

## Fe(II) and Fe(III) adsorption by chitosan-tripolyphosphate beads: kinetic and equilibrium studies

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### ABSTRACT

The purpose of this research was to analyze the adsorption behavior of Fe(II) and Fe(III) ions in aqueous solution onto beads of naturally derived chitosan cross-linked with tripolyphosphate in a batch system. Effects of solution pH, contact time and amount of adsorbent were regarded in the kinetic and equilibrium studies. The optimum conditions of adsorption for Fe(II) and Fe(III) were obtained as pH 5 and 3, amount of adsorbent 2 and 1.9 g and contact time 70 and 60 min, respectively. The kinetic and equilibrium experimental data were integrated into different models using the non-linear regression method. As a result, the pseudo-second-order and the Redlich–Peterson isotherm were the best evaluated models. The adsorption capacity, based on Langmuir, was 11.65 mg g<sup>-1</sup> for Fe(II) and 13.72 mg g<sup>-1</sup> for Fe(III). The beads of chitosan cross-linked with tripolyphosphate may be used as an effective bioadsorbent for the removal of Fe(II) and Fe(III) from an aqueous solution. This study confirms that the chitosan isolated from shrimp waste can be used to remove certain heavy metals in wastewater, without adversely affecting the ecosystem.

**Key words** | bioadsorbent, cross-linking, metal ions, polymers, shrimp chitin waste

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### NOMENCLATURE

$a_R$	Redlich–Peterson isotherm constant, (L mg <sup>-1</sup> ) <sup>g</sup>	$q_m$	Adsorption capacity obtained from the kinetic or isotherm models, mg g <sup>-1</sup>
$b$	Langmuir constant, L mg <sup>-1</sup>	$q_t$	Adsorption capacity of the adsorbent at time $t$ , mg g <sup>-1</sup>
$C_0$	Initial concentration of metal ions in the solution, mg L <sup>-1</sup>	$\bar{q}$	Average of $q_e$ or $q_t$ , mg g <sup>-1</sup>
$C_e$	Equilibrium concentration of metal ions in the solution, mg L <sup>-1</sup>	$R_L$	Separation factor
$C_f$	Final concentration of metal ions in the solution, mg L <sup>-1</sup>	$t$	Time, min
$g$	Redlich–Peterson isotherm exponent	$V$	Volume of solution, L
$K_1$	Pseudo-first-order rate constant, min <sup>-1</sup>	$\alpha$	Elovich initial adsorption rate, mg g <sup>-1</sup> min <sup>-1</sup>
$K_2$	Pseudo-second-order rate constant, g min <sup>-1</sup> mg <sup>-1</sup>	$\beta$	Elovich desorption constant, g mg <sup>-1</sup>
$K_F$	Freundlich constant, (mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup>		
$K_i$	Intra-particle diffusion rate constant, mg g <sup>-1</sup> min <sup>-0.5</sup>		
$K_R$	Redlich–Peterson isotherm constant, L g <sup>-1</sup>		
$m$	Dry mass of adsorbent, g		
$n$	Freundlich constant		
$Q_0$	Maximum adsorption capacity, mg g <sup>-1</sup>		
$q_e$	Equilibrium adsorption capacity of the adsorbent, mg g <sup>-1</sup>		

### INTRODUCTION

Urban wastewater, industrial effluents and agrochemicals can pollute the water with heavy metals which are characterized by their environmentally harmful effects. However,

trace amounts of some elements such as copper and iron are essential for the biological function of the human body (Ahalya *et al.* 2006; Acheampong *et al.* 2010; Senthil Kumar *et al.* 2010). With the aim of sanitizing water contaminated by heavy metals, various processes have been employed such as chemical precipitation, coagulation and flocculation, membrane filtration, ion exchange, electrochemical treatment and adsorption. The disadvantage of chemical precipitation and coagulation/flocculation is the production of sludge. Other methods for removal of metals such as membrane filtration processes, ion exchange and electrochemical treatments can be very expensive. Adsorption processes are therefore often preferred for removing heavy metals from wastewater. The adsorbent that has been traditionally used is activated carbon, but this has the disadvantage of high cost (Tahir & Rauf 2004; Debnath & Ghosh 2008; Acheampong *et al.* 2010; Fu & Wang 2011; Liu *et al.* 2011).

Finding low-cost alternatives to activated carbon has become a priority when seeking material for adsorption alternatives. In general, an adsorbent is considered as low cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry (Bailey *et al.* 1999). Chitosan (poly( $\beta$ -(1–4)-2-amino-2-deoxy-D-glucopyranose)), derived from chitin (poly( $\beta$ -(1–4)-2-acetamido-2-deoxy-D-glucopyranose)) of crustacean shells, is classified as one of these adsorbent materials. The industrial production of chitin is based on the treatment of various crustacean shells from the seafood industry (Guibal *et al.* 1995). The polymer chitosan can be obtained by deacetylation of chitin.

This research is part of an international project which is looking for an integrated way to use shrimp waste, head and shell, in the production of value-added products such as chitin and chitosan. Sonora, northwest México, has a large shrimp aquaculture production; during processing the industries generate enormous amounts of waste and effluents that are potential sources of coastal and marine pollution.

Chitosan has been used as flakes, powders and beads. Beads of chitosan are preferred in the adsorption process, due the fact that the flakes and powders have a low surface area and low porosity (Crini & Badot 2008). Nevertheless, chitosan beads have the disadvantage of weak mechanical strength and are soluble in diluted acids, which affect their

regeneration after adsorption. In order to improve these weaknesses, chemical modifications have been made to chitosan (Wan Ngah *et al.* 2004).

Chitosan has been cross-linked with different chemicals such as glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether (Ngah *et al.* 2005; Chen *et al.* 2008). Sodium tripolyphosphate is a non-toxic material that can be cross-linked with chitosan through ionic interactions between the positively charged amino groups of chitosan and negatively charged counter-ion of the tripolyphosphate, thereby improving the adsorption capacity of chitosan (Mi *et al.* 1999; Shu & Zhu 2002; Mi *et al.* 2003). The cross-linking of chitosan with sodium tripolyphosphate has been used by some researchers, who obtained good results in the adsorption of Cu(II), Mn(II), Pb(II) and U(VI) ions (Lee *et al.* 2001; Ngah & Fatinathan 2010; Sureshkumar *et al.* 2010). There are few studies on the adsorption of iron, however, which exists in the form of ferrous iron Fe(II) and ferric iron Fe(III). Laus *et al.* (2006) used this adsorbent to remove Fe(III) from coal mining wastewaters. The adsorption of Fe(II) on chitosan cross-linked with sodium tripolyphosphate has not been previously reported.

The aim of this research was to analyze the adsorption behavior of Fe(II) and Fe(III) ions onto beads of chitosan cross-linked with tripolyphosphate in a batch system. After studying the influence of pH on the solution containing Fe(II) or Fe(III), the required contact time and the amount of adsorbent, the optimum conditions for adsorption were determined. The kinetic tests allowed the fit of data to the pseudo-first-order and pseudo-second-order models; the Elovich and intra-particle diffusion; and the Langmuir, Freundlich and Redlich–Peterson isotherm models in the analysis of adsorption equilibrium data. The information gleaned from this research will be employed in the design of an adsorption system to treat water contaminated with iron.

## MATERIALS AND METHODS

### Chemical

Sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) was supplied by Productos Químicos Mardupol (México, DF, México). Ferrous

sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3$ ), ferrous ammonium sulfate  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) were purchased from Sigma-Aldrich (St Louis, MO, USA). Orthophenanthroline monohydrate, ( $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ ) and sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) were obtained from HYCEL de México (Zapopan, Jal, México). Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ), hydrochloric acid (HCl), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and sodium hydroxide (NaOH) were obtained from Productos Químicos Monterrey (Monterrey, NL, México). All aqueous solutions were prepared with Milli-Q water (Nanopure DIAMOND UV system, Barnstead International, Dubuque, IA, USA).

### Iron quantification methodology

The concentrations of Fe(II) and Fe(III) were determined by the phenanthroline method (APHA 1998) using a GENESYS 10 UV-Vis scanning spectrophotometer (Thermo Fisher Scientific, Madison, WI, USA) at 510 nm. The calibration curve was determined with iron solutions obtained from  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

### Preparation of chitosan

Chitosan was obtained by alkaline hydrolysis of chitin. An industry located in South Sonora (coast of the Gulf of México) provided the chitin, which is isolated from shrimp waste by lactic fermentation (López-Cervantes *et al.* 2010). The chitin was subjected to chemical treatment using the methodologies proposed by various researchers (Beaney *et al.* 2005; Abdou *et al.* 2008) with modifications. First, chitin was demineralized with 1 M HCl at room temperature for 4 h and subsequently deproteinized with 4.5% (w/v) NaOH at 65 °C for 4 h. The chitin was then treated with 45% (w/v) NaOH at 110 °C for 1.5 h to remove the acetyl residues (deacetylation). In all treatments the solid/liquid ratio was 1:15 (w/v) with constant agitation and the solids were washed with water until neutral pH after each treatment step.

The chitosan was characterized by the total nitrogen, moisture and ash contents and the degree of deacetylation. The total nitrogen was determined by the Micro-Kjeldahl method (AOAC 2005) using Rapid Digestor-4 and Rapidstill I

(Labconco, Kansas City, MO, USA). The ash content was obtained by using a muffle (Barnstead International, Dubuque, IA, USA) at 550 °C until the ash had a white or grayish color (AOAC 2005). The moisture content was determined in an oven (Felisa, Zapopan, Jal, México) at 60 °C for 5 h (AOAC 2005). The degree of deacetylation was assessed by following the method of Liu *et al.* (2006) which is based on the use of UV spectrophotometry, utilizing acetyl glucosamine and glucosamine hydrochloride as standards.

### Chitosan-sodium tripolyphosphate beads

Chitosan-sodium tripolyphosphate (CTPP) beads were prepared according to the procedure described by Ngah & Fatinathan (2010), with modifications. Chitosan flakes (2.5 g) were dissolved in 100 mL of 5% (v/v) acetic acid solution and then filtered. The chitosan solution was left for 24 h at room temperature, and was then dropped into 0.05 M sodium tripolyphosphate solution (pH 8) to form the beads. The beads were reposed for 24 h. Finally, the beads were filtered and rinsed with distilled water. The CTPP beads were stored in distilled water. Later the beads were filtered and the excess water was removed before being subjected to characterization and adsorption assays. The CTPP beads obtained were characterized in terms of diameter using a digital caliper (Cole-Parmer, IL, USA) and in terms of moisture (AOAC 2005) and solubility in 5% (v/v) acetic acid solution (Chen *et al.* 2008).

### Adsorption experiments

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3$  were used as ion sources for Fe(II) and Fe(III), respectively. Standard iron solutions were prepared the same day of use due to the instability of the ions. All utilized glassware was washed with concentrated HCl and rinsed with Milli-Q water. The assays were performed in batch mode, using 100 mL of the solution of Fe(II) or Fe(III) at room temperature, and these were carried out in 250 mL covered glass beakers to prevent entry of light and air. The concentrations of iron ions were measured immediately before and after each assay. The beads were kept in suspension using magnetic stirring (ceramic stirring hot plates, Cimarec, IL, USA).

The optimum conditions of adsorption were determined by testing the pH of the solution, the contact time and the amount of adsorbent. Assays were used with solutions with  $4 \text{ mg L}^{-1}$  of Fe(II) or Fe(III). The effect of pH was studied on a scale of 2–5 for the adsorption of Fe(II) and 2–3 for Fe(III) because both ions precipitate at higher pH values (Ngah *et al.* 2005; Ahalya *et al.* 2006). The pH was adjusted by adding HCl diluted solutions (0.01, 0.1, 6 and 12 M) and it was measured with a digital pH meter (Hanna Instruments, Woonsocket, RI, USA). A quantity of 3 g of wet CTPP beads were placed in the solutions, which were shaken for 30 min. To determine the optimal contact time, a series of solutions were adjusted to optimum pH, 3 g of beads were added to each solution and these were stirred at progressive time intervals. Finally, to determine the optimum amount of adsorbent, different amounts (0.5, 1.0, 1.5, 2.0 or 3.0 g) of wet CTPP beads were placed in solutions adjusted to optimum pH and these were agitated for the optimal time. For the three parameters studied, the optimum conditions were achieved when the highest percentage of adsorption was achieved, defined:

$$\text{Adsorption (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_f$  are the initial and final concentrations of iron ions in the solution ( $\text{mg L}^{-1}$ ), respectively.

Kinetic studies were carried out for four different initial concentrations (4, 6, 8 and  $12 \text{ mg L}^{-1}$ ). The solutions were adjusted to optimal pH. The optimal mass of wet beads were placed in 100 mL of Fe(II) or Fe(III). These were stirred at different time intervals. Finally, the beads were withdrawn and the remaining concentration was measured to estimate the adsorption capacity using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where  $q_t$  is the adsorption capacity of the adsorbent at time  $t$  ( $\text{mg g}^{-1}$ ),  $V$  is the volume of solution (L) and  $m$  is the dry mass of adsorbent (g).

For the adsorption equilibrium studies, a series of solutions of Fe(II) or Fe(III) at different concentrations ( $2\text{--}18 \text{ mg L}^{-1}$ ) were adjusted to optimal pH and agitated with the optimal mass of wet beads for a longer time than the optimum time

obtained previously. Finally, the remaining concentration was measured in each of the solutions to obtain the equilibrium adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ ):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where  $C_e$  is the equilibrium concentration of iron ions in the solution ( $\text{mg L}^{-1}$ ).

### Modeling of kinetics and isotherms

The experimental results of the kinetics and isotherms were adjusted to non-linear mathematical models using the solver add-in of Microsoft Excel. The model validation was performed by maximizing the coefficient of determination ( $r^2$ ) (Ho 2006a, b). The coefficient of determination used to test the goodness-of-fit of the isotherm and kinetic models with the experimental data is defined:

$$r^2 = \frac{\sum (q_m - \bar{q})^2}{\sum (q_m - \bar{q})^2 + \sum (q_m - q)^2} \quad (4)$$

where  $q_m$  is the adsorption capacity obtained from the kinetic or isotherm models ( $\text{mg g}^{-1}$ );  $q$  is  $q_e$  or  $q_t$ , and  $\bar{q}$  is the average of  $q_e$  or  $q_t$ , depending on whether the isotherm or kinetic model is used.

### Statistical analysis

The adsorption assays were conducted in completely randomized design with two repetitions. The chitosan and CTPP beads were characterized in triplicate. The mean values and the standard deviation were analyzed using a spreadsheet program.

## RESULTS AND DISCUSSION

### Iron quantification

The calibration curve for the iron quantification gave the equation  $y = 5.2043x - 0.0288$ , with a coefficient of determination  $r^2 = 1$ . This equation was obtained through the

measurement of the absorbance of 9 standard dilutions within a concentration range of 0–4 mg L<sup>-1</sup>. To measure concentrations higher than 4 mg L<sup>-1</sup>, corresponding dilutions were made before the measurement.

### Characterization of chitosan and CTPP beads

The results of the characterization of chitosan showed that the total nitrogen content was  $6.22 \pm 0.03\%$ , the ash content was  $0.26 \pm 0.02\%$ , the moisture content was  $7.15 \pm 0.56\%$  and the degree of deacetylation was  $81.68 \pm 1.16\%$ . The cross-linked chitosan beads were formed by interactions between positively charged amino groups and the negatively charged tripolyphosphate ions (Lee *et al.* 2001). With respect to its characterization, an average diameter of  $3.03 \pm 0.14$  mm with  $90.81 \pm 0.13\%$  humidity was recorded. The beads were insoluble in 5% (v/v) acetic acid solution. These results are consistent with those reported by other researchers (Wan Ngah *et al.* 2004; Beaney *et al.* 2005; Chen *et al.* 2008).

### Effect of solution pH

The initial pH of the solution is an important parameter in the adsorption process because it affects the surface charge of the adsorbent and the chemistry of the heavy metals (Crini & Badot 2008; Acheampong *et al.* 2010). Figure 1 shows the effect of solution pH on the adsorption of Fe(II) and Fe(III) by the wet CTPP beads. The adsorption was highly dependent on the pH mainly for Fe(II); increasing the pH value increases the percentage of adsorption. The

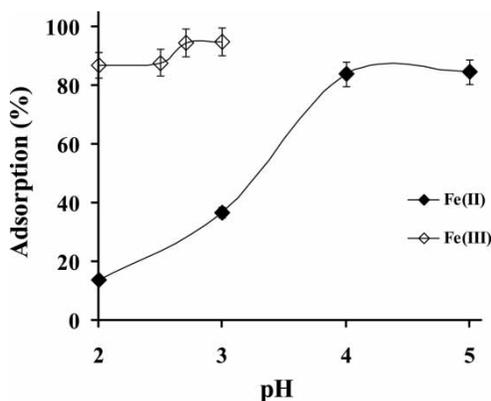


Figure 1 | Effect of pH on the adsorption of Fe(II) and Fe(III) by CTPP beads.

low adsorption at low pH is due to competition between the hydronium ions, protonated amino groups and the metal ions. As the pH increases, there is a decrease in positive sites on the adsorbent surface which reduces their electrostatic repulsion with the iron ions (Wan Ngah *et al.* 2004). The higher adsorption was performed at pH 5 and pH 3 for Fe(II) and Fe(III), respectively, so these values were the optimum pH. The values found in these studies are consistent with those reported for the adsorption on chitosan cross-linked with glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether (Ngah *et al.* 2005).

### Effect of contact time

Since time is an important parameter in the adsorption process, its optimization is necessary. During the process, the adsorbent surface is progressively occupied by metal ions until it has a constant value of adsorption capacity and cannot remove more metal ions from the solution (the equilibrium has been reached; Crini & Badot 2008). Figure 2 illustrates the effect of contact time on the adsorption of Fe(II) and Fe(III) with CTPP beads, showing that the adsorption of iron increases with the increase in contact time. During the first 30 min of treatment, over 80% of the adsorption was obtained for both cations. The adsorption remained constant after 70 min for the Fe(II) and after 60 min for the Fe(III). Thus 70 and 60 min of treatment were considered the optimum adsorption times. Based on these results, contact times higher than these values were used for the kinetic and equilibrium studies in order to ensure that the equilibrium time was reached.

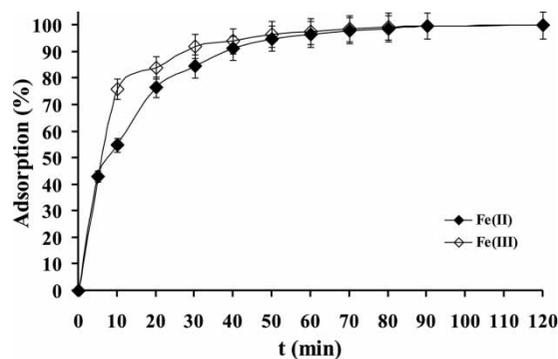
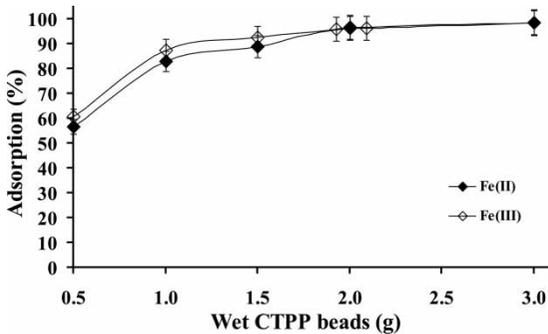


Figure 2 | Effect of contact time on the adsorption of Fe(II) and Fe(III) by CTPP beads.

### Effect of amount of adsorbent

The optimum amount of adsorbent used in an adsorption process affects the removal percentage of metal ions and the costs of the process. Figure 3 shows the effect of amount of adsorbent used in the adsorption of Fe(II) and Fe(III). The adsorption efficiency increases with the

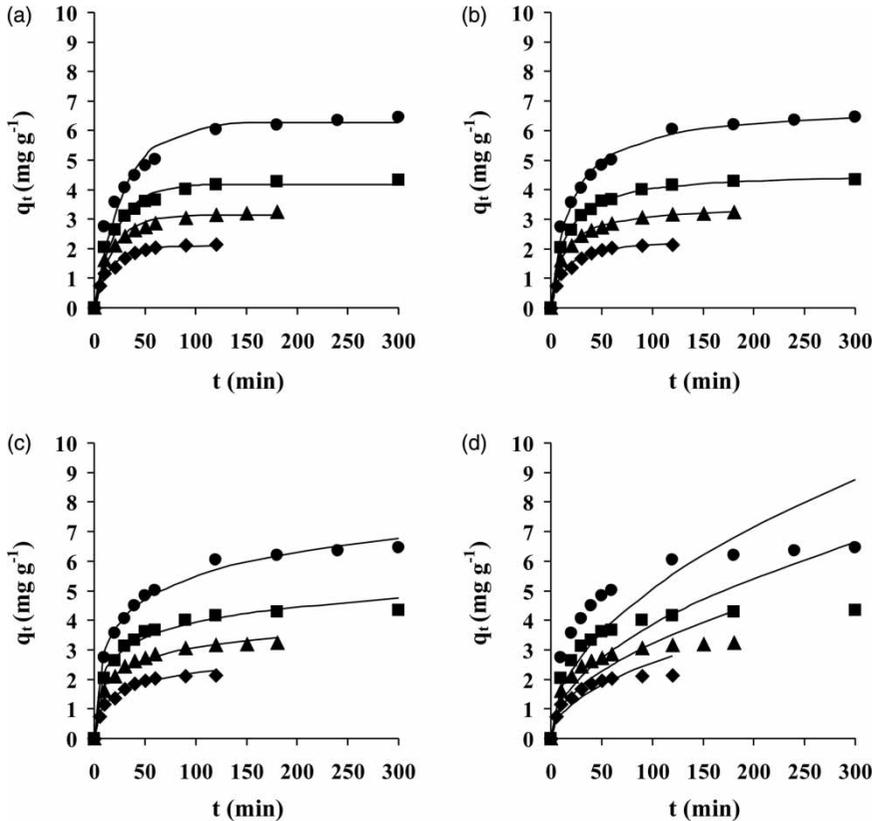


**Figure 3** | Effect of amount of adsorbent on the adsorption of Fe(II) and Fe(III) by CTPP beads.

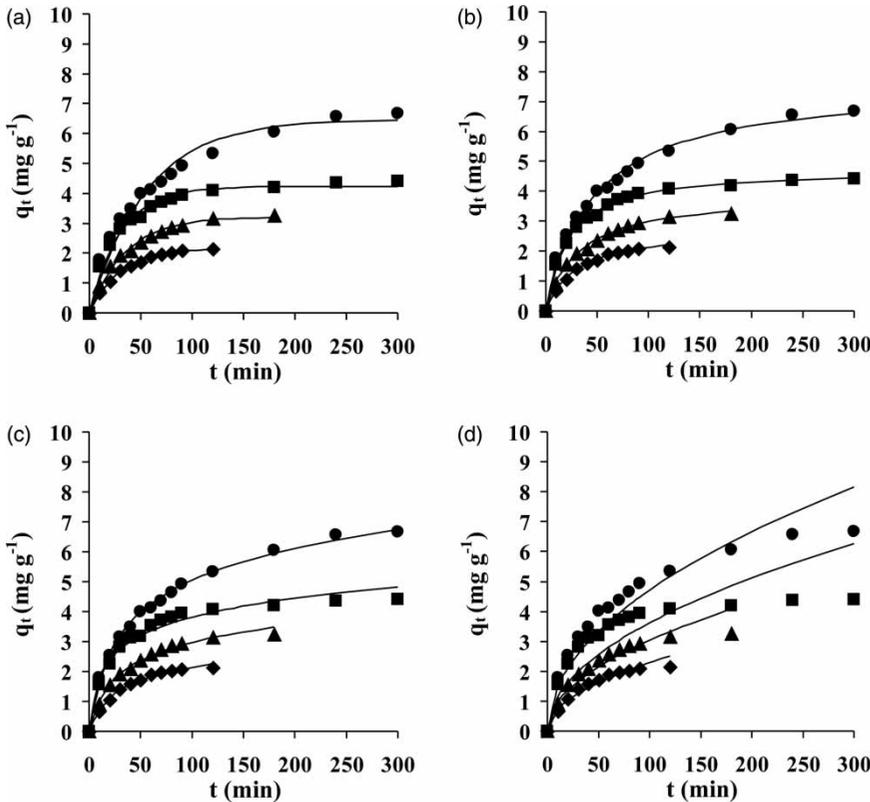
amount of adsorbent and remains constant with 2 g of wet CTPP beads for Fe(II) and 1.9 g for Fe(III). With an increasing dosage of adsorbent, the adsorption efficiency increases since there are more adsorption sites available to remove more iron ions, although the adsorption capacity of the adsorbent decreases (Crini & Badot 2008; Acheampong *et al.* 2010). Therefore, 2 and 1.9 g of wet CTPP beads were considered as the optimum amount of adsorbent for Fe(II) and Fe(III), respectively. These amounts will be used in subsequent kinetic and equilibrium studies.

### Kinetics of adsorption

Kinetic studies were carried out to determine the rate of adsorption and the mechanisms that control the adsorption process, used in the design of an adsorption system. The experimental data and theoretical plots of the kinetic studies of adsorption of Fe(II) and Fe(III) at four different concentrations are shown in Figures 4 and 5, respectively.



**Figure 4** | Modeling of adsorption of Fe(II): (a) pseudo-first-order; (b) pseudo-second-order; (c) Elovich; and (d) intra-particle diffusion. Initial Fe(II) concentration:  $\blacklozenge$  4 mg L<sup>-1</sup>;  $\blacktriangle$  6 mg L<sup>-1</sup>;  $\blacksquare$  8 mg L<sup>-1</sup>;  $\bullet$  12 mg L<sup>-1</sup>.



**Figure 5** | Modeling of adsorption of Fe(III): (a) pseudo-first-order; (b) pseudo-second-order; (c) Elovich; and (d) intra-particle diffusion. Initial Fe(II) concentration:  $\blacklozenge$  4 mg L<sup>-1</sup>;  $\blacktriangle$  6 mg L<sup>-1</sup>;  $\blacksquare$  8 mg L<sup>-1</sup>;  $\bullet$  12 mg L<sup>-1</sup>.

Figure 4 shows that for concentrations of 4 and 6 mg L<sup>-1</sup>, equilibrium was reached after 60 min of treatment. For concentrations of 8 and 12 mg L<sup>-1</sup>, equilibrium was reached after 120 min. Fe(III) shows similar behavior except for a concentration of 12 mg L<sup>-1</sup> where equilibrium was reached at 180 min. Kinetic models were investigated for their ability to determine the kinetic mechanisms of the adsorption of Fe(II) and Fe(III) with CTPP beads, including: pseudo-first-order (Ho & McKay 1998; Equation (5)); pseudo-second-order (Ho & McKay 1998, 2002; Equation (6)); Elovich (Ho & McKay 2002; Equation (7)); and intra-particle diffusion (Ho & McKay 1998; Equation (8)):

$$q_t = q_e(1 - e^{-K_1 t}) \quad (5)$$

$$q_t = \frac{t}{\frac{1}{K_2 q_e^2} + \frac{t}{q_e}} \quad (6)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

$$q_t = K_i t^{0.5} \quad (8)$$

where  $K_1$  is the pseudo-first-order rate constant (min<sup>-1</sup>);  $K_2$  is the pseudo-second-order rate constant (g min<sup>-1</sup> mg<sup>-1</sup>);  $\alpha$  is the Elovich initial adsorption rate constant (mg g<sup>-1</sup> min<sup>-1</sup>);  $\beta$  is Elovich desorption constant (g mg<sup>-1</sup>); and  $K_i$  is the intra-particle diffusion rate constant (mg g<sup>-1</sup> min<sup>-0.5</sup>).

The pseudo-first-order model did not present a good fit for the experimental data of Fe(II) (Figure 4(a)). Nevertheless, Fe(III) showed a good fit on all concentrations (Figure 5(a)) as demonstrated by the coefficients of determination listed in Table 1. Figures 4(b) and 5(b) show the pseudo-second-order model, which had the best coefficient of determination of the concentrations studied (consistent with other research on Fe(II) and Fe(III); Ngha *et al.* 2005)

**Table 1** | Evaluation of different kinetic models for adsorption of Fe(II) and Fe(III) by CTPP beads

$C_0$ (mg L <sup>-1</sup> )	Fe(II)				Fe(III)			
	4	6	8	12	4	6	8	12
Pseudo-first-order								
$K_1$ (min <sup>-1</sup> )	0.063	0.052	0.046	0.034	0.034	0.029	0.033	0.018
$q_e$ (mg g <sup>-1</sup> )	2.09	3.14	4.18	6.28	2.17	3.22	4.23	6.48
$r^2$	0.9603	0.9394	0.9410	0.9354	0.9965	0.9870	0.9691	0.9570
Pseudo-second-order								
$K_2$ (g min <sup>-1</sup> mg <sup>-1</sup> )	0.035	0.024	0.016	0.008	0.012	0.008	0.010	0.003
$q_e$ (mg g <sup>-1</sup> )	2.39	3.47	4.58	6.84	2.77	3.95	4.77	7.61
$r^2$	0.9875	0.9962	0.9928	0.9845	0.9935	0.9948	0.9946	0.9853
Elovich equation								
$\beta$ (g mg <sup>-1</sup> )	2.100	1.728	1.326	0.864	1.554	1.140	1.109	0.650
$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	0.498	1.172	1.384	1.338	0.182	0.260	0.625	0.410
$R^2$	0.9737	0.9721	0.9435	0.9817	0.9865	0.9855	0.9500	0.9930
Intra-particle diffusion								
$K_i$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	0.255	0.322	0.384	0.506	0.228	0.304	0.362	0.471
$r^2$	0.8262	0.7420	0.7019	0.7646	0.9252	0.8898	0.7519	0.9062

and other metal ions (Wan Ngah *et al.* 2004; Chen *et al.* 2008). The values for the constants of pseudo-second-order ( $K_2$ ) and equilibrium adsorption capacity of the adsorbent ( $q_e$ ) decrease and increase, respectively, for the four concentrations studied. The decrease of  $K_2$  with increasing concentration indicates that the adsorption of Fe(II) and Fe(III) with CTPP beads is faster when the adsorbent concentration in the solution is increased (Debnath & Ghosh 2008; Senthil Kumar *et al.* 2010).

The third model tested was Elovich; this yielded the second-best fit for Fe(II) (Figure 4(c)) and a good fit for Fe(III) (Figure 5(c)), suggesting that the chemisorption mechanism is probably rate controlling in the adsorption mechanism for both cations (Ho & McKay 2002). Figures 4 (d) and 5(d) show that the intra-particle diffusion model adapted poorly to the kinetic experimental data, because the mechanism that dominates the mass transfer is not due to internal diffusion (Ho & McKay 1998).

To summarize, the results showed that the adsorption of Fe(II) and Fe(III) ions on CTPP beads is best described by the pseudo-second-order equation. When comparing the values of the coefficient of determination ( $r^2$ ), the order of behavior of the kinetic models is pseudo-second-order > Elovich > pseudo-first-order > intra-particle diffusion for Fe(II) and

pseudo-second-order > pseudo-first-order > Elovich > intra-particle diffusion for Fe(III). These results suggest that the limiting step of the adsorption system for Fe(II) and Fe(III) is the chemical adsorption.

### Equilibrium studies

Data obtained from the equilibrium studies were adjusted for different isotherm models to find the best model to represent these experimental data. The equilibrium isotherms are essential for the effective use of adsorbent and for the design of an adsorption system (Crini & Badot 2008). The models used were Langmuir (Ahalya *et al.* 2006), Freundlich (Ho 2006a) and Redlich–Peterson isotherms (Debnath & Ghosh 2008). Equations (9), (10) and (11), respectively, correspond to these models:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (9)$$

$$q_e = K_F C_e^{1/n} \quad (10)$$

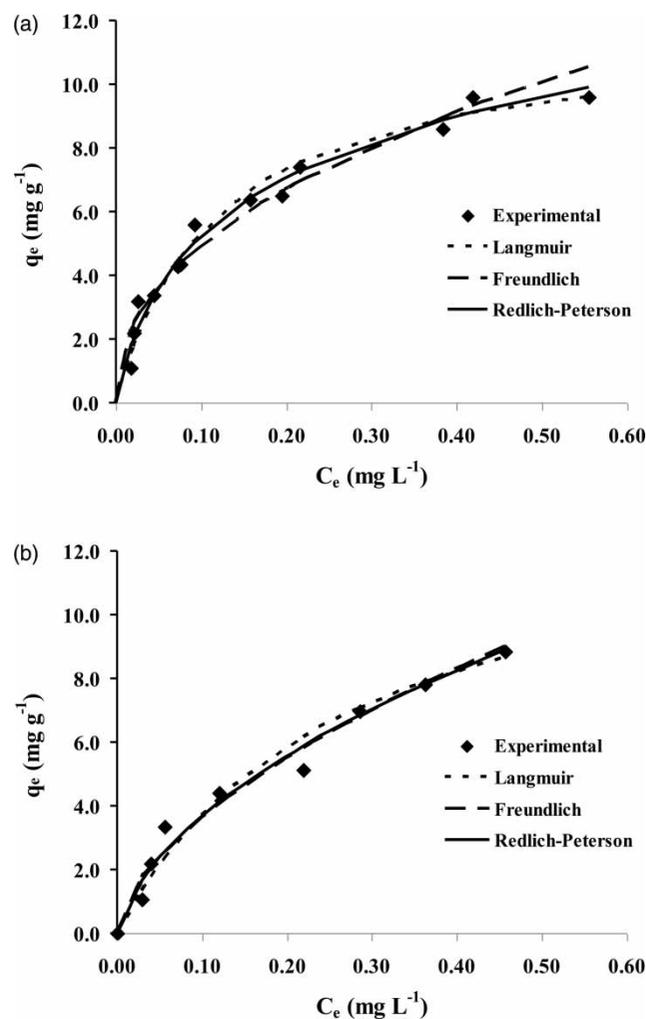
$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (11)$$

where  $Q_0$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) are the maximum adsorption capacity and Langmuir constant for the Langmuir equation;  $K_F$  ( $(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$ ) and  $n$  are Freundlich constants; and  $K_R$  ( $\text{L g}^{-1}$ ),  $a_R$  ( $(\text{L mg}^{-1})^g$ ) and  $g$  are the Redlich–Peterson isotherm constants.

Table 2 lists the values for the parameters evaluated in the three isotherm models. The theoretical data obtained from these isotherms and the experimental data are plotted in Figure 6. The Redlich–Peterson model provided the best fit for Fe(II) ( $r^2 = 0.9757$ ) and for Fe(III) ( $r^2 = 0.9704$ ), being very close to the value found for Langmuir. This behavior is similar to that reported by other researchers in the adsorption of metal ions (Ho 2006a; Debnath & Ghosh 2008). The Redlich–Peterson isotherm is a combination of the elements of the equations of Langmuir and Freundlich, and the fact that the Langmuir fit is very close to that of Redlich–Peterson suggests that the behavior of the adsorption equilibrium Fe(II) and Fe(III) ions by CTPP beads follows the Langmuir model. This model assumes that: the molecules are adsorbed into the defined sites of the adsorbent; each site can accommodate only one molecule (monolayer); the area of each site is a fixed amount, determined solely by the geometry of the surface; the adsorption energy is equal at all sites; and adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The value of the maximum adsorption capacity according to Langmuir is  $11.65 \text{ mg g}^{-1}$  for Fe(II) and  $13.72 \text{ mg g}^{-1}$  for Fe(III).

**Table 2** | Evaluation of different isotherm models for adsorption of Fe(II) and Fe(III) by CTPP beads

Isotherm	Parameters	Fe(II)	Fe(III)
Langmuir	$Q_0$ ( $\text{mg g}^{-1}$ )	11.65	13.72
	$b$ ( $\text{L mg}^{-1}$ )	8.49	3.73
	$r^2$	0.9709	0.9613
Freundlich	$K_F$ ( $(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$ )	13.68	14.38
	$n$	2.26	1.67
	$r^2$	0.9580	0.9695
Redlich–Peterson	$K_R$ ( $\text{L g}^{-1}$ )	141.46	134.27
	$a_R$ ( $(\text{L mg}^{-1})^g$ )	11.22	8.92
	$g$	0.82	0.53
	$r^2$	0.9757	0.9704



**Figure 6** | Adsorption isotherm by CTPP beads: (a) Fe(II) and (b) Fe(III).

The Freundlich model had the lowest fit ( $r^2 = 0.9580$ ) for Fe(II); this is not sufficient to predict the behavior of the adsorption equilibrium, confirmed by the shape of a graph with experimental data that tends to plateau in the final values. Fe(III) demonstrated a good fit for this model however, as observed in the shape of its graph of experimental data; the concentration of metal in the adsorbent increases with the concentration of metal ions in the liquid phase.

To determine whether the adsorption process is favorable or unfavorable, the separation factor ( $R_L$ ) was calculated with the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

where  $R_L$  indicates the shape of the isotherm and nature of the adsorption process. The adsorption is unfavorable if  $R_L > 1$ , linear if  $R_L = 1$ , favorable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$  (Wan Ngah et al. 2004).  $R_L$  values were calculated for all initial concentrations used in the studies of equilibrium (2–18 mg L<sup>-1</sup>). The results were 0.0540–0.0064 for Fe(II) and 0.1235–0.0163 for Fe(III), indicating that the adsorption of Fe(II) and Fe(III) on the CTPP beads was favorable.

## CONCLUSION

The beads of chitosan cross-linked with sodium tripolyphosphate may be used as an effective adsorbent for the removal of Fe(II) and Fe(III) ions from aqueous solution. The adsorption of iron ions was found to be dependent upon solution pH, contact time and amount of adsorbent. Kinetic experimental data were best fitted to the pseudo-second-order model, confirming that the limiting step of the adsorption process is the chemical adsorption. The Redlich–Peterson isotherm was the best evaluated model, followed closely by Langmuir. Chitosan from fermented shrimp waste can therefore be an environmentally friendly alternative in the treatment of wastewater.

## ACKNOWLEDGEMENTS

This research was financed by FONCICYT C002-2008-1/ALA – 127 249 (Project no. 95935) and by AGRINOS AS Bio Tech Company. The first author is grateful to CONACyT (333811). Michael A. Bryan offered suggestions and improvements in the wording of this manuscript.

## REFERENCES

- Abdou, E. S., Nagy, K. S. A. & Elsabee, M. Z. 2008 Extraction and characterization of chitin and chitosan from local sources. *Bioresource Technology* **99**, 1359–1367.
- Acheampong, A., Meulepas, R. J. W. & Lens, P. N. L. 2010 Removal of heavy metals and cyanide from gold mine wastewater. *Journal of Chemical Technology and Biotechnology* **85**, 590–613.
- Ahalya, N., Kanamadi, R. D. & Ramachandra, T. V. 2006 Biosorption of iron(III) from aqueous solutions using the husk of *Cicer arientinum*. *Indian Journal of Chemical Technology* **13**, 122–127.
- AOAC 2005 *Official Methods of Analysis of AOAC International*, 18th edition. AOAC International, Gaithersburg, MD.
- APHA 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC.
- Bailey, S. E., Olin, T. J., Bricka, R. M. & Adrian, D. D. 1999 A review of potentially low-cost sorbents for heavy metals. *Water Research* **33**, 2469–2479.
- Beaney, P., Lizardi-Mendoza, J. & Healy, M. 2005 Comparison of chitins produced by chemical and bioprocessing method. *Journal of Chemical Technology and Biotechnology* **80**, 145–150.
- Chen, A.-H., Liu, S.-C., Chen, C.-Y. & Chen, C.-Y. 2008 Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Journal of Hazardous Materials* **154**, 184–191.
- Crini, G. & Badot, P.-M. 2008 Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. *Progress in Polymer Science* **33**, 399–447.
- Debnath, S. & Ghosh, U. C. 2008 Kinetics, isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide. *Journal of Chemical Thermodynamics* **40**, 67–77.
- Fu, F. & Wang, Q. 2011 Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management* **92**, 407–418.
- Guibal, E., Jansson-Charrier, M., Saucedo, I. & Le Cloirec, P. 1995 Enhancement of metal ion sorption performances of chitosan: effect of the structure on the diffusion properties. *Langmuir* **11**, 591–598.
- Ho, Y. S. 2006a Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods. *Polish Journal of Environmental Studies* **15**, 81–86.
- Ho, Y. S. 2006b Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods. *Water Research* **40**, 119–125.
- Ho, Y. S. & McKay, G. 1998 Kinetic models for the sorption of dye from aqueous solution by wood. *Transactions of the Institution of Chemical Engineers, Part B* **76**, 183–191.
- Ho, Y. S. & McKay, G. 2002 Application of kinetic models to the sorption of Copper(II) on to peat. *Adsorption Science and Technology* **20**, 797–815.
- Laus, R., Laranjeira, M. C. M., Martins, A. O., Fávere, V. T., Pedrosa, R. C., Benassi, J. C. & Geremias, R. 2006 Microesferas de quitosana reticuladas com tripolifosfato utilizadas para remoção da acidez, ferro(III) e manganês(II) de águas contaminadas pela mineração de carvão. *Química Nova* **29**, 34–39.

- Lee, S.-T., Mi, F.-L., Shen, Y.-J. & Shyu, S.-S. 2001 Equilibrium and kinetic studies of copper(II) ion uptake by chitosan-tripolyphosphate chelating resin. *Polymer* **42**, 1879–1892.
- Liu, L., Li, L., Zuo, Y., Huang, Y. & Song, L. 2011 Adsorption of 2-methylisoborneol and geosmin by a low-cost hybrid adsorbent synthesized from fly ash and bentonite. *Journal of Water Supply: Research Technology-AQUA* **60** (8), 478–485.
- Liu, D., Wei, Y., Yao, P. & Jiang, L. 2006 Determination of the degree of acetylation of chitosan by UV spectrophotometry using dual standards. *Carbohydrate Research* **341**, 782–785.
- López-Cervantes, J., Adan-Bante, N. P. & Sánchez-Machado, D. I. 2010 Separation and biochemical characterization of the products from fermented shrimp wastes. In: *Sea By-products as Real Material: New Ways of Application* (E. L. Bihan, ed.). Transworld Research Network, Kerala, India, pp. 117–132.
- Mi, F.-L., Shyu, S.-S., Lee, S.-T. & Wong, T.-B. 1999 Kinetic study of chitosan-tripolyphosphate complex reaction and acid-resistive properties of the chitosan-tripolyphosphate gel beads prepared by in-liquid curing method. *Journal of Polymer Science, Part B: Polymer Physics* **37**, 1551–1564.
- Mi, F.-L., Sung, H.-W., Shyu, S.-S., Su, C.-C. & Peng, C.-K. 2003 Synthesis and characterization of biodegradable TPP/genipin co-crosslinked chitosan gel beads. *Polymer* **44**, 6521–6530.
- Ngah, W. S. W. & Fatinathan, S. 2010 Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: kinetic, equilibrium and thermodynamic studies. *Journal of Environmental Management* **91**, 958–969.
- Ngah, W. S. W., Ghani, S. A. & Kamari, A. 2005 Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresource Technology* **96**, 443–450.
- Senthil Kumar, P., Ramakrishnan, K., Dinesh Kirupha, S. & Sivanesan, S. 2010 Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk. *Brazilian Journal of Chemical Engineering* **27**, 347–355.
- Shu, X. Z. & Zhu, K. J. 2002 The influence of multivalent phosphate structure on the properties of ionically cross-linked chitosan films for controlled drug release. *European Journal of Pharmaceutics and Biopharmaceutics* **54**, 235–243.
- Sureshkumar, M. K., Das, D., Mallia, M. B. & Gupta, P. C. 2010 Adsorption of uranium from aqueous solution using chitosan-tripolyphosphate (CTPP) beads. *Journal of Hazardous Materials* **184**, 65–72.
- Tahir, S. S. & Rauf, N. 2004 Removal of Fe(II) from the wastewater of a galvanized pipe manufacturing industry by adsorption onto bentonite clay. *Journal of Environmental Management* **73**, 285–292.
- Wan Ngah, W. S., Kamari, A. & Koay, Y. J. 2004 Equilibrium and kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads. *International Journal of Biological Macromolecules* **34**, 155–161.

First received 31 May 2012; accepted in revised form 6 September 2012