Bioresource Technology 169 (2014) 750–762

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

Modification of agricultural waste/by-products for enhanced phosphate removal and recovery: Potential and obstacles

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HIGHLIGHTS

- Modification is critical in enhancing P removal ability of AWBs.
- Review focuses on metal loading and quaternization with potentials and drawbacks.
- P was adsorbed onto modified AWBs mainly via ligand and ion exchange mechanisms.
- Little has been done on beneficial use of modified AWBs for P recovery.
- Recommendations on proper use of modification methods were made.

ARTICLE INFO

Article history:
Received 8 June 2014
Received in revised form 9 July 2014
Accepted 10 July 2014
Available online 17 July 2014

Keywords:
Agricultural waste/by-products
Biosorbent
Modification
Phosphate
Removal efficiency

ABSTRACT

There is a growing trend to employ agricultural waste/by-products (AWBs) as the substrates for the development of phosphate biosorbents. Nevertheless, due to the lack of anion binding sites, natural AWBs are usually inefficient in phosphate decontamination. Consequently, modification plays a vital role in improving phosphate sorption's property of raw AWBs. This review paper evaluates all existing methods of modification. The literatures indicate that modification can significantly improve phosphate removal ability of AWBs by retaining phosphate ion onto modified AWBs principally via ion exchange (electrostatic interaction) and ligand exchange mechanisms. So far, little work has been done on the beneficial use of modified AWBs for the phosphorus recovery from aqueous solutions. The poor recyclability of modified AWBs could be responsible for their limited application. Hence, further study is essential to search for novel, cost-effective, and green methods of modification.

1. Introduction

Phosphorus plays an important role to the development of plants, animals and the industrial manufacture (Choi et al., 2012; Karachalios, 2012; Mezenner and Bensmaili, 2009). However, due to the over-exploitation for these purposes, the global phosphate rock reserve is probably going to be exhausted in the next 50–100 years (Cooper et al., 2011; Eljamal et al., 2013; Ogata et al., 2012). In another perspective, the phosphorus concentration in the aqueous medium above 0.02 mg/L can cause eutrophication, leading to the deterioration of water quality and threatening the life of aquatic creatures (Ismail, 2012; Jyothi et al., 2012). Therefore, the excessive amounts of phosphorus need to be removed from the water medium to prevent water bodies from this undesirable phenomenon, as well as pave the way to the phosphorus recovery (Anirudhan et al., 2006; Zhang et al., 2012).

Various technologies are available for controlling phosphorus pollution. These processes can be classified as chemical methods (precipitation, crystallization, anion exchange, and adsorption), biological methods (assimilation, enhanced biological phosphorus removal, constructed wetlands, wastewater stabilization pond), and physical methods (microfiltration, reverse osmosis, electrodialysis, and magnetic separation) (Benyoucef and Amrani, 2011; Bhojappa, 2009). However, each method represents its own demerits (Jeon and Yeom, 2009). The physical methods have

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http://dx.doi.org/10.1016/j.biortech.2014.07.047
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disadvantages of being too expensive or inefficient (Karachalios, 2012). The chemical precipitation is often prone to additional sludge, high chemical expense, effluent neutralization requirement, and inadequate efficiency for dilute phosphorus solutions (Kumar et al., 2010; Mallampati and Valiyaveettil, 2013; Zhang et al., 2011). Similarly, the major concerns with biological removal technologies are complicated operation; high energy consumption and large footprint (Ning et al., 2008; Peleka and Deliyanni, 2009). The use of wastewater stabilization pond with the water hyacinth is also restricted by land scarcity and the difficulty in water hyacinth utilization (Xi et al., 2010). On the other hand, adsorption is proven to be affordable, effective and best suited for low levels of phosphate (Zhang et al., 2011). Especially, it is believed that, adsorption enables the recovery of phosphorus, owing to its high selectivity toward phosphorus (Loganathan et al., 2014). Previously, activated carbon or anion exchange resins are commonly used for phosphorus decontamination. However, the problems associated with the high cost, no renewability, requirement of pre-concentration of anions, and disposal after use hinder their widespread application in developing countries (De Lima et al., 2012; Karachalios, 2012; Karthikeyan et al., 2004). Hence, increasing attention has been paid to AWBs based biosorbents in an attempt to search for a viable alternative option (Jyothi et al., 2012). The potential AWBs based phosphate biosorbents are expected to have low cost, high effectiveness, good selectivity, potential renewability, and high adaptability to various process parameters (Ning et al., 2008).

AWBs have several properties that make them attractive as the substrate for developing phosphorus biosorbents. To begin, AWBs are abundant, low-priced, and non-toxic. Additionally, as lignocellulosic materials, AWBs contain large amounts of functional groups (e.g. —OH, —CHO) in their cellulose, hemicellulose and lignin components. Therefore, AWBs can easily get involved in chemical reactions (e.g. condensation, etherification and polymerization). This provides a foundation for AWBs to be converted into some functional polymers (Benyoucef and Amrani, 2011; Xu et al., 2010b). Specifically, the —OH group of AWBs can combine with alkoxyamine ligands to improve their anion exchange abilities (Karthikeyan et al., 2002).

The utilization of AWBs as phosphate biosorbents may result in many benefits. Firstly, this practice can protect surface water from eutrophication. Secondly, there are large amounts of AWBs produced worldwide annually, posing a challenge to solid waste disposal. Thus, the recycling AWBs as phosphate biosorbents not only provides a viable solution to reduce waste materials in a cheap and eco-friendly way but also adds values to AWBs (Anirudhan et al., 2006; Eljamal et al., 2013; Ismail, 2012; Tshabalala et al., 2004). This also fits well with the principle "use of renewable resources" of Green Chemistry (Srivastava and Goyal, 2010). In addition, the production of anion exchange resins from abundant, cheap and renewable AWBs may help to the cost of phosphorus treatment (Liu et al., 2012). Moreover, by converting phosphorus in wastewaters into fertilizers, this practice can generate revenues (Huang et al., 2010; Peng et al., 2012). Also, the successful exploitation of phosphorus from wastewaters will diminish the use of mineral phosphorus, and hence saving the global phosphorus rock resource. Clearly, the use of AWBs based phosphate biosorbents may provide a sustainable, efficient and profitable solution for phosphorus pollution control.

There is increasing trend to use AWBs as phosphate biosorbents. Nevertheless, very few studies have been made for the ability of raw AWBs to adsorb phosphorus. Whereas some pristine AWBs can hardly remove any phosphorus from aqueous solutions (Huang et al., 2010; Namasivayam et al., 2005), others exhibit very low sorption abilities as compared to commercial adsorbents (Krishnan and Haridas, 2008; Marshall and Wartelle, 2004; Nguyen et al., 2013; Xu et al., 2011a; Zhang et al., 2012) (Table 1). The lack of efficiency in the phosphate removal of original AWBs can be explained by the abundant availability of negatively charged functional groups (e.g. —OH, —COOH), while absence of positively charged functional groups (e.g. $—NH_2$) on the surface of raw AWBs (Mallampati and Valiyaveettil, 2013; Nguyen et al., 2013). For these reasons, AWBs need to be modified to improve their phosphate sorption abilities. Besides, modification of AWBs was found to increase the strength of lignocelluloses materials, and hence mitigating the release of organic matters into aqueous solutions (Anirudhan et al., 2006).

Methods of modification of AWBs for better phosphate removal can be grouped into (i) cationization (e.g. metal loading, grafting with ammonium type chemicals), (ii) anionization (e.g. surface coating with sulphate), (iii) activation (e.g. thermal, chemical and steam activation) (Fig. 1). This paper aims to gain insight into each method of modification, with respect to the principle, procedure,

Table 1
The maximum phosphate adsorption capacity of commercial and natural AWBs based biosorbents.

Adsorbent	Maximum adsorption capacity (mg PO_4/g)	Reference
Unmodified AWBs based biosorbents		
Oyster shell	0	Huang et al. (2010)
Oyster shell	0	Namasivayam et al. (2005)
Giant reed	0.836	Xu et al. (2011a)
Sugarcane bagasse	1.10	Zhang et al. (2012)
Soybean milk residues (okara)	2.45	Nguyen et al. (2013)
Coir pith	4.35	Krishnan and Haridas (2008)
Date palm fibers	13.33	Riahi et al. (2009)
Scallop shells	23.00	Yeom and Jung (2009)
Palm surface fibers	26.05	Ismail (2012)
Granular date stones	26.66	Ismail (2012)
Commercially available 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)