Separation of Phosphate from Wastewater
Using an Ion Exchanger Based on Chitosan

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Abstract

Phosphate is a key contaminant that induces eutrophication in rivers, ponds and reservoirs. To control phosphates in wastewater, we developed a chitosan-bead-based ion exchanger using Cu^{2+} for immobilization. Changing the initial conditions, we investigated its phosphate removal efficiency from solutions. The optimal initial concentrations of chitosan, acid and base were determined to be 2.5% (w/w) chitosan, 1% (v/v) HCl, and 1M NaOH to maintain bead shape. The additional step of crosslinking reduced uptake (efficiency) by up to 10% due to the loss of amino group active sites. The phosphate removal efficiency was proportionally increased by copper uptake. A concentration of 5,000 mg/L of copper could achieve stable physical strength. The maximum phosphate uptake was 89 mg/g, fitted with a Langmuir equation. When 10% NaCl was used as a regenerate, the regeneration efficiency gradually decreased from 75% to 40% through seven cycles.

Key words: chitosan bead, eutrophication, phosphate

1. Introduction

Recently, green algae blooms in surface water such as rivers, ponds and reservoirs have been observed throughout the world, induced by eutrophication (Johnk *et al.*, 2008; Schindler *et al.*, 2012; Michalak *et al.*, 2013; Xu *et al.*, 2013; Ostfeld *et al.*, 2014). Growth of green algae is affected in a complex manner by a variety of factors like light, water temperature, nutrients, water depth and residence time (Ganf & Oliver, 1982; Lee *et al.*, 2012; Singh *et al.*, 2013). Nutrients in bodies of water have been reduced in an attempt to reduce blooms. The main causes of eutrophication are phosphate and nitrogen in bodies of water (Smith *et al.*, 1999; Anderson *et al.*, 2002). Furthermore, Schindler *et al.* (1974) claimed that phosphate is the main nutrient causing eutrophication. Even with very low concentrations of phosphorus in water, it has been recognized as a substance that can induce eutrophication (Cornell, 1998). In the Republic of Korea (ROK), the concentration of total phosphorus allowable in wastewater has been reduced from 2 mg/L to 0.2 mg/L in the first-grade zone since Jan. 2012 (Nam *et al.*, 2013). Therefore, improvement in phosphate removal efficiency in treatment processes is required.

Although physical, chemical and biological treatments have been widely used as techniques for the re-moval of phosphate (Mino *et al.*, 1998; Sarparastzadeh, 2007; Song *et al.*, 2007; Xu *et al.*, 2010; Zhao *et al.*, 2012), lately, simple operations and easy-to-manage methods are being actively investigated as alternatives; ion exchange and adsorption processes are being studied as ways to meet regulations. A variety of sorbents based on inorganic and organic materials such as chitosan (Chang & Juang, 2004), zeolites (Sakadevan & Bavor, 1998), furnace slag (Lu *et al.*, 2008), bentonite (Yan *et al.*, 2010), aluminum (Tanada *et al.*, 2003), iron oxide (Zeng *et al.*, 2004), and alginate (Silva *et al.*, 2008) have been used as substances of adsorption because of low cost and easy operation. Chitosan is known for not only being eco-friendly, biodegradable, nontoxic and low-cost, but also for having outstanding adsorption qualities with transition metals, making it useful as a permeable adsorbent (Steenkamp *et al.*, 2002; Cetinus *et al.*, 2009). Chitosan contains amino, hydroxyl and acetamide functional groups which serve as coordination and chelation sites for metal ions (Chang & Juang, 2004). Irving and Williams (1953) reported that the affinity order of the coordinated ligand with heavy metals is $Cu^{2+} > Ni^{2+} > Fe^{2+}$. The metal sorption capacity of chitosan is determined by the degree of deacetylation (DD), molecular weight, and pK_a value (Kawamura *et al.*, 1993; Paulino *et al.*, 2007; Osifo *et al.*, 2008). The immobilized transi-

tion metal ions as fixed functional groups interact with phosphate through Lewis acid-base (LAB) and electrostatic interaction, which enhances the efficiency of phosphate removal. However, although chitosan showed high capacity for heavy metal removal due to the presence of the amino and hydroxyl groups in the polymer chain, its weak chemical properties under acidic conditions have limited its practical application. Thus, it will be necessary to increase its strength for use in practical applications. The role of a cross-linking agent reinforces the chemical binding which is used to connect chitosan chains of amino groups. It leads to improved chemical stability, but the metal sorption capacity is reduced due to the loss of activation sites occupied by the cross-linking agents. Therefore, the effects of cross-linking agents on phosphate removal need to be studied.

In this study, chitosan beads were modified and developed to simplify the process and more effectively remove phosphate from water. The specific objectives of this study were to 1) determine optimized parameters for bead synthesis, 2) find physical and chemical properties of each prepared bead, 3) investigate the effect of a cross-linking agent on phosphate sorption, and 4) test the regenerability of phosphate-saturated chitosan beads.

2. Materials and Methods

2.1 Materials

Chitosan powder with 75%–85% deacetylation (DD) from chitin and medium molecular weight (215,000 g/mol) was purchased from Aldrich (USA). Glutaraldehyde (GLA) solution (25%, W/W) was obtained from SHOWA (Japan). All other reagents, copper chloride dehydrate ($CuCl_2 \cdot 2H_2O$), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), hydrochloric acid (HCl), sodium hydrate (NaOH), NaCl, $NaNO_3$, KH_2PO_4, Na_2SO_4 and $NaHCO_3$ were ACS grade reagents and used without further purification. Ultrapure deionized water (18.2 Ω) was used to prepare solutions in all experiments.

2.2 Preparation of the adsorbents

For the separation of phosphate from solution, chitosan-based beads (CBs) were prepared as described by previous studies (Rorrer & Hsien, 1993; Guibal *et al.*, 1998; Zhao *et al.*, 2007; Ashura & Liu, 2011; Sowmya & Meenakshi, 2013). In this study, the optimal conditions for efficient phosphate removal were studied by changing the initial concentration conditions of the chitosan and acid solutions.

CBs for phosphate removal can be prepared in two steps. The first step is formation of the chitosan beads and the second is an immobilization process for CBs (An *et al.*, 2014). In brief, chitosan powders ranging from 1 to 5 g were dissolved in 195g of 1% HCl aqueous solution (v/v) for at least 12 hours. The viscous chitosan solution was dropped into 200 mL of 1M NaOH through burettes with mild stirring (100 rpm). After the beads appeared, the mixing continued for 3 h to enhance their mechanical strength. The CBs were rinsed with deionized water until

the solution became neutral. To determine the effect of crosslinking, the CBs were treated with 400 mL of 0.02, 0.1, and 0.3 M GLA solution for three hours. GLA is a well-known crosslinking agent that improves chemical strength (Kulkarni *et al.*, 2006; Raut & Jassal, 2012). The crosslinked CBs which are referred to as CB−G were washed several times with DI until the pH became neutral.

The second step was a copper or nickel loading process for the CBs or CB−G with $CuCl_2 \cdot 2H_2O$ or $NiCl_2 \cdot 6H_2O$. To immobilize the copper or nickel, 6 g of each chemical was dissolved in 400 mL of DI and the pH was controlled to ~4.5 and ~5.0, respectively. The washed CBs or CB−G were mixed with the each solution for at least 24 hours to reach copper or nickel sorption equilibrium.

Finally, the beads loaded with copper or nickel were washed with DI and stored in DI or dried until used. For comparison of initial concentrations of copper, 3,000 mg/L of copper solution was used and tested. The copper- and nickel-loaded beads are referred to as CB−G−Cu or CB−G−Ni, respectively. To reduce the crosslinking process using GLA, these were mixed with the copper solution and the CBs were referred to as CB−G+Cu. Note that dashes (−) and pluses (+) on acronyms denote separate and mixed steps, respectively, during preparation.

2.3 Physical characterization of the beads

Physical properties of the beads before and after modification were investigated. The color of the beads was verified through a visual test and the sizes were measured using a ruler. The amount of immobilized copper was calculated after dissolution using 0.1M HCl. The rate of hydration (HR) was calculated according to the following equation (1) :

$$HR(\%) = \frac{(W_h - W_d) \cdot 100}{W_h} \qquad \text{(Eq. 1),}$$

where W_h and W_d are the weight of the hydrated and dried beads, respectively.

2.4 Batch adsorption test

Two kinds of batch experiment tests were performed to determine the phosphate separation behavior of CBs and modified CBs (CB−Cu, CB−G−Cu, CB−G+Cu). About 0.05g of each bead was added to 50 mL of mixed solution containing 50 mg/L of phosphate. Each sample was continuously shaken at 100 rpm with a platform shaker (JSSI−100C) for 24 hours to reach equilibrium. To find the phosphate sorption capacity, an isotherm test was carried out for CB−Cu and CB−Ni. Fifty milliliters of solution containing 100 mg/L of phosphate was mixed with known amounts of beads ranging from 0.011 g to 0.12 g. The pH of the solution was initially set at 7.5 (±0.2) and was adjusted with diluted HCl or NaOH at determined times. The following equation (2) was used to find phosphate uptake from the solution to the solid by mass balance.

$$q = \frac{(C_0 - C_e) \cdot V}{w} \qquad \text{(Eq. 2),}$$

where C_0 is the initial concentration (mg/L), C_e is the final concentration (mg/L), V is the volume of the solution (L), and w is the weight of the chitosan beads (g).

2.5 Regeneration

Regeneration was carried out to determine the reusability of CB−Cu in sorption-desorption batch cycles. Sorption tests were performed by adding 0.1 g of CB−Cu to 200 mL of a solution containing 50 mg/L of nitrate, phosphate and sulfate. After 24 hours of phosphate sorption, the phosphate-saturated CB−Cu was regenerated with 10% NaCl for 24 hours. Before each sorption-desorption test, the CB−Cu needed to be washed with DI several times until the pH became neutral, and the initial pH was adjusted to 7.0–7.5 during regeneration.

2.6 Analytical instrumental techniques

Concentrations of phosphate, sulfate, nitrate and chloride in solution were analyzed using a Dionex Ion Chromatogram (Model: ICS−1000, USA). The dissolved copper concentration was measured by Inductively Coupled Plasma (ICP, Nexion 300D, Agilent Technologies, USA). The pH was determined using a pH electrode (Orion Star A211, Thermo Scientific, USA).

3. Results and Discussion

3.1 Optimization of synthesis conditions

Chitosan powder is very stable in neutral and basic solutions, but it dissolves readily in acidic solutions (Rinaudo *et al.*, 1999; El-hefian *et al.*, 2009). To prepare gel beads of chitosan, it is necessary to determine the viscosity of the chitosan solution, which is dependent on the chitosan acid concentrations during dissolving. Different chitosan concentrations of 0.5, 1, 2, 2.5 and 3% (w/w) were tested for formation of hydrogel beads using a fixed acidic concentration of 1% (v/v) HCl. Photographs after CB synthesis are shown in Fig. 1 for concentrations of 2% (a) and 2.5% (b). The hydrogel beads broke easily at less than 1% chitosan concentration during solidification in NaOH (data not shown). Although hydrogel beads formed at 2% chitosan (Fig. 1(a)), some parts of the beads failed to keep their initial shape. It was difficult to dissolve 3% chitosan in 1% HCl. Therefore, 2.5% chitosan and 1% HCl were found optimal for chitosan shape and physical and chemical strength. Note that all of the chitosan beads used in following experiments were synthesized using a 2.5% (w/w) chitosan solution in 1% HCl.

3.2 Characteristics of CBs

Four types of chitosan-based sorbent were synthesized according to the parameters in Section 2.2 and tested to determine their physical and chemical properties. Details on their properties are listed in Table 1. After
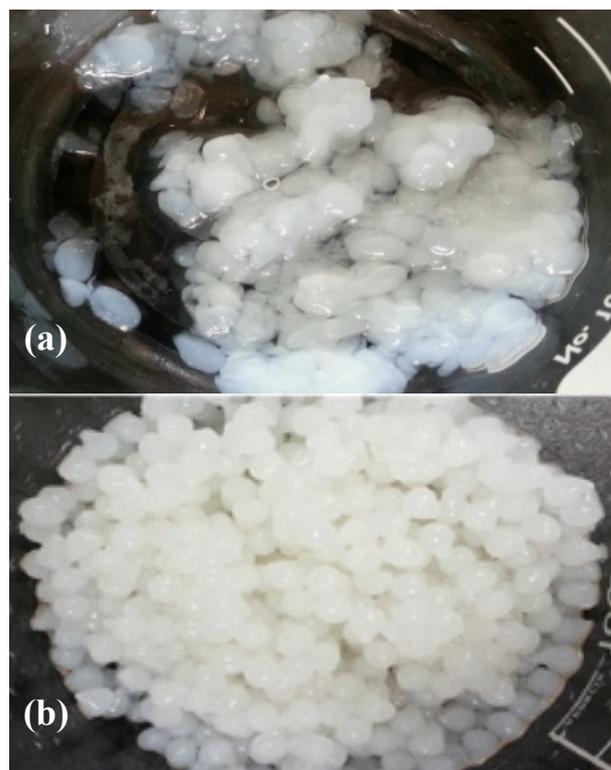

Fig. 1 Photograph of chitosan beads: (a) 2% chitosan in 1% HCl (b) 2.5% chitosan in 1% HCl.

Table 1 Size, hydration and immersed copper concentration of beads.

Bead	Size (mm)		Hydration (%)	Immersed copper (mg/g)
	gel	dry		
CB	5.0	2.5	96	0
CB−G−Cu	4.0	2.0	95	27.2
CB−G+Cu	3.0	2.5	89	25.6
CB−Cu	3.0	1.0	90	53.4

loading with copper (CB−G+Cu and CB−Cu), the size of the CBs (gel) decreased considerably from 5.0 mm to 3.0 mm, whereas the CB−G−Cu beads were slightly smaller in size. It is clear that crosslinking by GLA is likely to maintain the framework of the chitosan bead. One would suppose that the use of GLA would not modify the 3D geometric shape of CBs, but GLA seems to link amino groups from chitosan polymer chains with each other. For CB−Cu and CB−G+Cu, however, the copper is strongly coordinated with the amino group and the water molecules surrounding the CB are excluded. Therefore, it may result in decreased size of the CBs. After drying, resulting in contraction of the CBs, there were no notable differences in size between the four sorbents. It was found that most of the hydrogel beads were saturated with water. Thus the hydration rate for all of the beads was over 90%. Changes in bead color are shown in the photograph of Fig. 2. The color of CBs is ivory (a), but CB−G−Cu (b) and CB−G+Cu (c) turned dark green and brown, respectively. The CB−Cu (d) beads

Fig. 2 Colors of a chitosan bead and modified chitosan beads
(a) CB (b) CB−G−Cu (c) CB−G+Cu (d) CB−Cu.

Fig. 3 Uptake of copper at different GLA concentrations.

ultimately became a translucent blue due to copper ions. It is evident that the GLA and Cu ions strongly interact with the amino group of chitosan. The copper uptakes were 27.2, 25.6 and 53.4 mg/g for CB−G−Cu, CB−G+Cu and CB−Cu, respectively. The addition of a crosslinking agent reduced the copper sorption capacity of the chitosan beads by 50% and the copper sorption capacity was also affected by GLA addition. This result can be explained by the loss of active amino groups which were already occupied by GLA (Oyrton *et al.*, 1999; Guzman *et al.*, 2003; Jeon & Holl, 2003).

According to TOC measurement as an indicator of chitosan released into solution after batch experiments, among CB, CB−G−Cu, CB−G+Cu and CB−Cu, the highest TOC was obtained from CB. It can be predicted that the interaction between amino groups in chitosan polymers and transition metals may strengthen the physical, chemical and biological properties.

3.3 Effect of crosslinking on phosphate removal

To enhance the chemical strength of chitosan beads, GLA, a popular crosslinking agent for chitosan, was used when the CBs were prepared. By strongly crosslinking each polymer chain, CBs can acquire low pH resistance. The use of GLA, however, reduces active sorption sites. As Fig. 3 shows, copper uptake significantly decreases with an increase in GLA concentration. A maximum of 13 mg/g was achieved at 0.02 M, above which it decreased to ~3 mg/g. The loss of amino groups plays a key role in heavy metal sorption. As Fig. 4 shows, GLA interacts with each amino group and the nitrogen in the amino group is already occupied. As a result, the number of free amino groups capable of forming complexes with heavy metals decreases. Similar results were observed by Lee *et al.* (2001) and Ngah *et al.* (2002). Consequently, it is anticipated that reduced copper loading of CBs will be directly reflected in phosphate removal.

3.4 Effect of copper concentration during loading

As noted in Section 3.2, the number of free amino groups directly affects the uptake of copper. To observe the effect of the amount of copper ions on the removal of phosphate (Fig. 5), two concentrations, 3,000 and 5,000 mg/L of copper were used during loading. Phosphate removal efficiency reached more than 90% with 5,000 mg/L of copper, but only 70% with 3000 mg/L of copper, indicating that higher concentrations increase the uptake of copper in chitosan beads, and the interaction with phosphate through Lewis acid-base (LAB) and electrostatic interactions enhances the phosphate removal efficiency. Consequently, it is concluded that phosphate
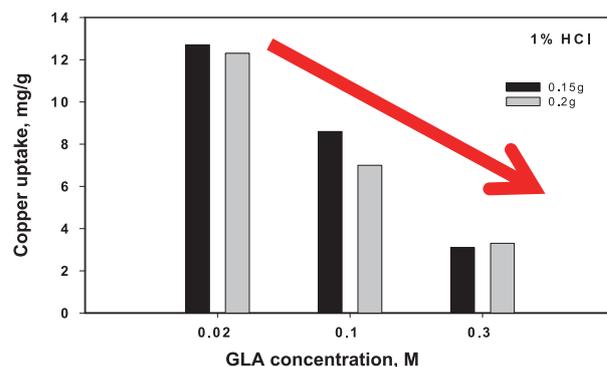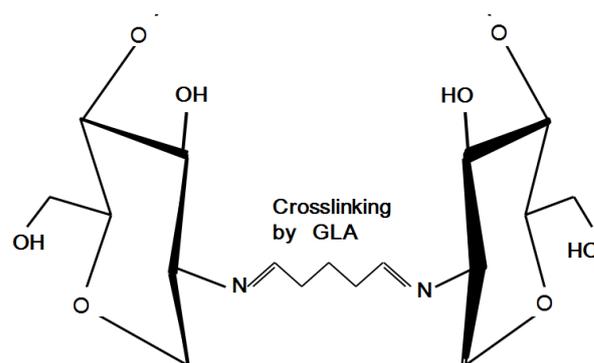

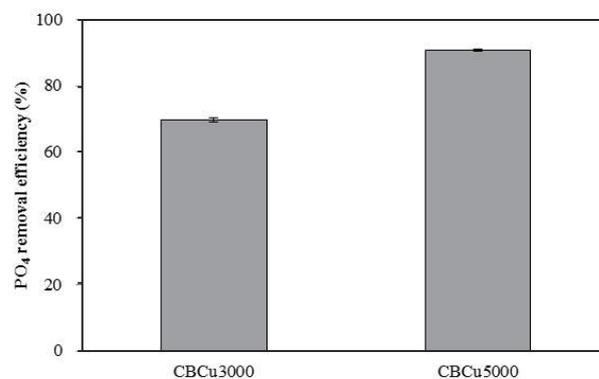**Fig. 4** The structure of a chitosan chain linked by GLA.

Fig. 5 Effect of initial copper loading concentration on phosphate removal efficiency.

removal is strongly affected by the amount of copper in the CBs.

3.5 Batch tests for phosphate removal

Batch tests were carried out to investigate the capacity of the four beads characterized in Section 3.2 for phosphate removal. In addition, in order to determine the effect of drying, two sets of each of the beads were prepared, with and without air drying (dry and gel type, respectively; Fig. 6). The phosphate removal efficiency for gel-type CBs, CB−G−Cu, CB−G+Cu and CB−Cu were about 11%, 86%, 84% and 91% respectively. The removal efficiency of 11% for CBs may indicate that protonated amino groups (H⁺) bind to phosphate by
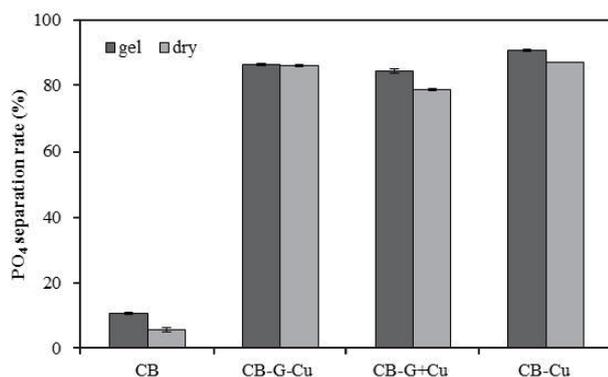
Fig. 6 Phosphate removal efficiency of four different beads (gel and dry type).

Fig. 7 Separation capacity of CB, CB−Cu, CB−Ni with competing ions.

Fig. 8 Two sorption equilibrium models: (a) Langmuir and (b)Freundlich.

electrostatic interaction. Among the copper-loaded chitosan beads, which showed much higher phosphate removal than CBs, CB−Cu obtained the highest phosphate removal efficiency of 91%. This corresponds to the copper loading capacity in Table 1, demonstrating that the addition of GLA reduces the copper loading capacity as a result of the loss of active amino groups. Consequently, phosphate is best separated from solution by using copper, which leads to LAB and electrostatic interactions. The effect of air drying shows no significant improvement in phosphate removal; instead a small reduction is found. This might be due to blockage of porosity in the chitosan beads.

3.6　The effect of copper and nickel

Like copper, nickel is a transition metal and has shown high complex stability (Irving & Williams, 1953). CB−Ni was prepared using the same procedures except that the solution pH was 5.0−5.5 during loading. In general, copper is known to be more selective for chitosan than nickel because copper is a stronger Lewis acid than nickel (Kawamura *et al.*, 1993; Seham Nagib *et al.*, 1999). However, it is possible to load as much nickel as copper by controlling the pH, due to the fact that nickel's solubility is higher than that of copper at high pHs. Batch tests were carried out for CB−Cu and CB−Ni to determine the effect of nickel on phosphate removal using artificial sewage consisting of nitrate with sulfate as the counter ion. Figure 7 shows phosphate uptake for CB−Cu and CB−Ni with nitrate and sulfate after 24 hours. There is no significant difference between CB−Cu and CB−Ni with regard to phosphate separation capacity. CB−Cu, however, is more affected by sulfate than CB−Ni.

3.7　Isotherm test

Equilibrium isotherm tests are essential in describing the interactive behavior between solutes and adsorbents. They were carried out to determine the maximum phosphate uptake at a fixed 100 mg/L of phosphate solution and pH 7. The experimental data (symbols) and model-fitted equation (plotted) are shown in Fig. 8 and the parameters are listed in Table 2. There are two sorption equilibrium models Langmuir (Fig. 8a) and Freundlich (Fig. 8b) commonly used to explain isotherm theories.
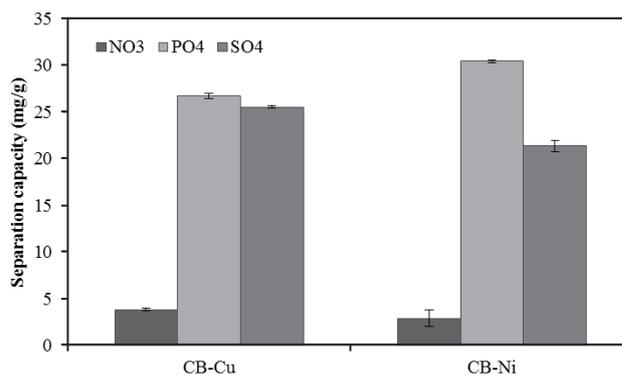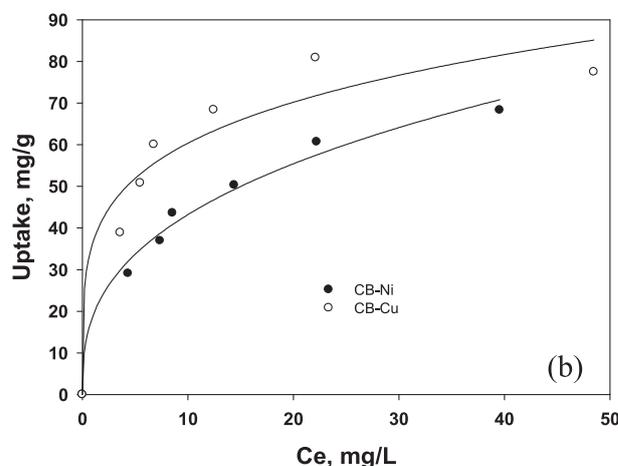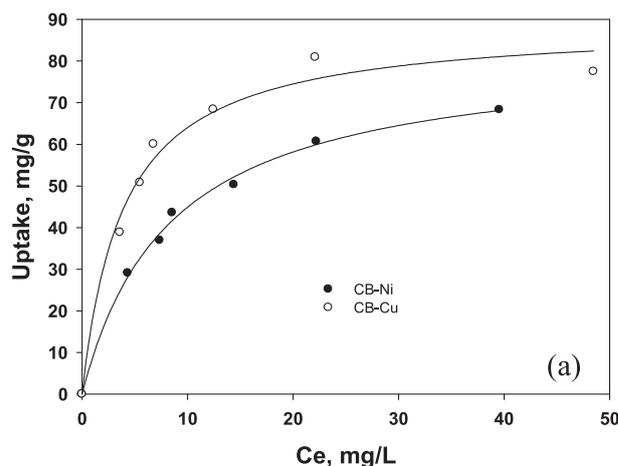
The classic Langmuir model (Eq. 3) and the Freundlich model (Eq. 4) that were used to fit the data and equations are as follows:

$$q_e = \frac{bQC_e}{1 + bC_e} \qquad \text{(Eq. 3),}$$

where q_e is the amount of phosphate adsorbed at equilibrium (mg/g), Q is the maximum phosphate uptake (mg/g), and b represents the Langmuir affinity coefficient (L/mg), a constant, between the sorbent and sorbate. C_e is the liquid-phase phosphate concentration at equilibrium (mg/L).

$$q_e = K_F C_e^{1/n}$$ (Eq. 4),

where K_F and n indicate adsorption capacity (mg/g) and the sorption intensity, respectively. According to Fig. 8 and Table 2, both adsorption models show a good fit to the experimental data with high r^2 of 0.99 and 0.99 using Langmuir, and 0.98 and 0.94 using Freundlich for CB–Ni and CB–Cu, respectively. The Langmuir isotherm model estimates that binding sites are homogeneously distributed over the adsorbent surface and chemical and physical bonding take place at the adsorption sites (Al-Asheh *et al.*, 2000). The value of the maximum adsorption capacity (Q) calculated by the Langmuir isotherm equation was 82.5 mg/g and 89.1 mg/g, for CB–Ni and CB–Cu, respectively. Based on the b value, which is associated with the affinity of the binding site, CB–Cu showed a higher affinity for phosphate than CB–Ni. The Freundlich parameter, n, indicates favorability of the adsorption. Treybal (1998) reported that the value of n in the Freundlich equation indicates the favorability of sorption; less than 1 is poor, 1–2 is moderately difficult, and 2–10 is good. The value for CB–Cu is 4.6, much higher than the 2.8 for CB–Ni resulting in a higher Q for CB–Cu.

3.8 Regeneration and reusability

For realistic application, adsorption and desorption experiments were repeated seven times to examine the potential of recycling using 10% NaCl. High concentrations of chloride can replace the phosphate from CB–Cu through the following equation (5) (Sowmya & Meenakshi, 2014).

$$CB\text{-}Cu^{2+}HPO_4^{2-} + 2Cl^-$$
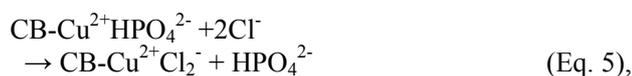$$\rightarrow CB\text{-}Cu^{2+}Cl_2^- + HPO_4^{2-}$$ (Eq. 5),

Figure 9 shows the recovered capacity efficiency of CB–Cu found at different cycles of regeneration. After the first regeneration, up to 75% of the phosphate removal capacity was recovered, gradually decreasing to 40% by the fourth regeneration. The reason was 10% NaCl is not enough to achieve 100% desorption of phosphate but suitable for obtaining ~40% desorption efficiency. How to dispose of the Cu^{2+} immobilized chitosan after use is also a big issue. Separation of the Cu^{2+} should be considered first, with the used chitosan remaining as an eco-friendly polymer that can be easily handled in the field of waste management.

4. Conclusions

To remove phosphate from wastewater, a variety of chitosan-based ion exchange beads with immobilizing copper (Cu^{2+}) or nickel (Ni^{2+}) were developed and tested with different initial experimental conditions. The main findings and conclusions are as follows:

– A chitosan solution at 2.5% (w/w) with 1% HCl and 1 M of NaOH was found optimal for forming physically and chemically stable chitosan beads.

– The use of GLA, which enhances chemical strength, reduced the amount of copper immobilization due to the loss of amino groups, and the phosphate removal efficiency decreased with increasing GLA concentration.

– Phosphate removal efficiency using CB–Cu, is strongly affected by the inclusion of nitrogen, phosphate and sulfate as counter ions, but the affinity for phosphate is higher than that for sulfate and nitrate. Therefore, use of CB–Cu in real wastewater can be expected to meet the current regulation level of 0.2 mg/L.

– The maximum phosphate uptake was 89.1 mg/g and 82.5 mg/g for CB–Cu and CB–Ni, respectively.

– The regeneration efficiency gradually decreased from 75% to 40% after four regeneration cycles and then stayed essentially constant through seven cycles.

Table 2 Equilibrium model fitted parameter values (Langmuir and Freundlich).

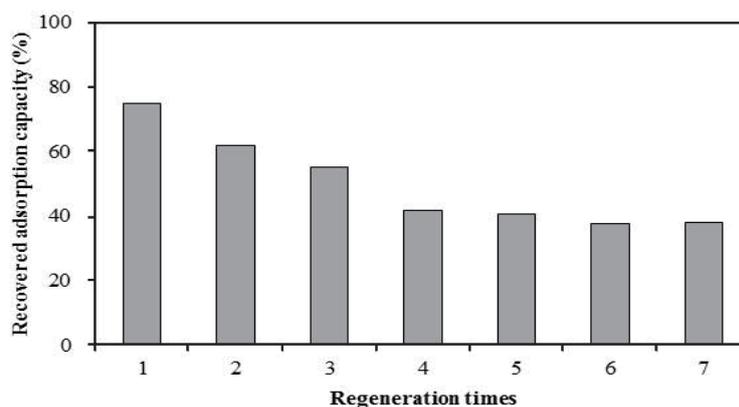|	Langmuir			Freundlich		
	Q	b	r^2	K_F	n	r^2
CB–Ni	82.5(2.5)	0.12(0.010)	0.99	18.9(1.7)	2.8(0.24)	0.98
CB–Cu	89.1(4.3)	0.25(0.046)	0.99	36.6(5.6)	4.6(1.1)	0.94

Fig. 9 Ratio of recovered adsorption capacity to that of fresh CB-Cu.

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