Feasibility of iron loaded 'okara' for biosorption of phosphorous in aqueous solutions

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ABSTRACT

This study investigated the feasibility of using soybean milk by-products (okara) as a sustainable biosorbent for phosphate removal in water and wastewater. The results show that raw okara could hardly decontaminate phosphate from aqueous solutions. Hence, in this work, okara was modified by being cationized using $FeCl_3$ 0.25 M (namely iron loaded okara, ILO) to enhance the phosphorus adsorption capacity. The phosphate sorption onto ILO was well achieved under the conditions of pH 3, initial phosphorous concentration of 25 mg/L, biosorbent dose of 20 mg/L and contact time of 7 hours. Based on Langmuir model, the maximum adsorption capacity of phosphate by ILO was 4.785 mg/g. The effects of interfering anions were in the order of $CO_3^{2-} > SO_4^{2-} > NO_3^-$. It was also observed that Fe(III) was detached during operation. This problem can hinder the sustainable usability of ILO. Thus, further research would be necessary for improving the modification method.

Keywords: Adsorption capacity; Cationization; Iron loaded okara; Phosphate removal

1. Introduction

Phosphorous plays a critical role in the development of agriculture and industry (Benyoucef and Amrani, 2011). However, the current phosphate rock reserve could be depleted in 50-100 years (Cooper et al., 2011). Meanwhile, eutrophication can be induced by high concentrations of phosphorous (> 0.02 mg/L) in receiving water bodies (Ismail, 2012). Therefore, the removal of phosphorous from water and wastewater is necessary to avoid water deterioration and diminish rely on limited phosphorous rock sources.

A variety of technologies have been employed for phosphate removal. Each of these methods has their own advantages and limitations (Table 1). However, biosorption has become a new trend in this field of study (Jyothi et al, 2012) which can effectively to purify wastewater with low contents of phosphorous (De-Bashan and Bashan, 2004; Han et al., 2005). Moreover, biosorption is believed to reduce the cost of water treatment, owing to the use of renewable, readily available and low-priced materials (Nguyen et al., 2012). Another advantage is the eco-friendly property of biosorption, which allows developing useful materials for water treatment from agricultural waste and byproducts (Li et al., 2012). Particularly, biosorption offers a potential of phosphorous recovery (Biswas et al., 2007; De-Basan and Basan, 2004). It is estimated that about 250,000 tones of phosphorous can be recovered from wastewater in Western Europe annually (Biswas et al. 2007).

Table 1

There is a growing interest in the use of renewable agricultural by-products to develop innovative, cost-effective and sustainable biosorbents for phosphorous decontamination. Earlier studies demonstrated that different agricultural by-products could be modified to effectively retain phosphorous, e.g. sawdust (Benyoucef and

Amrani, 2011); sugarcane bagasse fibers (Carvalho et al., 2011); date-palm wastes (Ismail, 2012); coir pith (Krishnan and Haridas, 2008); eggshell (Mezenner and Bensmaili, 2009); date palm fibers (Riahi et al., 2009); wheat straw (Xu et al., 2009); etc. This can be attributed to the fact that large amounts of hydroxyl groups in the cellulose, hemicelluloses, and lignin make agricultural by-products easily and effectively involve in chemical modifications (Benyoucef and Amrani, 2011; Xu et al., 2010).

Cationization of agricultural by-products using metal salts is widely used to activate their phosphorous capture ability. Many articles have been published so far, confirming the enhanced phosphorous removal of metal loaded biosorbents (Biswas et al., 2007; Carvalho et al., 2011; Eberhardt et al., 2006; Krishnan and Haridas, 2008; Mezenner and Bensmaili, 2009). However, little information is available on the leachability of metals, which plays a decisive role to the repeated utilization of biosorbents.

Okara is a by-product of soy beverage and tofu production. It is white and quite similar to wet sawdust in its texture and form. Okara is also named as soybean residue, soy pulp, bean curd dreg, tofuzha or douzha (Chinese), tofukasu (Japanese), or bejee (Korean). It contains 50% crude fiber, composing of cellulose, hemicellulose and lignin. Every 1,000 liters of soy milk make about 250 kg of okara. Thus, it is estimated that each year approximately 14 million tons of okara are generated all over the world, causing environmental burden. In addition, fresh okara degrades quickly. For that reason, though okara can be used for many purposes (e.g. animal food, fermentation substrate, fertilizer, etc.), it commonly dumped and burned as waste (Li et al., 2012). Some types of soybean by-products were used as environmentally friendly materials, such as soybean hulls (Marshall and Wartelle, 2004); lees materials (Adachi et al.,

2005) and bean dregs (Li, 2009). It was found that these materials exhibited good sorption abilities to heavy metals, organochlorine compounds, and some anions. However, no previous studies have reported the use of okara for phosphate elimination.

Okara was chosen in this study because of its dominant advantages, such as easy acquiring, abundant availability enough for large-scale applications, and low price. Consequently, the application of okara as a biosorbent of phosphate may help to reduce the cost of water treatment. Also, it allows eliminating okara as a waste product in a green way. Furthermore, okara contains phosphorous inside (400-440 mg P/g dry okara), giving a platform for phosphorous recovery from both original okara and wastewater (Li et al., 2012). The main objective of this study is to develop an innovative, cost-effective and sustainable biosorbent for phosphate removal from soybean milk by-product (okara). The material was cationized using $FeCl_3$ 0.25M to activate its phosphorous sorption capacity. The ILO before and after sorption was characterized using Fourier transform infrared spectroscopy (FTIR) analyzer. The influential factors (e.g. pH, dose, initial concentration, contact time, foreign anions) were investigated for the process optimization. The maximum adsorption capacity of phosphorous by ILO was determined from Langmuir isotherm model. Unusual results of desorption study and Fe(III) leachability was elucidated. Based on that, useful recommendations for improving the modification method were proposed.

2. Materials and Methods

2.1. Chemicals

All chemicals in this work are of analytical grade and supplied by Chemsupply, Australia. The phosphorous stock solution containing 1000 mg P/L was prepared by dissolving disodium hydrogen phosphate (Na_2HPO_4) powders in distilled water, using a

1000 ml volumetric flask. The phosphorous working solutions were prepared by diluting the phosphorous stock solution with distilled water to the desired concentrations.

The NaOH 0.05 M and $FeCl_3$ 0.25 M solutions were prepared by dissolving specific amounts of NaOH pellets and $FeCl_3.6H_2O$ in the distilled water.

2.2. Preparation of ILO

The biosorbent in this study was developed from okara. As okara is a by-product of tofu and soy milk production, it can be easily collected from soy milk factories or families at no cost or very little priced.

To prepare ILO, the raw okara was put on a sieve of 150 µm and washed with distilled water before it was kept in the dry oven at 110 ^{0}C for 24 h. Next, 40 g dried okara was stirred with 1 L NaOH 0.05 M at the speed of 120 rpm, room temperature for 24 h. NaOH pretreated okara was then washed with distilled water again until pH of the washing solution reached 7. After that, obtained okara was stirred with 800 mL $FeCl_3$ 0.25 M at the speed of 120 rpm, room temperature for 24 h. Consequently, Fe(III) pretreated okara was carefully washed with distilled water to remove all free Fe(III) cations remained on the surface of okara. Finally, it was dried in the oven at 110 ^{0}C for 24 h and powdered to a fine mesh of size with a Breville coffee ‘n’ spice grinder before it can be used for adsorption experiments.

2.3. Characterization of materials

Fourier transform infrared (FT-IR) spectroscopy is a useful technique. It allows a qualitative and preliminary analysis of the main functional groups on the biosorbent surface, which may be responsible for the phosphate retention. FTIR spectrum of pristine and phosphorous laden okara were recorded with SHIMADZU FTIR 8400S (Japan) in mid-IR wave number range (600-4000 cm^{-1}).

2.4. Adsorption kinetic experiments

The adsorption kinetic experiments were conducted using a series of 50 mL Erlenmeyer flasks, tightly covered with aluminum foil, without any pH adjustment. 0.5 g of ILO was taken into 25 mL of disodium hydrogen phosphate (Na_2HPO_4) of 100 mg P/L. The flasks were put on an orbital shaker and shaken vigorously at 120 rpm, room temperature for 24 h to ensure the equilibrium was reached. After different predetermined time intervals, each flask was taken and filtered with filter paper Whatman®, GF/C, Cat No 1822-047. All samples were kept for phosphorous analysis. The amount of adsorbed phosphorous was calculated based on the difference in the concentration between phosphorous solutions before and after adsorption.

2.5. Desorption experiments

To evaluate the desorption capacity of phosphorous from phosphorous bearing ILO, different elution solutions were employed, including the distilled water at various pH values (2, 4, 6, 8, 10, 12), NaOH 0.25 M and HCl 0.1 M.

The suspension from adsorption test was filtered with 0.45 μm filter paper. Next, the phosphorous laden solids remaining on the filter papers were washed with abundant amount of tap water and then with distilled water to remove all free phosphorous anions. After that, the solids were collected into 50 mL erlenmeyer flasks containing 25 mL of different desorption solutions. Consequently, all flasks were shaken on an orbital shaker at 120 rpm, room temperature for 24 h. When the contact time was over, all samples were filtered. The solutions were taken for determining the amount of desorbed phosphorous.

2.6. Phosphorous analysis method

The phosphorous concentrations were determined spectrophotometrically by molybdenum blue method on Spectroquant® NOVA 60 (Germany) machine, corresponding to its analysis procedure. The dilution was made where necessary to ensure the phosphorous concentrations in all samples were below 5 mg P/L. All measurements were conducted in triplicate. The data represented the average values.

2.7. Determination of iron

In order to identify the side effects of employing ILO as a biosorbent for the remediation of phosphorous, the samples after adsorption and desorption processes were taken for Fe(III) analysis. The iron concentration was determined by Microwave Plasma-Atomic Emission Spectrometer (MP-AES) - Agilent Technologies 4100.

3. Results and Discussion

3.1. Characterization of ILO

Table 2 presents functional groups and the corresponding infrared adsorption bands of ILO before and after adsorption of phosphorous. Numerous adsorption peaks are listed in Table 2, implying the complicated nature of ILO. Adsorption at 3548, 3423, 3405 and 3357 $cm^{-1}$is assigned to bonded hydroxyl groups (OH^-) of alcohols and phenols in modified okara (Riahi et al., 2009).The bands at 3290, 3162 and 3083 cm^{-1} are characteristics of O-H group in carboxylic acids & derivatives. The band at 2376 cm^{-1} is attributed to P-H of phosphine group (Ismail, 2012). The band intensity of alcohols & phenols as well as carboxylic acids & derivatives of ILO after adsorption has shifted compared with that before adsorption. The band shifts indicated that O-H (alcohols & phenols), O-H (carboxylic acids &derivatives) and P-H (phosphine) were major binding sites for the attachment of phosphorous onto ILO.

Table 2

3.2. *The phosphorus capture by ILO*

In this study, the Langmuir isotherm model was chosen to calculate the maximum adsorption capacity of phosphorous by ILO. The Langmuir equation and its linear form are described by the equation (1) and (2), respectively as follows (Mallampati and Valiyaveettil, 2013):

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (1)$$

$$\frac{1}{q_e} = \frac{1}{K_L C_e q_{max}} + \frac{1}{q_{max}} \qquad (2)$$

where C_e is the equilibrium phosphorous concentration in liquid phase (mg/L), and q_e is the amount of phosphorous adsorbed onto 1 g of the adsorbent (mg/g), K_L is a Langmuir constant (L/mg) relevant to the energy of adsorption, and q_{max} is the maximum phosphorous sorption capacity (mg/g), R^2 is the correlation coefficient. The linear regression method, which is based on the slope and intercept of the linear plot between $1/q_e$ and $1/C_e$, was used to calculate the values of q_m, K_L and R^2.

The Freundlich model is expressed as the equation (3) (Mallampati and Valiyaveettil, 2013), where K_f and n are Freundlich constants associated with sorption capacity and sorption intensity of the adsorbent, respectively. The Freundlich constants were calculated, using the same method as for Langmuir, for a comparison purpose. The results are presented in Table 3.

$$\ln q_e = \ln K_f + \frac{1}{n} * \ln C_e \qquad (3)$$

Table 3

As can be seen in Table 3, Langmuir model represented a better fit than Freundlich model, indicating that the sorption of phosphorous onto ILO was probably monolayer.

Also, the surface of ILO might be homogeneous. The Freundlich constant value 1 < n < 10 revealed that the sorption of phosphorous onto ILO was favorable (Boujelben et al., 2008). The 1/n value for PO_4^{3-} (0.225) was below 1, referring to the normal Langmuir isotherm (Mallampati and Valiyaveettil, 2013).

Table 3 indicates that the maximum adsorption capacity of phosphorous by ILO was 4.785 mg/g. Meanwhile, the initial investigations showed that raw okara exhibited very low adsorption capacity (0.8 mg P/g) and removal efficiency (4%) for phosphate ions (initial phosphorus concentration of 100 mg/L, biosorbent dose of 5 g/L, shaking speed of 200 rpm after 24 h of contact time at room temperature). It means that ILO was 5.98 times more efficient than raw okara in remediating phosphorus from aqueous solutions. Apparently, impregnation of okara with $FeCl_3$ 0.25 M considerably improved its phosphorous retention. In spite of the differences in nature and chemical composition between okara and sugarcane bagasse, the results of the present study fit well with the findings reported by Carvalho et al. (2011). The authors claimed that the phosphorous remediation capacity was increased by 45% due to the incorporation of Fe(II) onto of sugarcane bagasse fiber surface. By comparing the removal between carboxymethylated material (94%) and non-carboxymethylated material (97%), they concluded that the presence of Fe(II) in the fibers played a decisive role in enhancing phosphorous capture, whilst the carboxymethylation enabled the attachment of Fe(II). These results are in line with those reported by Jyothi et al. (2012). Accordingly, the presence of tenfold excess of cations, e.g. Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} boosted the removal percentage of phosphorous.

As shown in Table 4, the maximum adsorption capacity of phosphorous by ILO is not really high compared with the literature data. This implies that Fe(III) may be inappropriate for cationization of okara. To further improve the sorption capacity of phosphorous, other metals should be tested to substitute for Fe(III) ions. Besides, adsorption experiments need to be conducted at the optimum conditions. Despite of the limited adsorption capacity of phosphorous, original okara is still recommended for developing biosorbents of phosphorous, with the advantage of being abundantly available, cost effective, renewable and environmentally benign material.

Table 4

3.3. Optimization of phosphorous biosorption process

3.3. 1. Effect of pH

The pH plays an important role in the adsorption process by affecting the chemical speciation of phosphate anions and the ionization of active functional groups on sorbent surfaces. To evaluate the effect of pH on the sorption of phosphorous onto ILO, batch experiments were performed at a fixed initial phosphorous concentration (100 mg/L), biosorbent dose (20 g/L), shaking speed (130 rpm), room temperature, while varying pH values (3, 5, 7, 10). The NaOH and HCl solutions of different concentrations were used to adjust pH values of phosphorous solutions with a pH meter (HANA-HI 9126 model). It was found that, the removal percentage (%) of phosphorous decreased from 95.74% to 90.85% with an increase of pH from 3 to 10. The optimum pH for the removal of PO_4^{3-} by ILO was 3. The binding of PO_4^{3-} anions was most efficient in acidic medium. High pH values suppressed the attachment of PO_4^{3-} onto ILO surface. This can be explained by the fact that at high pH values, the surface of ILO became more negatively charged due to OH^- ions, leading to a higher competition with PO_4^{3-} anions. In contrast, low pH boosted the adsorption of PO_4^{3-} anions, because of the electrostatic interactions. It is interesting that, despite of fluctuations in pH, the minimum removal (90.85%) was still extremely high. Thus, pH did not show significant effects on the phosphorus removal using ILO.

Similar trend was observed by Ismail (2012) in case of adsorption of phosphorous onto date palm wastes. The results of the current study relative to the optimum pH fit well with the findings reported by Biswas et al. (2007) and Krishnan & Haridas (2008), who claimed that pH 3 favored the retention of PO_4^{3-} anions by Fe(III) loaded orange waste gel and Fe(III) coated coir pith, respectively. However, different pH values were found to be effective in previous studies conducted by Benyoucef and Amrani (2011); Jyothi et al. (2012); Kumar et al. (2010); Xu et al. (2010); Yue et al. (2010). This is probably due to the difference in nature and composition of various agro-based materials used.

To explore the effect of ILO dose on the removal of phosphorous, adsorption experiments were conducted at a constant initial phosphorous concentration (100 mg P/L); temperature (25 ^{0}C), pH (non-adjusted), and contact time (24 h) but with various Fe(III) loaded okara doses (1, 2, 5, 10, 15, 20 g/L). It was found that the phosphorous removal was augmented remarkably from 2% to 90.67% as the dose of ILO increased from 1 g/L to 20 g/L. The more efficient capture of PO_4^{3-} anions at a higher ILO dose resulted from a larger surface area (Kumar et al., 2010) or more available binding sites (Xu et al., 2009; Yue et al., 2010). Optimum dose was selected to be 20 g/L as the removal of PO_4^{3-} anions kept increasing until that dose. In addition, the ILO dose of 20 g/L resulted in exceptionally high removal efficiency (90.67%) at the initial phosphorous concentration of 100 mg/L. Furthermore, higher doses may lead to the decrease in the phosphorous removal because of particle aggregation, which is likely to reduce the total surface area of ILO (Mezenner and Bensmaili, 2009). The optimum dose in the present study (20 g/L) is higher when compared with the literature data, e.g. 2 g/L (Xu et al., 2009); 4 g/L (Kumar et al., 2010); 5 g/L (Ismail, 2012); 10 g/L (Mezenner and Bensmaili, 2009). Even so, the applicability of ILO as a biosorbent for the phosphorous removal should not be interfered because of its easy acquiring, abundantly available and low-priced characteristics.

3.3.3. Effect of initial phosphorous concentration

Figure 1

Batch experiments were conducted to examine the effect of different initial concentrations of phosphorous (10, 25, 50, 100, 200, 250, 350, 450, 100 mg/L) on the phosphorous removal by ILO at a fixed ILO dose of 10 g/L, pH values of 5-6, temperature of 298 K, shaking speed of 130 rpm and contact time of 24 h. The results are shown in Figure 1, showing that the higher the initial phosphorous concentration, the lower was the removal percentage of phosphorous attained. The removal percentage of PO_4^{3-} by ILO declined drastically from 96.03% to 20.30% with an increase in the initial concentration of phosphorous from 10 mg/L to 500 mg/L. The optimum initial concentration of phosphorous was 25 mg/L, as a further decrease in initial concentration did not result in a significant increase in the removal percentage of phosphorous. The removal percentage of phosphorous was lower at higher initial concentrations, owing to enhanced ratios between phosphate moles and available adsorption sites (Mezenner and Bensmaili, 2009). This can be explained by the fact that, the number of binding sites and thus the amount of phosphorous adsorbed are constant for a certain dose of ILO, whilst the quantity of phosphorous in the solution grows with increasing initial phosphorous concentrations. Likewise, the removal percentage of phosphate was found to decline from 95% to 64% with an increase in the phosphorous concentration from 2.8 mg/L to 110 mg/L (Mezenner and Bensmaili, 2009). These results are in harmony with those reported by Kumar et al. (2010) and Xu et al. (2009). The former attributed this to an increase in driving force at higher initial phosphorous concentrations, whereas the latter suggested that the phosphorous concentration gradient facilitated the sorption.

3.3.4. Effect of contact time

Figure 2

The influence of the contact time was examined by conducting experiments at a fixed phosphorous concentration (100 mg/L), biosorbent dose (20 g/L), temperature (298 K), pH values (5-6). The effect of contact time on the sorption of PO_4^{3-} onto ILO can be observed in Figure 2, indicating that the sorption of phosphorous occurred in three stages. A very rapid removal of phosphorous took place in the first stage, reaching above 55% within first 15 minutes. After this time, the removal kept rising but in a lower rate, achieving above 90.5% after 7 hours. Then the removal tended to be unchanged, reaching the maximum of 91.7% after 24 h. Hence, 7 hours was chosen as the optimum contact time for sorption of phosphorous onto ILO. However, to ensure the equilibrium is attained, 24 h is proposed as a contact time for next experiments. The results achieved in this study are more or less in agreement with those quoted by Biswas et al. (2007). Accordingly, it was noticed that, 15 h was necessary to attain the equilibrium in case of removing phosphate by Fe(III), La(III), Ce(III) loaded orange wastes.

3.3.5. Effect of foreign anions

The real wastewater usually contains many kinds of anions that may hinder the sorption of PO_4^{3-} anions. For that reason, the effect of coexisting anions on the sorption of phosphorous onto ILO was investigated to elucidate the practical applicability of ILO. A series of adsorption experiments were set up with the presence of SO_4^{2-}, NO_3^-, CO_3^{2-} individually and collectively. The concentration of coexisting anions was 10 times higher than that of phosphate ions in mol ratios. The operating conditions were initial phosphorous concentration (100 mg/L ~ 3 mmol), ILO dose (20 g/L), orbital shaking rate (130 rpm), temperature (298 K), and contact time (24 h). The ability of the above foreign anions to compete with PO_4^{3-} for binding sites on ILO was calculated using the Equation (4) given by Shin et al. (2005). The results are displayed in the Figure 3.

$$\text{Efficiency of competing anion (\%)} = \left(1 - \frac{\text{phosphorous sorbed in the presence of anion}}{\text{phosphorous sorbed when added alone}}\right) * 100 \qquad (4)$$

Figure 3

Figure 3 points out that the presence of SO_4^{2-} and NO_3^- anions separately could hardly hamper the sorption of phosphorous onto ILO, whereas CO_3^{2-} anions demonstrated the largest effect on the process, followed by a combination of 3 anions (SO_4^{2-} + CO_3^{2-} + NO_3^-). The removal of phosphorous using ILO was reduced by 79.29%, 57.66%, 4.81% and 3.06% in the addition of CO_3^{2-}, all three anions, SO_4^{2-} and NO_3^- anions, respectively. The efficiency of competing anions was in the order CO_3^{2-} (85.96%) > SO_4^{2-} + CO_3^{2-} + NO_3^- (62.51%) > SO_4^{2-} (5.22%) > NO_3^-(3.32%). Based on this, it would appear that ILO should not be applied for remediating phosphorous from wastewater with high levels of CO_3^{2-} anions. These findings agree with earlier studies performed by Biswas et al. (2007, 2008); Jyothi et al. (2012), associated with the effect of SO_4^{2-} and NO_3^- anions. On the other hand, the finding of the present study relative to the effect of CO_3^{2-} anions was just converse to the observations of above authors, who claimed that the interference effects of CO_3^{2-} were marginal.

3.4. Desorption of phosphorous from phosphorous bearing ILO

The recovery of phosphate anions and the reusability of ILO play critical roles to the actual application of this biosorbent. The desorption efficiencies of phosphorous from phosphorous bearing ILO with diverse eluents are depicted in Figure 4. It can be inferred that the distilled water at pH values of 2, 4, 6, 8, 10 exhibited very poor desorption capacities (< 20%). In contrast, the distilled water at pH 12, NaOH 0.25 M and HCl 0.1 M were found to be excellent elution solutions with extremely high desorption efficiencies (> 94%). It is worth mentioning that the desorption percentage in cases of using NaOH 0.25 M and HCl 0.1 M as elution solutions were even higher than 100%. The unusual desorption results can be explained by the assumption that raw okara may contain some phosphorous, which was eluted together with phosphorous adsorbed onto ILO. This hypothesis was strongly supported by the experimental data, which displayed that significant amounts of phosphorous can be eluted into aqueous solutions from dry okara by H_2SO_4, HCl, and NaOH 0.05 M. These findings more or less agree with a preceding study conducted by Li et al. (2012), revealing that the phosphorous content in original okara was 396-444 mg/ 100 g dry matter. These results imply that, the extraction of phosphorous from native okara via the pretreatment with NaOH 0.05 M was incomplete. This also highlights the potential of enhancing the efficiency of phosphorous recovery via conducting it with both original okara at the beginning and with phosphorous bearing ILO at the end of the process. For that reason, there is room for improvement of procedures for phosphorous removal and recovery by metal loaded okara.

Figure 4

3.5. Iron released during sorption and desorption tests

The detachment of Fe(III) from ILO during its sorption performance is undesirable, owing to the possible losses in its sorption capacity in next sorption cycles together with the deterioration of the effluent water quality. To investigate the leachability of Fe(III) from ILO during adsorption and desorption tests, batch experiments were undertaken under specific operating conditions as follows: initial phosphorous concentration of 100 mg/L, ILO dose of 10 g/L, orbital shaking rate of 130 rpm, temperature of 298 K, contact time of 24 h. Different elution solutions were employed, including the distilled water at different pH values (2, 4, 6, 8, 10, 12), NaOH 0.25 M, and HCl 0.1 M.

Figure 4 reveals that free Fe(III) ions could be found in the aqueous solutions at the end of desorption tests. The elution of Fe(III) ions was trivial with such eluents as distilled water at pH values of 4, 6, 8, and 10. Conversely, the significant amounts of Fe(III) were detected when the distilled water at pH values of 2, 12, NaOH 0.25 M and HCl 0.1 M were used. It would seem that, the extreme pH values of desorption solutions resulted in higher detachment of Fe(III) from ILO. Due to a significant leachability of Fe(III) during operation, Fe(III) may not be appropriate for cationization of okara. Hence, it needs replacing by alternative metals.

Equally, it was found that, the detachment of Fe(III) ions from ILO was significant in the adsorption test. The concentration of Fe(III) ions fluctuated in the range from 12.285 mg/L to 17.916 mg/L. The further investigations showed that the release of Fe(III) decreased from 32.56 mg/L to 15.13 mg/L with an increase in the initial phosphorous concentrations from 2 mg/L to 100 mg/L (Figure 5). The release of Fe(III) was lower at higher initial concentrations of phosphorous. This can be explained by the fact that more Fe(III) ions involved in complexation with PO_4^{3-}, leading to a reduction in the number of free Fe(III) ions eluted into aqueous solutions.

Figure 5

Similar observation was noticed by Biswas et al. (2007) in case of removal of phosphorous with La(III) loaded orange waste gel. They explored that La(III) was released into aqueous solutions when HCl 0.4 M was employed as a desorption solution. Unfortunately, the detail data could not be detected. These results are in harmony with those reported earlier by Shin et al. (2005), who discovered that the leachability of La(III) from La(III) loaded bark fiber was above 85% at pH of 2.5.

3.6. The prospect of using metal loaded biosorbents for phosphorous elimination

In general, biosorbents do not show significant affinity towards PO_4^{3-} in water bodies, owing to the lack of available binding sites, which are responsible for sorption of anions (Eberhardt and Min, 2008; Marshall and Wartelle, 2004). Consequently, to enhance their sorption capacity of phosphorous, biosorbents need to be cationized via impregnating with metal compounds or grafting with ammonium type chemicals (Han et al., 2005; Mallampati and Valiyaveettil, 2013; Nguyen et al., 2012; Orlando et al., 2002). Due to its simplicity and effectiveness, the former is usually method of choice. The common metals used for this purpose include Fe(II, III), Zr(IV), La(III), Ce(III), and Zn(II). The biosorbents which are directly immersed into metal solutions usually exhibit insufficient capacity for phosphate sequestering (Eberhardt et al., 2006). Thus, base treatments or grafting of carboxylate groups are necessary for improving the attachment of metals onto the material surface (Biswas et al., 2008; Carvalho et al., 2011; Eberhardt et al., 2006). Many articles have been published so far, confirming the enhanced phosphorous removal of metal loaded biosorbents (Biswas et al., 2007; Carvalho et al., 2011; Eberhardt et al., 2006; Krishnan and Haridas, 2008; Mezenner and Bensmaili, 2009). It is worth mentioning a study performed by Krishnan and Haridas (2008), reporting that the phosphorous uptake by coir pith expanded up to 6 times, as a result of impregnating with $FeCl_3$. However, little information is available on the leachability of metals during operation, which may significantly influence the repeated utilization of metal loaded biosorbents. Table 5 reveals that Zr(IV) is superior to other metals used for cationization of biosorbents, because of its low leachability. However, the relatively high cost and toxicity of Zr(IV) compounds may hinder its widespread applications. Therefore, further improvements are required in this direction of research. The appropriate metals for this purpose should meet such requirements as high phosphate removal efficiency, minor elution during operation, low price, and low toxicity to the public and environmental health. From that point of view, this study may be considered as a starting point for further research on enhancement of phosphate removal from water and wastewater using metal loaded okara.

Table 5

4. Conclusions

ILO demonstrated a relatively high phosphorous sorption capacity (4.785 mg/g). The CO_3^{2-} anions interfered the phosphorous biosorption the most, whilst competing effects of SO_4^{2-} and NO_3^- anions were negligible. Despite extremely high phosphorous removal efficiency (> 90% at initial phosphorus concentration of 100 mg/L, biosorbent dose of 20 g/L), the demerit of ILO was found from the strong detachment of Fe(III) during operation. As a final remark, alternative metals for cationization should be examined in the future study.

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FIGURE CAPTIONS

Figure 1

Effect of initial phosphorous concentration on the biosorption of PO_4^{3-} anions onto ILO (T = 298 K, t = 24 h, shaking speed = 130 rpm, C_0 = 10 ÷ 500 mg/L, dose = 10 g/L; pH = 5 - 6).

Figure 2

Effect of contact time on the removal of PO_4^{3-}anions using ILO as a biosorbent (T = 298 K, t = 24 h, shaking speed = 130 rpm, C_0 = 100 mg/L, dose = 20 g/L; pH = 5 - 6).

Figure 3

Phosphorous removal percentage of ILO in the presence of competing anions and the efficiency of competing anions

Figure 4

Desorption of phosphorous from phosphorous bearing ILO using different eluents and Fe(III) detachment during desorption tests.

Figure 5

The release of Fe(III) from ILO during adsorption tests.

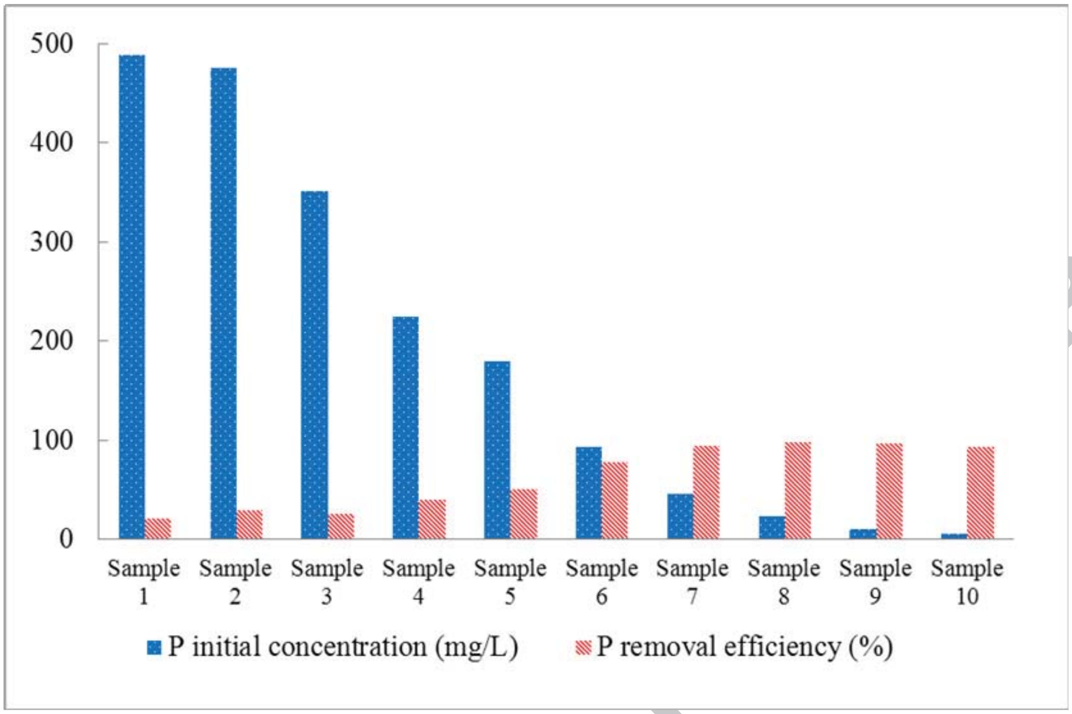
500
400
300
200
100
0
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
P initial concentration (mg/L)
P removal efficiency (%)

Figure 1

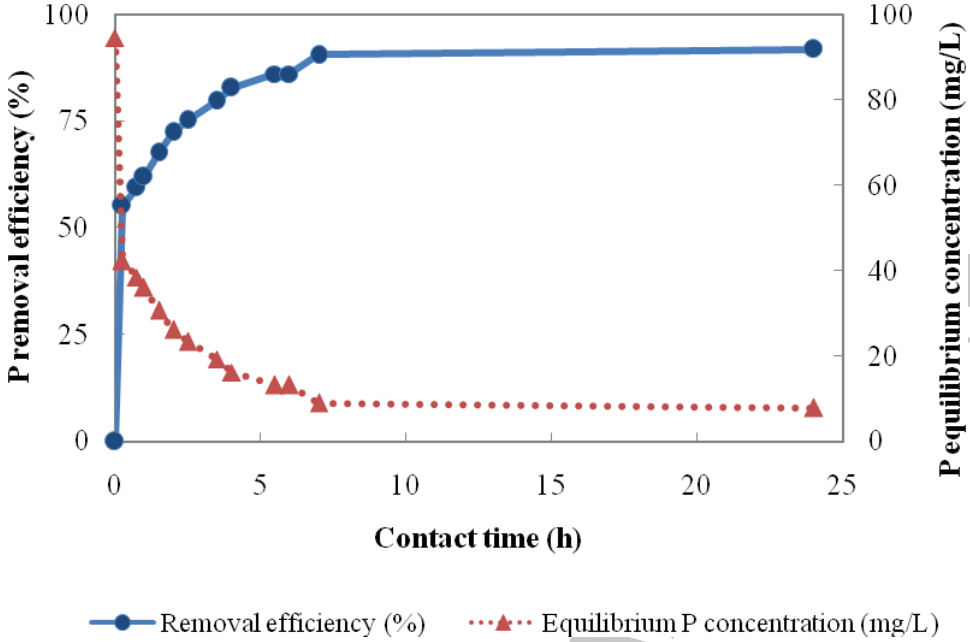
P removal efficiency (%)
100
75
50
25
0
P equilibrium concentration (mg/L)
100
80
60
40
20
0
0
5
10
15
20
25
Contact time (h)
Removal efficiency (%)
Equilibrium P concentration (mg/L)

Figure 2

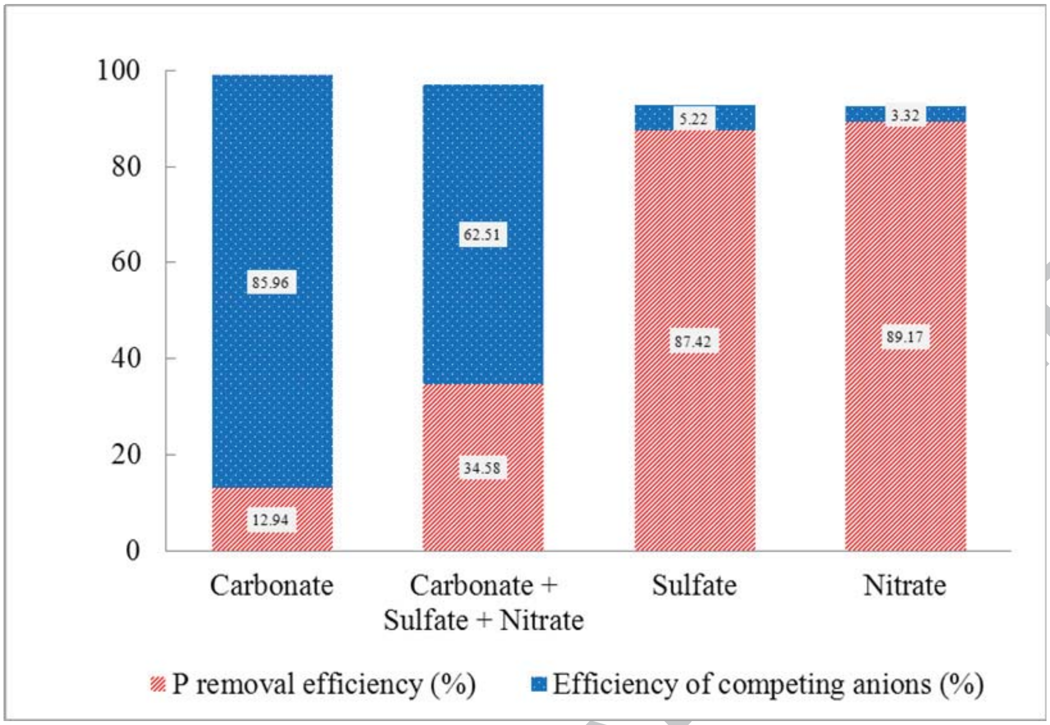
100
80
60
40
20
0
85.96
12.94
62.51
34.58
5.22
87.42
3.32
89.17
Carbonate
Carbonate + Sulfate + Nitrate
Sulfate
Nitrate
P removal efficiency (%)
Efficiency of competing anions (%)

Figure 3

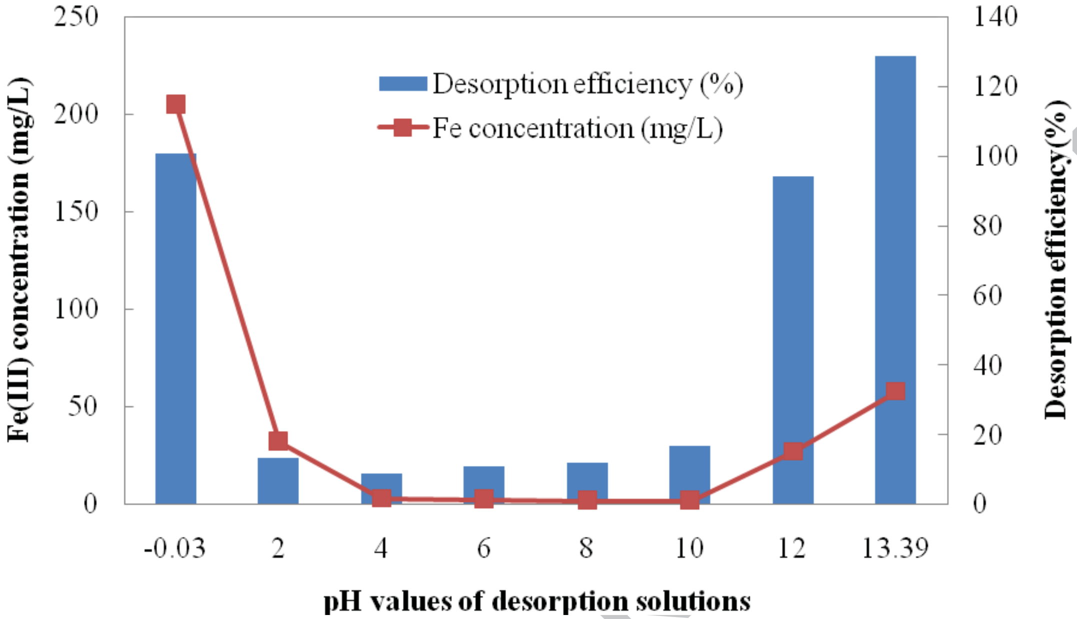
Desorption efficiency (%)
Fe concentration (mg/L)
Fe(III) concentration (mg/L)
Desorption efficiency(%)
pH values of desorption solutions
250
200
150
100
50
0
140
120
100
80
60
40
20
0
-0.03
2
4
6
8
10
12
13.39

Figure 4

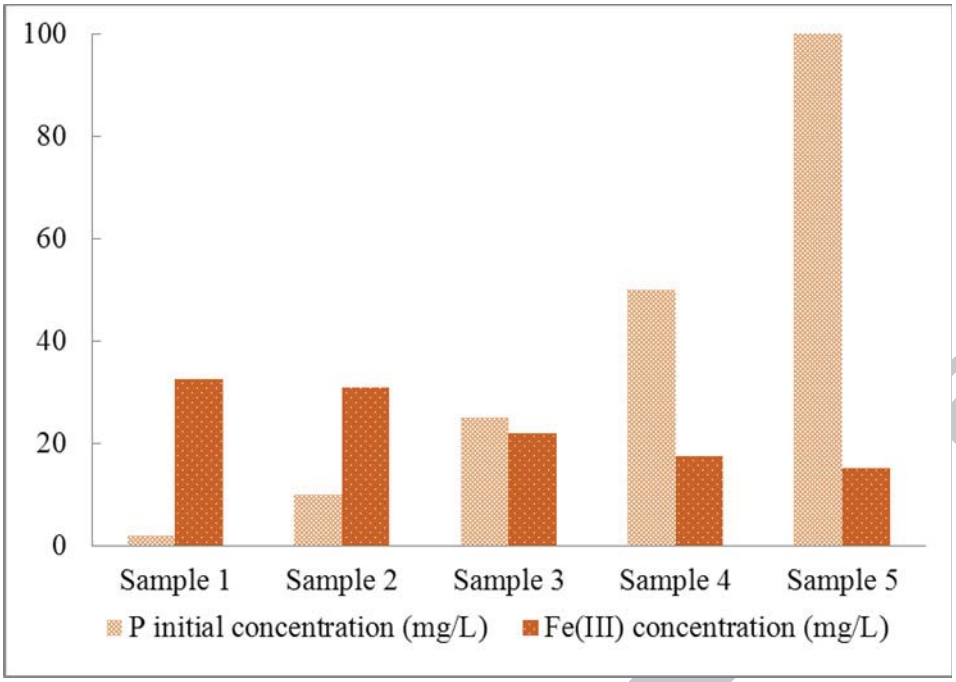
100
80
60
40
20
0
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
▨ P initial concentration (mg/L)
■ Fe(III) concentration (mg/L)

Figure 5

TABLES

Table 1 Comparison of different technologies for phosphorous removal.[a]

Technology	Advantages	Disadvantages
Chemical precipitation	Most commonly used method Easy to install, can be applied at any stage during wastewater treatment High P removal	Chemicals required Sludge production
Biological P removal	Widely used method Avoiding chemical use	External carbon source may be required Sensitive to changes in P load and temperature More complex technology Difficult sludge handling Inefficient P recovery
Crystallization	Produce more marketable end-product	Chemicals and operation skills necessary
Ion exchange	High P removal Struvite produced can be reused in agriculture	High cost Chemicals required Complex technology Low selectivity with the presence of co-anions Materials originated from nonrenewable resources
Magnetic	High P removal	Chemicals required Technology is complex
Adsorption	Appropriate for low P levels Potential P recovery Multiple regeneration of sorbents Few chemicals involved Without additional sludge	Experimental technology Disposal problems after use
Biosorption	Cost-effectiveness Originated from abundantly available, low cost, environmentally friendly, renewable materials	Experimental technology
Tertiary filtration	Technology is simple	High capital cost Useless recovery product

[a] Adapted fromBiswas et al. (2007); Ismail (2012); Karthikeyan et al. (2004); Ngo and Guo (2009); Riahi et al. (2009); Tshabalala et al. (2004).

Table 2 Functional groups analysis of ILO before and after phosphorous adsorption by FTIR.

IR peak	Adsorption bands (cm^{-1})			Assignment
	Before biosorption	After biosorption	Differences	
1	3546	3548	+ 02	Alcohols & Phenols: O-H (H-bonded), usually broad (strong)
2	3421	3423	+ 02	Alcohols & Phenols: Bonded hydroxyl groups (OH$^-$)
3	3386	3405	+ 19	Alcohols & Phenols: Bonded hydroxyl groups (OH$^-$)
4	3356	3357	+ 01	Alcohols & Phenols: Bonded hydroxyl groups (OH$^-$)
5	3289	3290	+ 01	Carboxylic acids & Derivatives: O-H (very broad) (strong)
6	3163	3162	- 01	Carboxylic acids & Derivatives: O-H (very broad) (strong)
7	3080	3083	+ 03	Carboxylic acids & Derivatives: O-H (very broad) (strong)
8	2374	2376	+ 02	Phosphorous functions: P-H phosphine (medium)

Table 3 Isotherms used for describing the sorption of PO_4^{3-}anions onto ILO.

Freundlich			Langmuir		
K_F(mg/g)(L/g)^n	n	R^2	K_L(L/mg)	q_m	R^2
1.516	4.44	0.924	0.568	4.785	0.981

Table 4 Comparison of ILO with diverse adsorbents, based on the phosphorous adsorption capacity.

Adsorbents	Phosphorous adsorption capacity (mg P/g)	References
CONVENTIONAL ADSORBENTS		
Zirconium ferrite	13.00	Biswas et al., 2008
Goethite	6.42	Han et al.,2005
Commercial anion exchange resins	13.80-42.10	Park and Na, 2006
Natural zeolite	2.15	Wu et al., 2006
Iron oxide tailings	8.21	Zeng et al.,2004
UNMODIFIED BIOSORBENTS		
Sawdust	47.61	Benyoucef and Amrani, 2011
Granular date stones	8.70	Ismail, 2012
Palm surface fibres	8.50	Ismail, 2012
Coir pith	4.35	Krishnan andHaridas, 2008
Date palm fibres	4.35	Riahi et al., 2009
Raw okara	0.8	THIS STUDY
MODIFIED BIOSORBENTS		
Sawdust of Aleppo pine (modified with urea)	116.25	Benyoucef and Amrani, 2011
Orange waste(loaded with La(III), Ce(III), Fe(III))	13.94	Biswas et al., 2007
Orange waste gel (loaded with Zr(IV))	57.00	Biswas et al., 2008
Sugarcane bagasse fibres (carboxymethylation + $FeCl_2$)	152.00	Carvalho et al., 2011
Aspen wood fiber(treated with carboxymethyl cellulose + $FeCl_2.4H_2O$)	4.30	Eberhardt et al., 2006
Juniper fiber(treated with acid mine drainage)	2.31	Han et al., 2005
Coir pith(impregnated with $Fe(NO_3)_3.9H_2O$)	70.92	Krishnan and Haridas, 2008
Eggshell(treated with iron hydroxide)	14.49	Mezenner and Bensmaili, 2009
Wheat straw (grafted with aminated intermediate)	45.70	Xu et al., 2010
Giant reed	19.89	Yue et al., 2010
Fe(III) loaded okara	4.785	THIS STUDY

Table 5 A summary of studies using metal loaded biosorbents for the decontamination of phosphorous.

Biosorbent	Modification method	Phosphorous adsorption capacity (mg/g)	Side effects	References
La(III)-, Ce(III)-, Fe(III)- loaded orange waste gel	$Ca(OH)_2$ + La(III) or Ce(III) or Fe(III) solutions	13.94 (for 3 types of gels)	La(III) was eluted during operation	Biswas et al., 2007
Zr(IV) loaded orange waste gel	$Ca(OH)_2$ + NaOH + Zr(IV) solution	57.00	Negligible detachment of loaded Zr(IV)	Biswas et al., 2008
Fe(II) loaded sugarcane bagasse	Carboxylmethylation + $FeCl_2$	152.50	N/A	Carvalho et al., 2011
Fe(II) loaded aspen wood fiber	Carboxymethyl cellulose + $FeCl_2$	4.30	Fe(III) wasleaked during sorption test	Eberhardt et al., 2006
Fe loaded juniper fiber	Acid mine drainage (Fe, Al, Pb, Zn)	2.31	Fe released during reaction	Han et al., 2005
Fe(III) loaded coir pith	$Fe(NO_3)_3$	70.92	N/A	Krishnan and Haridas, 2008
Zr(IV) loaded apple peels	$ZrOCl_2.8H_2O$	20.35	N/A	MallampatiandValiyaveettil, 2013
Iron hydroxide eggshell	$FeCl_3$	14.49	N/A	Mezenner and Bensmaili, 2009
Zn(II) activated coir pith carbon	$ZnCl_2$	5.10	N/A	Namasivayamand Sangeetha, 2004
Zr(IV) loaded activated carbons from rice straws	$ZrO(NO_3)_2.\ xH_2O$	11.10	N/A	Shindo et al., 2011

Note: N/A Information is not available.

Highlights

- Iron loaded okara was evaluated as a biosorbent for phosphate removal.
- Effects of process factors on phosphate capture were fully investigated.
- P can be effectively desorbed from native okara and P laden modified okara.
- The release of Fe(III) from modified okara during operation was significant.
- Alternative metals were proposed to replace Fe(III) in cationization of okara.