., Omori, A., Shimizu, T., Kawaguchi, Y., Kassai, K., and Murakami, T. (2008). "Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high−speed adsorbent." *Water Science and Technology*, 58(8), 1601−1607.

Namasivayam, C., Sakoda, A., and Suzuki, M. (2005). "Removal of phosphate by adsorption onto oyster shell powder − kinetic studies." *Journal of Chemical Technology and Biotechnology*, 80(3), 356−358.

Namasivayan, C., and Sangeetha, D. (2004). "Equilibrium and kinetic studies of adsorption of phosphate onto $ZnCl_2$ activated coir pith carbon." *Journal of Colloid and Interface Science*, 280, 359−365.

Nada, A. M. A., and Hassan, M. L. (2006). "Ion exchange properties of carboxylated bagasse." *Journal of Applied Polymer Science*, 102, 1399−1404.

Nieminen, J. (2010).*Phosphorus recovery and recycling from municipal wastewater sludge*, Master Thesis, Aalto University, Espoo, Finland.

Ning, P., Bart, H., Li, B., Lu, X., and Zhang, Y. (2008). "Phosphate removal from wastewater by model La(III) zeolite adsorbents." *Journal of Environmental Sciences*, 20, 670−674.

Neethling, J. B. (2011). *Impact of Phosphorous Removal to Low Limits*, available at http://www.azwater.org/common/files/committees/e8fbf236-e225-4d3b-8e17-d94ae7beb19d/Phosphorus%202.pdf. (Accessed on January 20, 2013).

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., and Nguyen, T. V. (2012). "Phosphorus removal from aqueous solutions by agricultural by-products: A critical review." *Journal of Water Sustainability*, 2(3), 193−207.

Ogata, F., Tominaga, H., Kangawa, M., Inoue, K., and Kawasaki, N. (2012). "Characteristics of granular boehmite and its ability to adsorb phosphate from aqueous solution." *Chemical & Pharmaceutical Bulletin*, 60(8), 985−988.

Ohura, S., Harada, H., Biswas, B. K., Kondo, M., Ishikawa, S., Kawakita, H., Ohto, K., and Inoue, K. (2011). "Phosphorus recovery from secondary effluent and side stream liquid in a sewage treatment plant using zirconium loaded saponified orange waste." *Journal of Material Cycles and Waste Management*, 13, 293−297.

Peleka, E. N., and Deliyanni, E. A. (2009). "Adsorptive removal of phosphates from aqueous solutions." *Desalination*, 245, 357−371.

Peng, F., He, P., Luo, Y., Lu, X., Liang, Y., and Fu, J. (2012). "Adsorption of phosphate by biomass char deriving from fast pyrolysis of biomass waste." *CLEAN – Soil, Air, Water*, 40(5), 493−498.

Penn, C. J., Bryant, R. B., Kleinman, P. J. A., and Allen, A. L. (2007). "Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials." *Journal of Soil and Water Conservation*, 62, 269−276.

Ren, Z., Shao, L., and Zhang, G. (2012). "Adsorption of phosphate from aqueous solution using an iron−zirconium binary oxide sorbent." *Water, Air, & Soil Pollution*, 223, 4221−4231.

Riahi, K., Thayer, B. B., Mammou, A. B., and Ammar, A. B. (2009). "Biosorption characteristics of phosphates from aqueous solution onto Phoenix dactylifera L. date palm fibers"*Journal of Hazardous Materials*, 170, 511−519.

Rodrigues, L. A., Maschio, L. J., Coppio, L. S. C., Thim, G. P., and Silva, M. L. C. P. (2012). "Adsorption of phosphate from aqueous solution by hydrous zirconium oxide." *Environmental Technology*, 33(12), 1345−1351.

Sartorius, C., Horn, J. V., and Tettenborn, F. (2012). "Phosphorus recovery from wastewater–expert survey on present use and future potential." *Water Environment Research*, 84(4), 313−322.

Schick, J., Kratz, S., Adam, C., and Schnug, E. (2009). "Techniques for P recovery from wastewater and sewage sludge and fertilizer quality of P recycling products." *Phosphorus Recycling Conference in Berlin*, available at http://www.mmm.fi/attachments/mmm/ministerio/5n8h6xg9T/presentation_judith_schick.pdf. (Accessed on September 14, 2013).

Shin, E. W., Karthikeyan, K. G., and Tshabalala, M. A. (2005). "Ortho phosphate sorption onto lanthanum treated lignocellulosic sorbents." *Environmental Science & Technology*, 39, 6273−6279.

Srivastava, S., and Goyal, P. (2010). *Novel biomaterials, decontamination of toxic metals from wastewater*, Springer, Heidelberg.

Tian, S., Jiang, P., Ning, P., and Su, Y. (2009). "Enhanced adsorption removal of phosphate from water by mixed lanthanum/aluminium pillared montmorillonite." *Chemical Engineering Journal*, 151, 141−148.

Tshabalala, M. A., Karthikeyan, K. G., and Wang, D. (2004). “Cationized milled pine bark as an adsorbent for orthophosphate anions.” *Journal of Applied Polymer Science*, 93, 1577−1583.

Tyagi, V. K., and Lo, S. (2013). “Sludge: a waste or renewable source for energy and resources recovery.” *Renewable & Sustainable Energy Reviews*, 25, 708−728.

Unnithan, M. R., Vinod, V. P., and Anirudhan, T. S. (2002). “Ability of iron(III)−loaded carboxylated polyacrylamide−grafted sawdust to remove phosphate ions from aqueous solution and fertilizer industry wastewater: Adsorption kinetics and isotherm studies.” *Journal of Applied Polymer Science,* 84(13), 2541−2553.

Wang, W., Yue, Q., Xu, X., Gao, B., Zhang, J., Li, Q., and Xu, J. (2010). “Optimized conditions in preparation of giant reed quaternary amino anion exchanger for phosphate removal.” *Chemical Engineering Journal*, 157, 161−167.

Wang, Z., Nie, E., Li, J., Yang, M., Zhao, Y., Luo, X., and Zheng, Z. (2012). “Equilibrium and kinetics of adsorption of phosphate onto iron doped activated carbon.” *Environmental Science and Pollution Research*, 19, 2908−2917.

Wang, S., Yuan, R., Yu, X., and Mao, C. (2013). “Adsorptive removal of phosphate from aqueous solutions using lead−zinc tailings.” *Water Science and Technology*, 67(5), 983−988.

Wartelle, L. H., and Marshall, W. E. (2006). “Quaternized agricultural by−products as anion exchange resins.” *Journal of Environmental Management*, 78, 157−162.

Xu, X., Gao, B., Wang, W., Yue, Q., Wang, Y., and Ni, S. (2009). “Adsorption of phosphate from aqueous solutions onto modified wheat residue: Characteristics, kinetic and column studies.” *Colloids and Surfaces B*, 70, 46−52.

Xu, X., Gao, B., Yue, Q., and Zhong, Q. (2010). “Preparation of agricultural by−product based anion exchanger and its utilization for nitrate and phosphate removal.” *Bioresource Technology*, 101, 8558−8564.

Xu, X., Gao, B., Yue, Q., and Zhong, Q. (2011a). “Sorption of phosphate onto giant reed based adsorbent: FTIR, Raman spectrum analysis and dynamic sorption/ desorption properties in filter bed.” *Bioresource Technology*, 102, 5278−5282.

Xu, X., Gao, B., Tan, X., Zhao, Y., Yue, Q., and Wang, Y. (2011b). “Characteristics of diethylenetriamine−crosslinked cotton stalk/ wheat stalk and their biosorption capacitites for phosphate.” *Journal of Hazardous Materials*, 192(3), 1690−1696.

Xu, X., Gao, B., Yue, Q., Zhong, Q., and Li, Q. (2011c). “Preparation of new types of anion exchange resins from agricultural by−products and their utilization in the removal of various toxic anions from solutions.” *Chemical Engineering Journal,* 167, 104−111.

Yan, L., Xu, Y., Yu, H., Xin, X., Wei, Q., and Du, B. (2010). “Adsorption of phosphate from aqueous solution by hydroxyl aluminium, hydroxyl iron and hydroxyl iron aluminium pillared bentonites.” *Journal of Hazardous Materials*, 179, 244−250.

Yeom, S. H., and Jung, K. (2009). “Recycling wasted scallop shell as an adsorbent for the removal of phosphate.” *Journal of Industrial and Engineering Chemistry*, 15(1), 40−44.

Yu, S., Dong, X., Gong, H., Jiang, H., and Liu, Z. (2012). “Adsorption kinetic and thermodynamic studies of phosphate onto tantalum hydroxide.” *Water Environment Research*, 84(12), 2115−2122.

Yue, Q., Wang, W., Gao, B., Xu, X., Zhang, J., and Li, Q. (2010). “Phosphate removal from aqueous solution by adsorption on modified giant reed.” *Water Environment Research*, 82(4), 374−381.

Zhang, T. C., Dahab, M. F., Nunes, G., Hu, C., and Surampalli, R. Y. (2007). “Phosphorus fate and transport in soil columns loaded intermittently with influent of high phosphorus concentrations.” *Water Environ. Res.*, 79, 2343−2351.

Zhang, G., Liu, H., Liu, R., and Qu, J. (2009). “Removal of phosphate from water by a Fe-Mn binary oxide adsorbent.” *Journal of Colloid and Interface Science*, 335, 168−174.

Zhang, L., Wan, L., Chang, N., Liu, J., Duan, C., Zhou, Q., and Li, X. (2011). “Removal of phosphate from water by activated carbon fiber loaded with lanthanum oxide.” *Journal of Hazardous Materials*, 190, 848−855.

Zhang, J., Shan, W., Ge, J., Shen, Z., Lei, Y., and Wang, W. (2012). “Kinetic and equilibrium studies of liquid phase adsorption of phosphate on modified sugarcane bagasse.” *Journal of Environmental Engineering*, 138(3), 252−258.