Bioresource Technology 170 (2014) 30–37

Contents lists available at ScienceDirect

Bioresource Technology

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

Phosphorus elimination from aqueous solution using 'zirconium loaded okara' as a biosorbent

T.A.H. Nguyen [a], H.H. Ngo [a,*], W.S. Guo [a], J.L. Zhou [a], J. Wang [b], H. Liang [c], G. Li [c]

[a] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), 15 Broadway, Ultimo, NSW 2007, Australia
[b] School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[c] School of Municipal and Environmental Engineering, Harbin Institute of Technology, 150090, China

HIGHLIGHTS

- ZLO exhibited reasonably high phosphorus adsorption capacity (44.13 mg/g).
- Except pH 12, pH 2–11 had a minor effect on phosphorus retention by ZLO.
- Phosphorus removal by ZLO was rapid with the efficiency reached 95% in 30 min.
- The adsorption process had feasible, spontaneous, and endothermic nature.
- Phosphorus was captured by ZLO predominantly as chemisorption.

ARTICLE INFO

Article history:
Received 19 June 2014
Received in revised form 16 July 2014
Accepted 17 July 2014
Available online 24 July 2014

Keywords:
Biosorbent
Isotherms
Kinetics
Okara
Phosphate removal

ABSTRACT

This work deals with the capture of phosphorus from aqueous solutions by biosorption onto zirconium loaded okara (ZLO). The batch-mode experiments were conducted to examine the effect of pH, biosorbent dose, initial phosphorus concentration, contact time, and temperature on the process. It was found that, the adsorption was most favored in the pH range of 2–6. The optimal doses for the adsorption, at initial phosphorus concentrations of 5, 10, 25, 50 mg/L were 2, 3, 7, 10 g/L, respectively. The maximum adsorption capacity of ZLO was approximately 44.13 mg PO_4/g at 298 K. The phosphate removal was rapid, reaching 95% in 30 min. Freundlich model best fitted the equilibrium data, while Pseudo-second order model satisfactorily described the kinetic results. Thermodynamic analysis revealed feasible, spontaneous, and endothermic nature of the process. The research would be beneficial for developing a promising, eco-friendly phosphorus biosorbent from a plentiful AWB – okara.

1. Introduction

Phosphorus is essential 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, the global phosphate rock reserve is predicted to be exhausted in the next 50–100 years (Cooper et al., 2011; Eljamal et al., 2013). 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 aquatic medium to protect water bodies from this undesirable phenomenon, as well as pave the way to the phosphorus recovery.

A wide variety of phosphorus pollution treatment methods have been developed and applied, including chemical precipitation, biological processes, electrodialysis, reverse osmosis, ion exchange, and adsorption (Biswas et al., 2008; Boujelben et al., 2008; Xu et al., 2011a). The latter is usually a method of choice, because of being simple, effective, applicable, most appropriate for the low levels of phosphorus, favorable to the phosphorus recovery (Loganathan et al., 2014). Nevertheless, the drawbacks of commercial adsorbents (e.g. high cost, non-renewability) prevent the adsorption from widespread use in developing countries.

Abbreviations: AWBs, agricultural wastes/byproducts; ZLO, zirconium loaded okara.

* Corresponding author. Address: School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), P.O. Box 123, 15 Broadway, Ultimo, NSW 2007, Australia. Tel.: +61 2 95142745; fax: +61 2 95142633.

E-mail address: ngohuuhao121@gmail.com (H.H. Ngo).

http://dx.doi.org/10.1016/j.biortech.2014.07.069
0960-8524/

In an attempt to diminish the cost of treatment, there is lately an emerging trend to use agricultural wastes/by products (AWBs) as phosphorus biosorbents (Zhang et al., 2012). Normally, AWBs are abundantly available but have low economic values. Hence, AWBs often cause the environmental burden and require disposal to mitigate their adverse impacts on the environment. Conversely, the recycling of AWBs as biosorbents for the remediation of phosphorus pollution helps the environment by reducing waste in a green way (Ismail, 2012). Moreover, it gives a chance to add values to AWBs, and to develop attractive, economical alternative to existing treatment methods (Peng et al., 2012). Nevertheless, due to the lack of binding sites for anions on their cell walls, AWBs need to be cationized via metal impregnation or quaternization reaction to efficiently remove phosphorus (Han et al., 2005; Mallampati and Valiyaveettil, 2013). Whereas many articles have been published so far, confirming the efficiency of various phosphorus – AWBs adsorption systems (Benyoucef and Amrani, 2011; Biswas et al., 2008; Carvalho et al., 2011; de Lima et al., 2012; Eberhardt and Min, 2008; Karachalios, 2012; Mallampati and Valiyaveettil, 2013), the search for innovative, cost-effective, and sustainable phosphorus biosorbents is still a challenge to the adsorption researchers.

Among various methods of modifying AWBs for better phosphate removal, metal loading seems to be preferred, because of its simplicity and effectiveness. In this study, zirconium was employed as a loading metal since it has several favorable characteristics, such as strong affinity toward phosphate, high selectivity, large surface area, and chemical stability. In an earlier study conducted with different metal loaded orange waste gel (SOW), Biswas et al. (2008) explored that Zr(IV) loaded SOW demonstrated a superior adsorption capacity (174.68 mg/g) when compared to those loaded with La(III) or Ce(III) or Fe(III) (42.72 mg/g for all three gels). Similarly, in the previous paper, zirconium loaded okara (ZLO) exhibited better adsorption capacity of phosphate (47.88 mg/g) than iron/zirconium loaded okara – IZLO (40.96 mg/g) and iron loaded okara – ILO (16.39 mg/g) (Nguyen et al., 2014).

The results indicate that Zr(IV) has the stronger affinity toward phosphate than other metal ions used for metal loading of AWBs. While La(III) and Fe(III) was found to be vigorously released from metal loaded biosorbents into aqueous solutions during operation, no Zr(IV) leakage could be detected (Biswas, 2008; Mallampati and Valiyaveettil, 2013; Nguyen et al., 2013). Due to its chemical stability during operation, Zr(IV) can be used as a metal loading without any harmful effects on the aquatic life or public health. The high cost of Zr(IV) salts can be considered as a limitation that currently exists. However, this drawback can be overcome once the Zr(IV) loaded biosorbents can be recycled and used sustainably. These findings prove that Zr(IV) can be used as a promising loading metal for modification of AWBs.

Okara, known as soybean milk residue, soy pulp, soy fines, bean mash, bean curd dregs, is a byproduct of soy beverage and tofu production. The production of every 1000 L of soy beverage can result in 250 kg of okara (Soy 20/20, 2005). Accordingly, it is estimated that, approximately 14 million tons of okara are generated worldwide annually (Nguyen et al., 2013). Due to the rapid degradation, okara needs to be dried or frozen for further use in food. However, this is costly because of intensive use of energy and special equipment requirement. Therefore, okara is mostly dumped or burned as waste, posing the environmental concern (Li et al., 2012). In this work, okara was used as a substrate to develop an innovative biosorbent for phosphorus removal because of its dominant advantages, such as easy acquiring, abundant availability enough for large scale utilization, low cost, insolubility in water, non-toxicity. Additionally, the existence in large amounts of hydroxyl and carboxyl groups on its cell walls makes okara easily and efficiently involve in chemical modifications (Benyoucef and Amrani, 2011). Moreover, okara has phosphorous inside (396–444 mg P/100 g dry matter), enabling the phosphorous recovery from both original okara and waste water (Li et al., 2012). Eventually, to the best of the author's knowledge, the use of okara as a phosphorus biosorbent has never been reported in the previous studies.

In a previous paper, we have made a comparison of three kinds of metal loaded okara. Zirconium loaded okara (ZLO) was proven to be superior to iron/zirconium loaded okara (IZLO) and iron loaded okara (ILO), with respect to adsorption, desorption, reusability and stability. Conversely, ILO and IZLO exhibited several drawbacks, as thus demonstrating unsuitable when used as phosphate biosorbents. As the next stage, the present study extensively investigates 'zirconium loaded okara' as a selected biosorbent, with the emphasis has been placed on kinetics, isotherms and thermodynamics studies. In doing so, batch-mode experiments were conducted to identify the effect of pH, adsorbent dose, initial phosphorus concentration, contact time and temperature on the retention of phosphorus by ZLO. The adsorption isotherms, kinetics, and thermodynamics were analyzed using nonlinear regression method in Curve Expert Professional 2.0.4. The results revealed the sorption mechanisms and nature, along with provided useful information for designing and operating the phosphorus – ZLO adsorption scheme in the future. Hence, this study has both theory and practical values.

2. Methods

2.1. Materials

2.1.1. Biosorbent

The fresh okara was collected from soybean milk production at the family with Lumina glass blender (Model No BL-805C). Every four liters of soybean milk made can result in one kg of fresh okara. To eliminate the residual milk, the pristine okara was washed with tap and distilled water on a 300 μm sieve. After being dried in the oven at 105 °C for 24 h, it was cooled down to the ambient condition and kept in a glass bottle for further chemical treatments.

ZLO as a modified biosorbent was developed by a two-step pretreatment of okara with NaOH and Zr(IV) salt. Firstly, the dried raw okara was impregnated in 0.05 M NaOH solution to enhance its metal capture ability (solid/liquid ratio: 1 g/20 ml, 120 rpm, 25 °C, 24 h). Then, NaOH treated okara was saturated with 0.25 M Zr(IV) solution at the above conditions. Due to the cationization, Zr(IV) loaded okara can efficiently remove phosphate species from aqueous solutions.

2.1.2. Adsorbate

Analytical grade chemicals used in this study was provided by Chem supply, Australia. The stock solution of phosphorus (1000 mg/L) was prepared by dissolving 4.58 g of disodium hydrogen phosphate (Na_2HPO_4) in a 1000 ml of milli−Q water. The working phosphorus solutions were made afterward by appropriate dilution of the stock solution with milli−Q water. The solutions of 0.05 M NaOH and 0.25 M Zr(IV) were produced by liquefying proper amounts of sodium hydroxide (NaOH) and zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) in the milli−Q water.

2.2. Methods

2.2.1. Analytical method

The phosphorus concentration in the solutions was determined using molybdenum blue method on Spectroquant® NOVA 60 machine. The phosphorus adsorption capability (mg/g) was calculated from the changes in the phosphorus concentrations before and after adsorption: