Phosphorous Removal from Aqueous Solutions by Agricultural By-products: A Critical Review

Thi An Hang Nguyen, Huu Hao Ngo[*], Wenshan Guo, Tien Vinh Nguyen

Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, FEIT, University of Technology, Sydney, City Campus, Broadway NSW 2007, Australia

ABSTRACT

Phosphorous plays an essential role in the development of living organisms. Nevertheless, phosphorous pollution, known as the eutrophication, is regarded as one of main causes of water quality deterioration. Hence, the decontamination of phosphorous from aqueous solutions is of importance for eutrophication control and phosphorous recovery. This review paper investigates the potential use of agricultural by-products (ABPs) as biosorbents in remediation of phosphorous contaminated waters. It was found that the modified ABPs exhibit equivalent or higher sorption capacity of phosphorous compared to conventional adsorbents. The efficient removal of phosphorous by ABPs requires some chemical modifications. The application of ABPs is highly recommended because of their significant advantages, including the abundant availability, low cost, high efficiency and without detrimental impacts on the environment. As adsorptive removal of phosphorous by ABPs is a relatively new process, there are still many aspects for future research, such as development of novel and cost-effective modification techniques, modeling for process optimization, desorption, cost-benefit analysis etc. The improvements in these aspects are expected to make it the method of choice in the future.

Keywords: Agricultural by-products; biosorbents; phosphorous; removal efficiency; uptake capacity

1. INTRODUCTION

1.1 Significance of phosphorous and major sources of phosphorous pollution

Phosphorous is one of 16 elements that are necessary for the plant growth (Mullins, 2009). It is also the key component of acid dezoxiribonucleic (ADN), teeth and bones (Biswas, 2008). In water bodies, it is a main factor limiting the development of aquatic plants (The Everglades hub, 2013). In addition, phosphorous is a principal material of many industries, such as fertilizers, detergents, paints, corrosion inhibitors, beverages, and pharmaceuticals (Biswas et al., 2007). However, the over-exploitation of phosphorous ores leads to the fact that these natural resources can be exhausted in the near future (Aryal and Liakopoulou - Kyriakides, 2011).

A large amount of phosphorous in receiving water bodies may come from different sources. Biswas (2008) divided the sources of phosphorous pollution into natural sources (e.g. precipitation, dry fall, decomposition of organic materials, soil erosion) and artificial sources (e.g. use of fertilizers, detergents, human and animal wastes). Wentzel et al. (2008) classified them as diffuse sources (e.g. run-off from agricultural fields) and point sources (e.g. wastewater treatment sites). It is estimated that the amount of phosphorous entered the

aquatic medium through artificial activities is three times larger than that via natural processes (Everglades hub, 2013). Each person discharges 2-3 g of phosphorous to wastewater through feces and urine every day (Biswas, 2008).

Understanding the existence forms of phosphorous is crucial to the selection of treatment technologies (Neethling, 2011). In natural waters, phosphorous can exit in various species as shown in Table 1. The orthophosphate presented in the forms of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ can accelerate the algae growth.

1.2　Potential environmental and well-being impacts of phosphorous

The presence of phosphorous in natural waters in excessive amounts is responsible for the eutrophication. de Bashan and Bashan (2004) defined eutrophication as the extraordinary growth of algae as a result of over enrichment of water bodies by nutrients, such as phosphorous and nitrogen. The two common symptoms of eutrophication are algae blooms and oxygen depletion (Everglades hub, 2013). In aquatic solution, high phosphorous concentration accelerates the development of phytoplankton, algae and macro aquatic plants. When they die, a large amount of oxygen is used for their decomposition, through oxidizing organic carbon and nitrogen into carbon dioxide and nitrate, respectively. Consequently, natural waters become lack of dissolved oxygen, threatening the life of aquatic plants and animals (Benyoucef and Amrani, 2011, Biswas, 2008). There are also many other adverse effects, e.g. decline of sub aquatic plants, the formation of dead zones. These may put the whole ecosystem to a risk of disappearance. It does not only affect aesthetic and ecological values of the ecosystems but also cause severe economic damages. According to Everglades hub (2013), a red tide event occurred near Hong Kong in 1998 affected 90% of Hong Kong's aquaculture farms and caused the estimated economic loss to 40 million USD. People's health may be negatively affected by consuming poisonous fish and shellfish in eutrophication regions. These people may suffer from skin irritation, gastrointestinal illnesses, neurological damage and death. Obviously, as eutrophication has severe impacts on the environment and people's well-being, the USEPA recommends that the acceptable level of total phosphorous in natural waters should be under 0.05 mgP/L (Mullins, 2009). Thus, this leads to a need to develop cost-effective technologies to achieve this water quality goal.

Table 1　Different forms of phosphorous in aqueous solutions (adapted from Wiesmann et al., 2006)

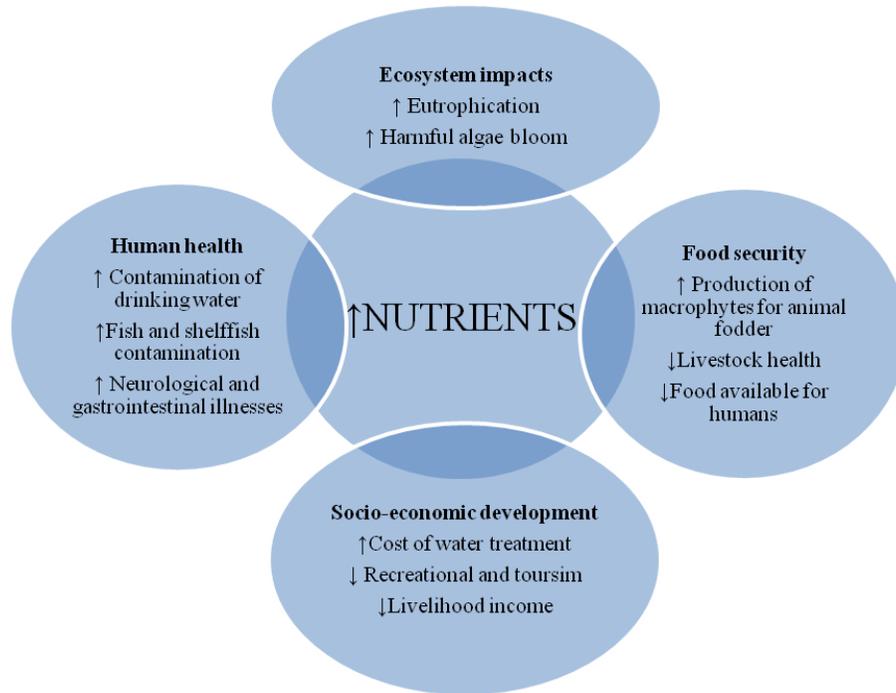| Total phosphorous, P_t			
Particulate phosphorous, P_p (organic and inorganic)	Dissolved phosphorous, P_d		
	Dissolved Polyphosphate, P_{Dp} (inorganic)	Hydrolyzed dissolved phosphorous, P_{Dh}	
		Orthophosphate P-PO$_4$ (inorganic)	Dissolved phosphorous, P_{Ox} (organic)

Figure 1 The effects of excessive amount of nutrients on ecosystem and human well-being
(adapted from UNEP-GEO, 2009)

1.3 Phosphorous removal technologies

Phosphorous removal is necessary for controlling eutrophication in natural waters and phosphorous recovery. This process was first studied in 1950s (Biswas, 2008). To date, a wide variety of phosphorous removal technologies are available to meet more strict regulations. According to Strom (2006), phosphorous removal technologies can be grouped into physical treatments (filtration of particulate phosphate, membrane technologies, magnetic separation); chemical treatments (precipitation, crystallization, anion exchanger, adsorption); and biological treatments (assimilation, enhanced biological phosphorous removal – EBPR, constructed wetlands). However, there is a general operation principle for all these methods. The phosphorous ions are initially changed into insoluble compounds, in the forms of salt precipitates or phosphorous built-in in microorganisms (in activated sludge) and plant (constructed wetlands). The

insoluble compounds are then separated from wastewater (Rybicki). de Bashan and Bashan (2004) argued that all these methods were not sustainable. The reason is that the phosphorous is usually simultaneously removed with other pollutants, including poisonous substances, leading to the fact that phosphorous cannot be recycled.

Regarding the development trend of phosphorous removal technologies, Biswas (2008) claimed that, currently chemical precipitation is widely applied for its high efficiency and space saving. However, such problems as high chemical expenditure, additional sludge production, effluent neutralization requirement have limited its use in phosphorous decontamination (Strom, 2006). Besides, it is difficult to recycle phosphorous in this method as it is unintentionally precipitated with other pollutants (de-Bashan and Bashan, 2004). There is an increasing trend in using EBPR for phosphorous elimination (Tanyi).

Table 2 Comparison of different treatment methods for phosphorous removal

Process	Effluent features	Advantages	Limitations	References
MBRs	EPC = 0.04 mgP/L			Strom (2006)
Tertiary membrane filtration	EPC = 0.04 mgP/L			Strom (2006)
RO	EPC = 0.008 mgP/L			Strom (2006)
Electro dialysis	EPC < 0.005 mgP/L			Everglades hub (2013)
Magnetic separation	EPC = 0.1-0.5 mgP/L	High performance, Compact process, Low power input		Rybicki (1998)
Chemical precipitation	EPC = 0.005-0.04 mgP/L; RE = 99% - Fe_2O_3/CaO; RE = 99% - Al_2O_3; RE = 97%-$Mg(OH)_2$	Better water quality Less space	High cost of chemicals; Chemical sludge; Neutralization of effluent; Do not recycle P	Biswas (2008); De-Bashan and Bashan (2004); Strom (2006); Tanyi (2010)
Crystallization	EPC = 0.3-1.0 mgP/L	Final product can be used as a fertilizer without further processing	Complex process; Increased salinity	De-Bashan and Bashan (2004); Rybicki (2010)
Anion exchanger		Operational simplicity, Adaptability to aqueous solution compositions and flow rates	Low selectivity; High cost	Awual and Jyo (2011); Biswas (2008)
Conventional adsorbents	EPC= 0.005 – 0.01 mgP/L; RE > 80%		High cost	Biswas (2008); Rybicki; Everglades hub (2013)
Bio-sorbents	EPC = 0.02 mgP/L	Abundant availability, Cost-effective, Minimum harmful effect on environment		Biswas (2008); Everglades hub (2013)
Biological P removal	EPC = 0.1 – 0.3 mgP/L; RE <30%	Less sludge production; Lower cost of chemicals; Opportunities for recovering P	Biological sludge; Bioavailability of P min.~0.02 mg P/L is required	Biswas (2008); Tanyi (2010); Everglades hub (2013)
EBPR	EPC = < 0.02 to < 0.1 mgP/L, depending on duration; RE = 100%	Can remove P to very low levels; Modest cost; Minimal sludge production	More energy consumption; More space;	De-Bashan and Bashan (2004); Strom (2006)
Constructed wetlands	EPC = 0.02 mgP/L RE = 39-99%, depending on plant type	Low cost; low tech	Sediments; deposits	De-Bashan and Bashan (2004); Everglades hub (2013)

EPC: Effluent phosphorous concentration
RE: Removal efficiency

EBPR can reduce phosphorous to low concentration (<0.02 mgP/L) with modest cost and minimal sludge production. Nevertheless, the major concerns with EBPR are large energy and space requirements (de-Bashan and Bashan, 2004; Strom, 2006). Although the membrane technologies can help to reduce the phosphorous concentration to extremely low level (<0.005 mg P/L), its application is limited due to extraordinarily high cost caused by membrane fouling (Everglades hub, 2013; Strom, 2006). Adsorptive removal of phosphorous by ABPs is relatively new process. The significant advantages of this method are cost effective, high efficiency with minimum detrimental effects on the environment (Biswas, 2008). In addition, the reuse of ABPs as bio-sorbents for phosphorous removal provides a low-cost and environmentally friendly means to eliminate wastes (Ismail, 2012).

A comparative study conducted by Tanyi using EFOR software found that the chemical treatment was better than biological treatment, with respects to the total phosphorous effluent concentration (0.28 compared with 0.40 mg P/L), space saving (4.079 m^3), and energy savings (500 kg O$_2$/h). However, 25% more sludge production and 520.000 SEK/year more chemical cost are significant constraints of the chemical method. They concluded that each technology presents its own merits and demerits, and thereby for the maximization of the treatment efficiency, a combination of different technologies is required. However, the assessment of treatment technologies should base on several factors, such as effluent figures, cost, side effects etc. The quantitative information is meaningful for this purpose. Unfortunately, there is lack of this information in the literature.

2.   PHOSPHOROUS ADSORPTION ON AGRICULTURAL BY-PRODUCTS

2.1   Merits of using agricultural by-products as biosorbents of phosphorous

The use of ABPs as biosorbents of phosphorous has many benefits. Firstly, modified ABPs exhibit comparable or even higher adsorption capability of phosphorous than conventional adsorbents. In addition, most of them are abundantly available, relatively cheap or free of charge (de Lima et al., 2012). The use of ABPs as biosorbents of phosphorous does not cause environmental adverse impacts. Contrarily, it provides an economic, effective and environmentally benign means for eliminating agricultural wastes. Besides, phosphorous loaded ABPs can be used as fertilizers for agricultural production (Ismail, 2012).

2.2   Phosphate adsorption mechanisms

Different mechanisms have been reported for the adsorption of phosphate by various ABPs biosorbents. Benyoucef and Amrani (2011) found that the removal of phosphorous by adsorption on the sawdust of Aleppo pine was fast, indicating that the dominant mechanism might be the chemisorption. The Scanning Electron Microscopy (SEM) results indicated that modification with urea resulted in a large number of pores. Krishnan and Haridas (2008) reported the ligand exchange was the principal mechanism in case of removing phosphate ions by iron impregnated coir pith and natural coir pith. Yue et al. (2010) concluded that the adsorption of phosphorous on modified giant reed mainly occurred via physisorption based on the result of low activation energy. The zeta potential and spectra analysis led to a conclusion that the nature of adsorptive removal of phosphorous using diethylenetriamine-crosslinked cotton stalk and wheat stalk was electrostatic attraction between phosphate ions and biosorbents (Xu et al., 2011). These diverse findings may be attributed to the dif-

ference in the number and composition of functional groups on the cell wall of various ABPs.

2.3 Factors affecting phosphorous biosorption

2.3.1 pH

Numerous studies investigated the influences of pH on the adsorption of phosphorous by different ABPs. Biswas et al. (2007) reported that % removal of phosphate by metal loaded orange waste increased quickly as pH increased from 5 to 7, then obtained the highest value (≈100%) and remained unchanged until pH10. However, the percent removal declined after pH10. Biswas et al. (2008) explored that the low pH favored the maximum removal efficiency of phosphorous, whereas high pH interfered the phosphate ions removal. These findings were in good agreement with those reported by Krishnan and Haridas (2008). They observed that natural coir pith effectively removed phosphorous in the pH range of 2.0-3.5. The optimum pH was 3.0. They attributed these findings by pHzpc, presence of different phosphate species in the solution and affinity of phosphate ions towards binding sites. Despite the difference in types of biosorbents used for phosphorous decontamination, both Xu et al. (2011) and Yue et al. (2010) observed that the effective removal of phosphate ions by cotton stalk/wheat stalk and modified giant reed occurred in the pH range of 4-9. They suggested that, at these pH values, the dominant phosphate ions were $H_2PO_4^-$ and HPO_4^{2-}, which had a strong affinity for the adsorption sites. Kumar et al. (2010) indicated that the pH range of 6-10 favored the highest adsorption of phosphorous on coir-pith carbon activated by H_2SO_4. These results were in line with a study performed by Benyoucef and Amrani (2011). They considered 7.5 as the optimum pH for the decontamination of

phosphate ions by Aleppo pine sawdust. They explored that the phosphate % removal increased from 83.86% to 88.53% in the pH range of 3.5-7.5 and decreased from 88.53% to 86.34% as pH kept increasing to 10.6. They attributed this decline to the increasing repulsive interaction between phosphate ions and hydroxyl ions. It is interesting from the report of de Lima et al. (2012) that pH hardly affected the adsorption rate of phosphorous by coconut fibers. Different results on the effect of pH imply the complicated nature of the adsorption process by ABPs. For this reason, further investigation in this field is required.

2.3.2 Temperature

Some researchers reported that the adsorptive removal of phosphorous ions by ABPs was endothermic while others claimed the exothermic nature of the process. Mezenner & Bensmaili (2009) observed that the phosphorous uptake capability of iron hydroxide-eggshell increased as the temperature of the solution increased from 20 to 45 °C. They confirmed this process was endothermic based on the positive $\Delta H^°$ (81.84 kJ/mol). The similar conclusions were made by Kumar et al. (2010) and Benyoucef and Amrani (2011). While Kumar et al. (2010) attributed the higher phosphorous adsorption ability with increasing temperature to the increase in the rate of intra-particle diffusion of phosphate ions, Benyoucef and Amrani (2011) ascribed this to the expansion in pore size and activation of adsorbent surface at a higher temperature. On the other hand, Xu et al. (2009) stated that there was a decrease in the phosphorous sorption capability of modified wheat residue as the temperature declined from 20 to 60 °C. They suggested that the higher temperature of the phosphate solution accelerated the escape of phosphate ions from the biosorbent surface to the solution. These results were supported by a study conducted by Yue et al. (2010), us-

ing modified giant reed as a biosorbent. They found that the phosphate uptake capacity reduced from 19.89 to 17.79 mg/g as the temperature increased from 20 to 60 $^{\circ}$C. They concluded this adsorptive removal has exothermic nature as the lower temperature favored the process.

2.3.3 Adsorbent dosage

The phosphorous removal increased with increasing adsorbent dose up to a specific level, and then it remained unchanged. The removal efficiency of phosphate increased substantially from 52.1% to 92.5% as wheat residue dosage rose from 0.5 to 2 g/L (Xu et al., 2009). They explained that, there were more binding sites available for phosphorous adsorption when higher adsorbent dose was used. However, further increase of adsorbent dose did not accelerate further the % removal of phosphorous. By that time, though there were additional adsorption sites, there was no more phosphate ions left in the solution as most of them were adsorbed. These results suit findings quoted by Ismail (2012), Kumar et al. (2010), Mezenner and Bensmaili (2009), Yue et al. (2010).

2.3.4 Initial phosphate concentration

In general, the adsorption capacity of phosphate ions increased while their % removal decreased with increasing initial concentration of phosphate species. Mezenner and Bensmaili (2009) observed that the % removal of phosphate by iron hydroxide eggshell decreased from 95% to 64% when beginning phosphate concentration increased from 2.8 mg/L to 110 mg/L. Xu et al. (2009) explored that phosphate uptake capacity of modified wheat residue at the initial phosphate concentration of 300 mg/L was higher than those at 100 and 200 mg/L. They suggested that the concentration gradient facilitated the adsorp-

tion process. Kumar et al. (2010) observed that the phosphorous sequestering ability of coir pith activated carbon increased with increasing initial phosphorous concentration and reached the highest value at the equilibrium time. The authors attributed this to the increase in the driving force.

2.3.5 Interfering ions

The effects of interfering anions on the adsorption of phosphorous onto ABPs were investigated by many researchers in an attempt to enhance its practical application of these biosorbents. Biswas et al. (2007) explored that foreign anions such as SO_4^{2-}, Cl^-, CO_3^{2-} did not show any substantial influence on phosphate adsorption by La (III) loaded orange waste. Similar observation was noticed in their 2008 research with zirconium loaded orange waste, in which the interference effects of SO_4^{2-}, Cl^-, CO_3^{2-} were minimal. They explained this by the fact that the affinity between the gel and phosphate was stronger than that between the gel and competing anions. This behavior can be detected in a study performed by Divya et al. (2012). The authors released that such anions as Cl^-, SO_4^{2-}, NO_3^-, F^- and CO_3^{2-} hardly affected the adsorption of phosphorous, whilst the presence of cations like Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} accelerated the phosphate adsorption. Yue et al. (2010) reported that, even with the presence of interfering ions, high % removal of phosphate ions, ranging from 70.28% to 96.89%, could be achieved with modified giant reed. These results indicate the ABPs can be efficient biosorbents for phosphorous decontamination in the real wastewater with the existence of various competing ions.

2.3.6 Adsorbent particle size

Eberhardt and Min (2008) investigated the effect of particle size on phosphate adsorption

by aspen wood. It was found that the larger wood particles demonstrated better phosphorous adsorption capacity, owing to the possession of a higher number of carboxylate to complex iron. However, they recommended using the smallest wood particles (35-80 mesh) because of the highest ratio between the amount of phosphate removed and the quantity of iron liberated into the solution.

2.3.7　Contact time

In most cases, the equilibrium time for the adsorption of phosphate by ABPs was under 1h. Xu et al. (2009) observed that the removal of phosphate by modified wheat residue reached equilibrium in 10 - 15 min. Mezenner & Bensmaili (2009) revealed that phosphate sorption using waste iron hydroxide-eggshell reached 73% of the total adsorption capacity in 30min. Yue et al. (2010) reported that the adsorption of phosphorous on modified giant reed reached the equilibrium after 25 minutes, whereas 40 min was needed in case of using modified sawdust (Benyoucef and Amrani, 2011). Conversely, the longer contact time was noted by other authors. Based on the study of Biswas et al. (2007), 15 h was necessary to reach equilibrium for the phosphate removal using orange waste loaded with La (III), Ce (III) and Fe (III). Kumar et al. (2010) showed that the phosphate elimination by coir pith activated carbon was a gradual process, reaching equilibrium in 3h. The higher the initial concentration of phosphate (10, 20 and 40 mg/l), the longer the contact time (60, 120 and 180 min) was required to attain equilibrium.

2.4　Phosphate adsorption performance by agricultural by-products

Various ABPs have been tested as biosorbents for the removal of phosphorous from aqueous solutions. They include pine sawdust (Benyoucef and Amrani, 2011a), orange waste (Biswas et al., 2007, 2008), coir pith (Krishnan and Haridas, 2008, Kumar et al., 2010), eggshell (Mezenner and Bensmaili, 2009), wheat residue (Xu et al., 2009, 2011), cotton stalk (Xu et al., 2011), giant reed (Yue et al., 2010). Tables 3 and 4 present the adsorption performance of phosphorous by ABPs, in both natural and modified forms. Meanwhile, the phosphorous sequestering abilities of conventional adsorbents are summarized in Table 5. It is clearly that, most of studies on the removal of phosphorous by adsorption on ABPs are performed with modified biosorbents. There are uncommonly few papers employing biosorbents in natural/raw form for this purpose. While the removal of heavy metals can occur naturally through functional groups, which are already available on the cell wall of ABPs, the efficient removal of phosphate requires proper chemical modifications (Eberhardt and Min, 2008). Natural ABPs showed extremely poor adsorption capacities of phosphorous in scarce studies performed by Benyoucef and Amrani (2011b), Eberhardt and Min (2008), Ismail (2012), Krishnan and Haridas (2008). Contrarily, in the remaining research reviewed in this paper, a majority of modified ABPs demonstrated equivalent or much better adsorption capability of phosphorous when compared with that of conventional adsorbents. However, in some instances, this principle could not apply. The phosphorous uptake abilities of Wood particles modified with carboxymethyl cellulose + ferrous chloride and Juniper fiber treated by AMD were (2.32 and 1.85 mg P/g) much lower than that of natural Sawdust of Aleppo pine (47.64 mg P/g) (Benyoucef and Amrani, 2011b; Eberhardt and Min, 2008;Han et al., 2003). This indicates the significance of developing appropriate modification methods and the selection of potential ABPs for phosphorous elimination.

Table 3 The phosphorous adsorption performance by agricultural by-products and influential parameters

Biosorbents	Uptake capacity (mg/g)	RE (%)	Opt. pH	Opt. sorbent dose (g)	Initial P conc. (mg/L)	T (°C)	ET (min.)	References
Sawdust of Aleppo pine (natural and modified forms)	47.64 & 116.25		7.5	0.5	300	25	80 & 40	Benyoucef and Amrani (2011b)
Orange waste (La(III)-, Ce(III)- and Fe(III)- loaded)	13.94 (for 3 gels)		7				15	Biswas et al. (2007)
Orange waste gel (modified form)	57	>85	3			30	(6h)	Biswas et al. (2008)
Coconut shell (modified form)	200			0.1	20-1000	25	(4h)	De Lima et al. (2012)
Barks/stems powders of F. *religiosa;* C.*gigantean;* P.*granatum;* C. *auriculata* (natural form)		87; 97; 89; 90	10	1.0; 1.5; 2.0; 2.0				Divya, et al. (2012)
Ashes of F. *religiosa;* C.*gigantean;* P.*granatum;* C. *auriculata*		93; 100; 93; 94		0.75; 1.0; 1.5; 1.25				Divya, et al. (2012)
Wood particles (modified)	2.32			4	100	25	(6h)	Eberhardt and Min (2008)
Granular date stones (natural form)	8.7	87	7-7.5	5	50	25		Ismail (2012)
Palm surface fibers (natural form)	8.5	85	7-7.5	5	50	25		Ismail (2012)
Coir pith (natural and modified)	4.35 & 22.05	17.4 & 88.2	3	0.1	50	30	(12h)	Krishnan and Haridas (2008)
Coir pith (activated carbon)	7.74		6-10	4	40	35; 50; 60	3h	Kumar et al. (2010)
Iron hydroxide-eggshell	14.49	95÷65 (depending on Ci)		10 (2.5-20)	2.8-110	20-45		Mezenner and Bensmaili (2009)
Wheat residue (modified form)	67.1 (column test)			2	50	20±2	10-15 (80)*	Xu et al. (2009)
Cotton stalk and wheat straw (modified form)	51.54 & 60.61	80.3 & 81.4	4-9	0.1	50	20	15	Xu et al. (2011)
Giant reed (modified form)	19.89	96.89	4-9	0.8	50	20±2	25	Yue et al. (2010)

Note: RE= Removal Efficiency; opt.= optimum; conc.= concentration; T= Temperature; ET= Equilibrium time;

*10-15: equilibrium time; (80): interaction time.

Table 4   Effect of modification of agricultural by-products on phosphorous removal from
wastewater

Agricultural by-products	Modifying agents	AC before Mod. (mg/g)	AC after Mod. (mg/g)	Imp. in AC (%)	References
Sawdust of Aleppo pine	Urea	47.64	116.25	144	Benyoucef & Amrani (2011)
Orange waste	La (III)-, Ce (III)- and Fe (III)-loaded		13.94 (for all 3 types of gels)		Biswas et al. (2007)
Orange waste gel	Zirconium (IV)		57		Biswas et al. (2008)
Coconut shell fibers	Ammonium quaternary salt (2-hidroxypropyltrimethyl ammonium chloride)	Negligible/ Not significant	200	~ 200	De Lima et al. (2012)
Ficus religiosa bark; Cassia auriculata bark; Punica granatum bark; Calotropis gigantean stem	Ash	87; 97; 89; 90 (%)	93; 100; 93; 94 (%)	6; 3; 4; 4	Divya et al. (2012)
Wood particles	Carboxymethyl cellulose + Ferrous chloride		2.32		Eberhardt and Min (2008)
Juniper fiber	AMD		1.85		Han, Hur and Choi (2003)
Coir pith	$Fe(NO_3)_3.9H_2O$	4.35	22.05	>400	Krishnan and Haridas (2008)
Coir pith activated carbon	H_2SO_4		7.74		Kumar et al. (2010)
Wheat residue	Epichchlorohydrin + N,N-dimenthylformamide + Ethylenediamine + Triethylamine		67.1		Xu et al. (2009)
Cotton stalk and wheat straw	Epichlorohydrin-diethylenetriamine-trimethylamine		51.54 & 60.61		Xu et al. (2011)
Giant reed	Epichchlorohydrin + N,N-dimenthylformamide + Ethylenediamine + Triethylamine		19.89		Yue et al. (2010)

Note: AC= Adsorption Capacity; Mod.= Modification; Imp.= Improvement.

Table 5   The sorption capacity of phosphorous by conventional adsorbents

Adsorbents	Adsorption capacity (mg P/g)	References
Weak base Diaon WA20 resins	43 – 153	Awual and Jyo (2011)
Strong base DiaionSA10A resins	12	Awual and Jyo (2011)
Zirconium ferrite	13	Biswas et al. (2008)
Zr(IV)-loaded MUROMAC	43	Biswas et al. (2008)
Goethite	6.42	Han et al. (2005)
Activated alumina	9.90	Li et al. (2009)
Commercial anion exchange resins	13.8-42.1	Park and Na (2006)
Property changed zeolite	15.62	Wang et al. (2007)
Natural zeolit	2.15	Wu et al. (2006)
Iron oxide tailings	8.21	Zeng et al. (2004)

2.5 Modification of agricultural by-products for better phosphorous treatment

Most studies used modified ABPs for phosphate removal, e.g. chemically modified sawdust of Aleppo pine (Benyoucef and Amrani, 2011), metal loaded orange waste (Biswas et al., 2007), zirconium loaded orange waste (Biswas et al., 2008), surface modified coir pith (Krishnan and Haridas, 2008), activated carbon coir pith (Kumar et al., 2010), waste iron hydroxide eggshell (Mezenner and Bensmaili, 2009), modified wheat residue (Xu et al., 2009), diethylenetriamine-crosslinked cotton stalk/wheat stalk (Xu et al., 2011), modified giant reed (Yue et al., 2010). According to Eberhardt and Min (2008), the natural ABPs can efficiently remove metal ions from wastewater due to the presence of functional groups in biomass. Contrarily, it needs to do some chemical modification of raw ABPs to obtain a remarkable sequestering of phosphorous. The principle of chemical modification is to improve the adsorption of iron, and thereby enhance the phosphorous capture capability. This can be done by ordinary treatments with bases or grafting of carboxylate groups.

Regarding the performance of ABPs as biosorbents, typically, it was found that the modification vastly enhances the removal efficiency of phosphorous. Biswas et al. (2008) explored that zirconium loaded orange waste gel could be use as an effective biosorbent for phosphate removal. The phosphorous uptake capacity of zirconium loaded orange waste gel was 57 mg P/g, four times higher than that of zirconium ferrite. Krishnan and Haridas (2008) conducted a comparative study of the phosphorous adsorption using iron impregnated coir pith (CP-Fe-I) and coir pith (CP). The results showed that the former one was five to six times more effective than the latter. The highest removal capacities of phosphorous were 88.2% (22.05 mg/g) and 17.4% (4.35 mg/g) for CP-Fe-I and CP, respectively. Yue et al. (2010) found that modified giant reed could be a promising solution to the decontamination of phosphorous from real waste waters with extremely high removal efficiency of 96.89%. The modification of Aleppo pine sawdust with urea resulted in 2.44 times improvement in phosphorous adsorption capacity when compared with the pristine biosorbent. This finding was confirmed by the SEM analysis, which indicated that there were many pores formed after modification (Benyoucef and Amrani, 2011b). de Lima et al. (2012) reported that whereas the phosphorous sequestering capability of natural Coconut shell fibers was negligible, the modification of this

biosorbent with Ammonium quaternary salt resulted in extremely good adsorption capacity of phosphorous (200 mg P/g). Divya et al. (2012) conducted a comparative study on the phosphorous removal, between bark/stems and ashes of four types of biosorbents. It was found that the removal percentages of phosphate by the ashes of F. *religiosa*, C. *auriculata*, P. *granatum*, C. *gigantean* (93% - 100% - 93% - 94%) were higher than those of their powders (87% - 97% - 89% - 90%).

Although modification plays a key role in enhancing the adsorptive capacity of phosphorous by ABPs, some side effects have been reported. The positive influence was noted by Divya et al. (2012). They explored that the ash of biosorbents helped to reduce the optimum sorbent dosage required for the maximum removal of phosphate. Regarding the adverse effects, the use of F.*religiosa*, C.*auriculata*, P.*granatum* and C.*gigantean* as biosorbents, in the ash form at optimum conditions, did not cause water quality deterioration, in terms of DO, BOD, COD, color and turbidity (Divya et al., 2012). Contrarily, Han et al. (2003) claimed that the adsorptive removal of phosphorous by juniper fiber, modified with acid mine drainage (AMD), resulted in iron release into the water. This disagreement leads to a need for further investigation on the detrimental effects of the chemical modification in the future.

2.6   Desorption

Regeneration of biosorbents has received increasing attention of researchers. Xu et al. (2011) reported that NaCl and HCl were excellent eluent solutions for diethylenetriamine - crosslinked cotton stalk and wheat straw. They also explored that, after three adsorption - desorption cycles, the column removal efficiency of these biosorbents were still higher than 92%. However, the use of HCl for regeneration resulted in 5% of biosorbent weight

loss. On the contrary, de Lima et al. (2012) found that the regeneration of modified coconut fibers with HCl led to a reduction by 70% of removal efficiency compared to that of the third cycle of reuse. The reduction of phosphorous uptake ability to zero was a result of the second cycle of reuse. These findings demonstrate the limited reuse and regeneration of modified coconut fibers for phosphorus removal. Ismail (2012) found that the desorbabilities of phosphorous for granular date stones and palm surface fibers were 10-11.2% and 12.1-13%, respectively. Due to the low values of desorbability of phosphorous, the adsorptive removal of phosphate ions by these two biosorbents is not reversible. Thus, these may be significant challenges to the application of ABPs as phosphorous biosorbents.

CONCLUSIONS AND FUTURE WORK

- Natural ABPs exhibit extremely poor affinity to phosphorous. On the contrary, modified ABPs present comparable or higher biosorption capacity of phosphorous when compared with conventional adsorbents. The extremely good sequestering capability of phosphorous requires proper chemical modifications. However, existing modification methods have some shortcomings. This leads to a need to develop novel and cost-effective modification methods for better phosphorous treatment and less harmful environmental impacts.
- Different mechanisms and various influential factors are reported for the adsorption of phosphorous onto ABPs. This gives platform for further research on process modeling and optimization.
- In many cases, ABPs based biosorbents demonstrate low desorbability of phosphorous. However, this does not have significant impacts on their practical application as phosphorous loaded materials

can be used as fertilizer for agricultural production.

- There is lack of information in literature for cost-benefit analysis of the development and application of ABPs based biosorbents at both the laboratory and industrial scales.

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