



Preparation of a chitosan-based anionic exchanger for removal of bromide, chloride, iodide and phosphate ions from aqueous solutions

Affonso Celso Gonçalves Junior^{1*}, Herbert Nacke¹, Daniel Schwantes¹, Valfredo Tadeu de Fávère² and Mauro Cesar Marghetti Laranjeira²

¹Centro de Ciências Agrárias, Programa de Pós-graduação em Agronomia, Universidade Estadual do Oeste do Paraná, Rua Pernambuco, 1777, 85960-000, Marechal Cândido Rondon, Paraná, Brazil. ²Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, Santa Catarina, Brazil. *Author for correspondence. E-mail: affonso133@hotmail.com

ABSTRACT. The development of a chitosan anion exchanger, obtained from shrimp shells, and its adsorption capacity for chloride, bromide, iodide and phosphate anions are provided. Dependence of exchange processes with the anions as a function of pH and contact time between exchanger and anions were initially investigated. Results showed that the best adsorption of ions occurred at pH 3.0. Exchange isotherms were then developed by the Langmuir, Freundlich and Dubinin-Radushkevich mathematical models. Results demonstrated that chitosan produced from shrimp shells may be used as feedstock in the manufacture of anion exchange microspheres.

Keywords: anion exchange, microspheres, reticulated chitosan.

Preparo de um trocador aniônico a base de quitosana para remoção de íons brometo, cloreto, iodeto e fosfato de soluções aquosas

RESUMO. Este trabalho estudou o desenvolvimento de um trocador aniônico de quitosana obtida a partir de cascas de camarão e sua capacidade de adsorção dos ânions cloreto, brometo, iodeto e fosfato. Inicialmente foi estudada a dependência dos processos de troca com os ânions em função do pH e do tempo de contato entre o trocador e os ânions, os resultados mostraram que em pH 3,0 ocorreu a melhor adsorção dos íons. Após isso, isotermas de troca foram desenvolvidas pelos modelos matemáticos de Langmuir, Freundlich e Dubinin-Radushkevich. Pelos resultados pode-se afirmar que a quitosana produzida a partir de cascas de camarão tem o potencial para ser utilizado como matéria-prima na fabricação de microesferas de troca iônica.

Palavras-chave: troca iônica, microesferas, quitosana reticulada.

Introduction

Biomasses are a renewable source of energy and thus highly interesting in research. Chitin, the second most abundant polysaccharide in biomasses, is produced by several sea animals (such as crabs, shrimps, lobsters, etc.), insects and fungi (MUZZARELLI, 1978; MATHUR; NARANG, 1990; BECKER et al., 2000; OLIVEIRA; VIEIRA, 2006). The glycoside units that form chitin are united by $\beta(1\rightarrow4)$ bonds forming a linear polymeric chain with a polymerization degree of about 2000 to 4000 (McKAY, 1996).

One single chitin molecule contains two chains with intra- and inter-molecular hydrogen bonds and simulates the cellulose molecule with a bent conformation (MATHUR; NARANG, 1990; MUZZARELLI, 1978).

It is important to highlight that the obtaining of chitin from byproducts of crustacean industrialization is hardly used in Brazil which may be considered a

waste due to the great quantity of these species on the Brazilian coast. Since the crustaceans are generally used as protein sources, the use of biopolymers as raw material for different industrial applications is essential (KIMURA et al., 1999; GONÇALVES JUNIOR, et al., 2010).

For many years, the US, Japan and India have been producing commercial polyelectrolytes derived from chitosan on a large scale. It is derived from chitin, a material extracted from shrimp shells (MATHUR; NARANG, 1990; MUZZARELLI, 1978). In Brazil, some studies are being developed on the rational use of shrimp shells by the fishing industry. Usually these residual components are thrown back into the sea, buried or merely deposited on the ground with significant damage to the environment (KIMURA et al., 1999; GONÇALVES JUNIOR, et al., 2010; WESKA, et al., 2007). Interest in the use of shrimp shells may be justified because of pigments, calcium salts, proteins and, in

particular, natural chitin polymer (MATHUR; NARANG, 1990; GACÉN; GACÉN, 1996).

The change from chitin into chitosan is an extremely important process since the biopolymer may be employed as an adsorbent in the form of grains, powder or microspheres (BECKER et al., 2000; SPINELLI et al., 2004; RAO et al., 2008; NGAH et al., 2004; DEBBAUDT et al., 2004). The protonation of the amino groups makes this material adequate as ionic exchanger (GONÇALVES JUNIOR et al., 2010; RORRER; HSIEN, 1993; HERNÁNDEZ et al., 2007).

Chitosan is obtained from the partial chitin deacetylation reaction in concentrated alkaline solutions (OLIVEIRA; VIEIRA, 2006). It presents itself as a 2-amino- β (1-4)-2-desoxi-D-glicopiranosose and 2-acetamide- β (1-4)-2-desoxi-D-glicopiranosose copolymer (LARANJEIRA; FÁVERE, 2009) where most of the acetamide ($-\text{NHCOCH}_3$) groupings in chitin during the alkaline hydrolysis reaction are transformed into amino (NH_2) groups along the polymeric chain.

Ion exchangers are solid substances with electric charges in their structures which are compensated by opposite ion charges, adsorbed on the surface, called exchangeable ions (MARHOL, 1982). They are extensively used in Analytical Chemistry to separate and pre-concentrate elements found in many kinds of samples for later analytical determinations (STURGEON et al., 1981; SPINELLI et al., 2005; JUSTI et al., 2005; COELHO et al., 2007; VITALI et al., 2008).

The ions studied in current research are important water pollutants. Iodide, bromide and chloride are widely used in the pharmaceutical industry (AGUIAR et al., 2006; SOUZA-MACHADO et al., 2008; GARCÍA et al., 2011) and are present in the effluents generated by this activity. Moreover, chloride and bromide compounds are determined in the assessment of drinking water quality (GONÇALVES et al., 2004; SALAMI et al., 2009). In the case of phosphate, the ion is mainly found in agricultural, domestic and industrial effluents (PRIOR et al., 2009; ALVES et al., 2012) and is a major cause of water eutrophication.

Owing to the high variety of substances in potentially contaminated waters, the development of exchangers and clean methods for *in situ* determination of different chemical compounds in the water is advantageous because of low waste and low consumption of reagents (LINDINO et al., 2011).

Current research evaluates the use of chitosan, obtained from shrimp shells, to develop an anionic exchanger. The use of the fishing industry's co-

product for the production of chitin and chitosan synthesis provides a breakthrough in the activity's sustainable development. Adsorption capacity of the anionic exchanger for the anions chloride, bromide, iodide and phosphate was determined and results interpreted by adsorption isotherms. The recovery of chitosan microspheres to be reused in a new study of phosphate adsorption was undertaken to prove sustainable usage of the biosorbent.

Material and methods

Materials

Chitin was extracted from shrimp shells, *Peneaus shimit* (white shrimp), native to the southern region of Brazil, and provided by sellers at the public market of Florianópolis, Santa Catarina State, Brazil.

Extraction of chitin and obtaining chitosan

Shrimp shells were dried, shredded and immersed in HCl 2 mol L^{-1} for 5h for the extraction of chitin. The material was then washed in distilled water until it reached neutral pH and dried at 70°C for 48h. The dry mass obtained was again immersed in HCl 2 mol L^{-1} for 24h, under agitation, and once again washed with abundant water until neutral pH. So that proteins could be eliminated, the material was put in contact with NaOH 1 mol L^{-1} for 12h, at 80°C, under reflux. The extraction using alkali was repeated two times more and finally the material was washed sequentially with water, until neutral pH, and then with ethanol and ethylic ether, and dried at 60°C for 24h (HACKMAN, 1953). Chitin mass obtained was approximately 20% of the initial shrimp shell mass.

Previously extracted chitin was submitted to deacetylation reaction with Broussignac method (BROUSSIGNAC, 1970). The reaction's medium was composed of a solution of KOH in an ethanol/ethylene glycol solvent system which was refluxed for 2h under a nitrogen atmosphere, at 120°C. The semi-anhydrous reaction environment was kept in inert atmosphere to avoid the depolymerization of the chitosan. The obtained sample was washed with distilled water and dried at 70°C for 36h. The mass of chitosan obtained was approximately 16% of the initial shrimp shell mass.

The synthesized chitosan was purified by dissolution in acetic acid 3% (m v^{-1}) and filtrated to eliminate any insoluble residue. The obtained material was then dried with a Büchi Mini Spray Dryer (model B-191). The product of the synthesis consisted of approximately 20.5% of chitin and 16.2% of chitosan from every 100 g of shrimp shells.

Chitosan characterization

The purified chitosan was submitted to elemental analysis (C, H, N), using a CHN Perkin Elmer Elements Analyzer-240 to obtain carbon, hydrogen and oxygen rates. It was also characterized by an infrared spectrum, using FT Perkin Elmer Infrared Spectrophotometer – Model 16 PC, and by a ¹³C nuclear magnetic resonance, using a Bruker¹H and ¹³C Nuclear Magnetic Resonance – Model AC-200F (HIRAI et al., 1990). Further, the deacetylation degree (DG) or the percentage of amino groups was determined by conductometric titration (DOMSZY; ROBERTS, 1985), using a Micronal conductometer – Model B330 and a Schott Geräte automatic titrator – Model T80/20 (RAYMOND et al., 1993).

The deacetylation degree is represented by the percentage of amino groups in chitosan. Its determination is done by conductometric titration of the chitosan in strong mineral acid and performed with a strong base. The conductance is obtained by the addition of each ion in the solution. H₃O⁺ and OH⁻ ions are those that most contribute towards conductance. The conductometric titration monitors change the conductance of these ions because of the added titrate volume. Percentage of amino groups was determined by the equation 1:

$$DG(\%) = \frac{C(V_2 - V_1)161}{W} \times 100 \quad (1)$$

being:

C is the concentration of NaOH solution in mol L⁻¹;

V₁ is NaOH volume to neutralize the hydrochloric acid;

V₂ is the NaOH volume to neutralize the hydrochloric acid and the protonated chitosan;

161 is the molar mass of the monomer unit of the polymer;

W is the sample mass in mg taken through titration.

Preparation, reticulation and characterization of the chitosan microspheres

The preparation of microspheres was carried out by the dissolution of chitosan in 5% (m v⁻¹) acetic acid. The viscous solution obtained was poured in drops with a peristaltic pump (Ismatec brand) attached to a precipitation shower containing a solution of NaOH 2 mol L⁻¹ (inversion of phases method). The jellied microspheres were washed with distilled water until neutral pH (RORRER; HSIEN, 1993).

The chitosan microspheres were reticulated by contact with a solution of glutaraldehyde 2.5% (m v⁻¹). The mixture was kept under agitation for 18 h at room temperature. The material was washed with distilled water to eliminate excess of reticulating agent and the microspheres were dried in an oven at 45°C for approximately 18h.

After the preparation and reticulation of the chitosan microspheres, the morphology of the external and internal surfaces were analyzed by scanning electron microscopy (SEM), with a Philips equipment, Model XL30 (KIMURA et al., 1999). Average diameter of the chitosan's microsphere was determined with micrograph figures of 20 microspheres, analyzing the vertical and horizontal axes of each microsphere.

Mercury porosimetry analysis was performed with a device from Micromeritics, model Poresizer 9320, to measure the distribution of the pores in the reticulated microspheres. The average size of the pores was determined by the Young-Laplace equation (KIMURA et al., 1999).

Conversion and determination of the anionic exchanger's theoretical capacity

The reticulated chitosan microspheres were put in contact with HNO₃ 7% (v v⁻¹) solution for 3h, under agitation. When the microspheres were washed and filtrated, exchanger was converted from RNH₂ to RNH₃⁺NO₃.

Samples of the reticulated chitosan microspheres were put in contact with different solutions of NaOH 0.097 mol L⁻¹. When they reached apparent equilibrium, approximately 3 h later, solutions' pH was measured by a pH-meter. The graphic of pH *versus* NaOH volume was provided to determine the quantity of –NH₃⁺mmol per exchanger gram.

Ion adsorption dependence in the chitosan microspheres as a function of pH

The ion adsorption dependence of pH was carried out by placing samples of reticulated chitosan microspheres in contact with different solutions containing a constant concentration of the anion (chloride, bromide, iodide, and phosphate).

Solutions' pH was adjusted with several buffer solutions and then transferred to a mechanic agitator at room temperature and agitated for 3h at 50 rpm. After agitation, pH measurements were made and aliquots were extracted to determine the anions according to the most suitable method for each. The anions chloride, bromide, and iodide were determined by volumetry, whereas the phosphate anion was

assessed by spectroscopy with Visible-UV at $\lambda = 720$ nm (RAIJ et al., 2001).

The adsorbed quantity of each anion was determined by the equation 2:

$$q = \frac{(C_0 - C_f)}{W} V \quad (2)$$

being:

q is the amount of anion adsorbed (mmol g^{-1});

W is the chitosan microsphere mass (g);

C_0 is the initial concentration of the solution (mmol L^{-1});

C_f is the anion concentration after the equilibrium time in the solution (mmol L^{-1});

V is the solution's volume (L).

Adsorption isotherms and selectivity coefficients

For isotherms, the stock solutions were prepared at a concentration of 5 mmol L^{-1} of the anions chloride, bromide, iodide and phosphate. They were then placed in Erlenmeyer flasks with different volumes of the stock solutions at an interval of 5, up to 45 mL, with the final volume gauged at 50 mL, at constant pH. Finally, samples of the reticulated chitosan microspheres (100 mg) were added in the solutions.

After reaching equilibrium, the aliquots of the supernatant were withdrawn to determine anion concentration. Bromide, chloride, and iodide ions were determined by volumetric methods and phosphate ion by UV-Vis Spectrophotometry, according to above references.

Anion concentration was determined for the supernatant by the equation 3:

$$q = \frac{(C_0 - C_{eq})}{m} V \quad (3)$$

being:

q is the number of anions adsorbed in the exchanger surface;

C_0 is the initial concentration;

C_{eq} is the final or balanced concentration;

V is the solution's volume used in the adsorption process, in liters; m is the chitosan mass in grams.

After reaching the exchange isotherms for the studied anions, the microspheres were recovered with HNO_3 1 mol L^{-1} solution at 24h under slow agitation. The microspheres were then separated from the HNO_3 1 mol L^{-1} solution, washed and stocked in deionized water at room temperature. The exchanger was once again converted into $\text{RNH}_3^+\text{NO}_3^-$. After the recovery of the microspheres, an exchange isotherm for the phosphate anion was again carried out to test the exchange capacity after the use and recovery of the

anion exchanger. All the analysis procedures were performed in triplicate.

Results and discussion

Chitosan characterization

The conductometric titration was calculated and represented by the average of three determinations from which 94% deacetylation were obtained. The deacetylation degree from three replicates by conductometric titration was higher than chitosan sold on the Brazilian market with 90% deacetylation (SPINELLI et al., 2004; GONÇALVES JUNIOR et al., 2010).

The chitosan microanalysis provided carbon 40.78%; hydrogen 7.18%; nitrogen 7.67%; and by deduction, oxygen 44.37%. The chitosan molecular formula $(\text{C}_8\text{H}_{13}\text{NO}_5)_{0.06} (\text{C}_6\text{H}_{11}\text{NO}_4)_{0.94} \cdot 5.64 \text{ H}_2\text{O}$ was established from the analysis of the elements, deacetylation degree and humidity rate.

Figure 1 shows chitosan infrared spectrum. The 3454 cm^{-1} absorption bands are very intense due to OH^- and H_2O stretching vibrations, whereas the 2900 cm^{-1} absorption bands correspond to C-H stretching vibration. The bands at 1654 and 1590 cm^{-1} refer to the amides $\text{C}=\text{O}$ stretching and the deforming vibrations of medium intensity of the N-H primary amide. The 1380 cm^{-1} band is attributed to C-N low intensity vibration of the CH_3 group and refers to the acetamide group still present in the polymer chain in small proportions while deacetylation has not been completed. The 1068 cm^{-1} band originates the C-O vibration stretching of primary alcohol (KIMURA et al., 2002).

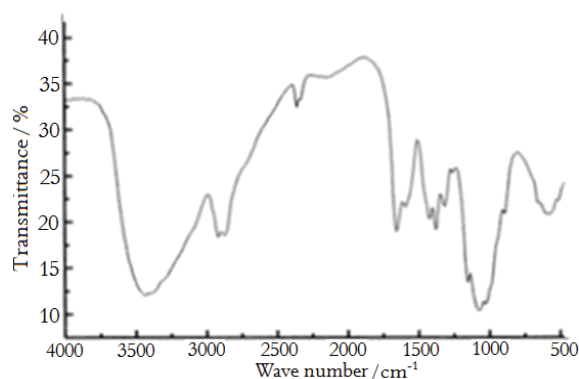


Figure 1. Infrared spectrum of chitosan in KBr.

Figure 2 illustrates the nuclear magnetic resonance spectrum of chitosan ^{13}C . The spectrum shows the chemical dislocation of the anomeric carbon C_1 in 98 ppm, well separated from the other signs. The two other signs, close to 80 ppm, are related to C_4 . Further, C_3 and C_5 carbons dislocate at

about 77 ppm. The 60 ppm sign is distinct due to the alcohol primary carbon, while the signs at 56 and 57 ppm refer to C_2 . Due to the deacetylation incompleteness, there are still lines correspondent to $C=O$ and CH_3 , dislocating at about 177 and 21 ppm, respectively (PERLIN; HAMER, 1979).

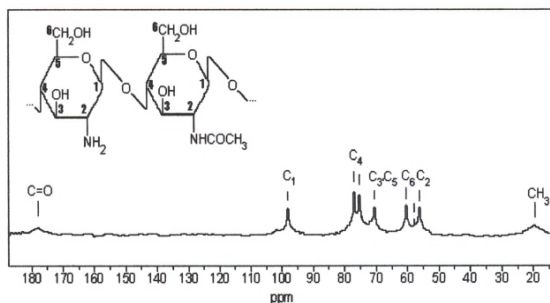


Figure 2. Spectrum of ^{13}C nuclear magnetic resonance of chitosan.

Characterization of the reticulated chitosan microspheres

The average diameter of chitosan microspheres found was 1.01 ± 0.06 mm (Figure 3). Mercury porosimetry analysis of the chitosan microsphere revealed that most of the pore size distributions presented a diameter with approximately 60 Å, confirming SEM studies. Results corroborated those found in studies with commercial chitosan (GONÇALVES JUNIOR et al., 2010).

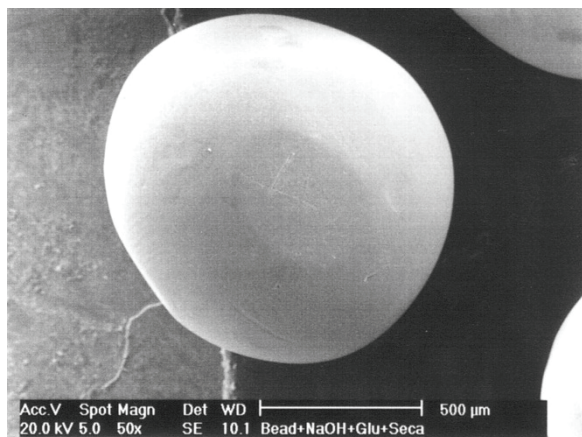


Figure 3. SEM photomicrographs of the reticulated chitosan microsphere morphology with a 50X increase

Determination of the anion exchanger's theoretical capacity

Figure 4 shows the neutralization curve of the chitosan-based anion ($pH \times NaOH$ volume in mL). The point of maximum inflection in the curve corresponds to the stoichiometric point of the protonated exchanger. The inflection point was determined from the first derivative of the curve

($\Delta E/\Delta V$) and corresponds to 0.908 mmol of $-NH_3^+$ groups per polymer gram. In current study, this rate was used as a reference for maximum adsorption capacity of the ions.

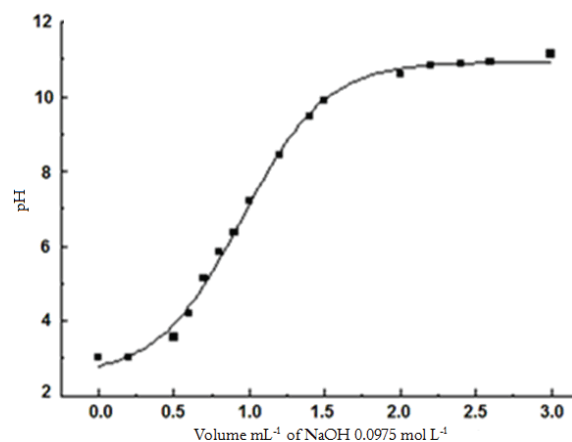


Figure 4. Neutralization curve of the chitosan anionic exchanger

Adsorption pH dependence

Results of pH adsorption dependence indicate that the adsorption of the ions iodide and phosphate were very dependent on pH variation. Maximum adsorption of anions by the chitosan occurred at pH close to 3.0 (Figure 5).

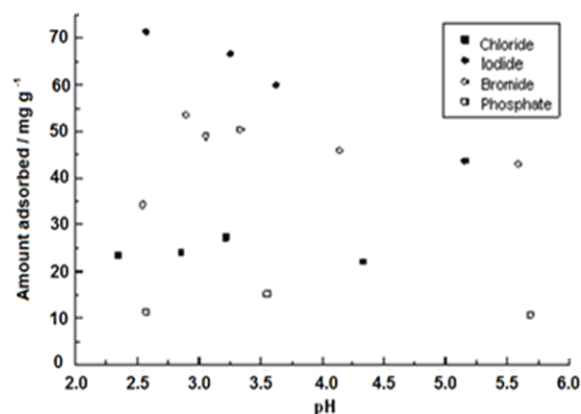
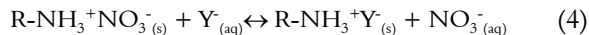


Figure 5. pH effect on the adsorption of chloride, bromide, iodide and phosphate on chitosan microspheres. Temperature 25°C; contact time 3h; QTS mass 100 mg; stirring speed 150 rpm.

Results obtained in this research on ions adsorption in dependence of pH by the chitosan microspheres showed that the pH interval where the greatest adsorption of chloride, bromide, iodide, and phosphate anions occurred (Figure 5) was between 2.7 and 3.0. Buffer agents were not necessary to reach this pH interval and pH after adsorption did not vary. Isotherms were obtained after defining the best pH interval for anion adsorption.

Adsorption isotherms of the anions chloride, bromide, iodide, and phosphate

When the adsorption process of chemical species is studied, the functional group connected to the adsorbent surface should be highlighted. Consequently, groups that cause ion-anion interaction in current experiment are amine protonated groups ($-\text{NH}_3^+$), with NO_3^- as counter-exchangeable ion. Chitosan interactions with halides and dihydrogen phosphate solutions studied in this paper may be expressed by the equation 4:



being:

Y^- is the Cl^- , Br^- , I^- and H_2PO_4^- anions.

From the results of the analysis after equilibrium, the q and C_{eq} rates were calculated. Figures 6 and 7 illustrate the concentration curves in the solid phase (q) versus the anion concentration in the liquid phase (C_{eq}). The Langmuir mathematical model is used because of the behavior of some of the adsorption curves. Such model considers the adsorbent surface as homogeneous and the sites with same energy. In current study, the $-\text{NH}_3^+$ groups were the adsorption sites and the NO_3^- ions were exchanged by the solution anions.

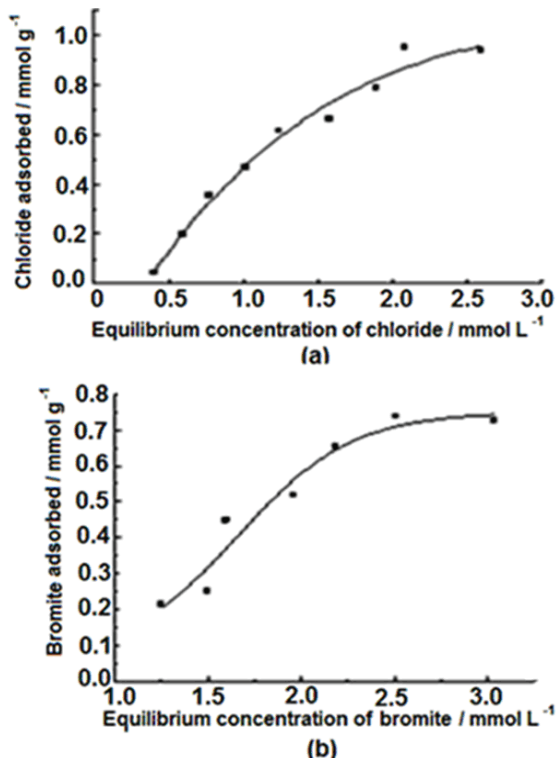


Figure 6. Adsorption isotherms of chloride ions (a) and bromide (b). Temperature 25°C; contact time 3h; QTS mass 100 mg; stirring speed 150 rpm.

The occurrence of the saturation of adsorption sites for iodide is reported (Figure 7a), while, in the case of the adsorption of chloride (Figure 6a), bromide (Figure 6b) and phosphate ions (Figure 7b), the saturation point should be reached for concentrations just above the maximum used in this experiment.

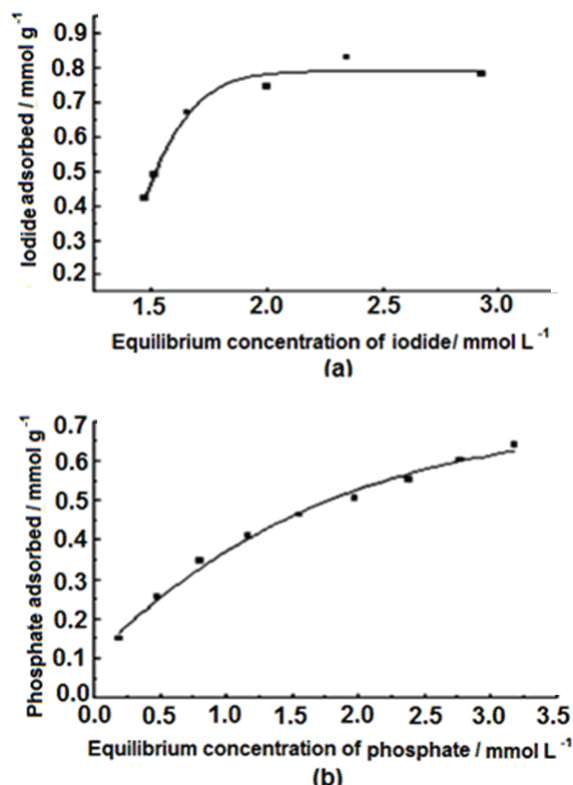


Figure 7. Adsorption isotherms of iodide ions (a) and phosphate (b). Temperature 25°C; contact time 3h; QTS mass 100 mg; stirring speed 150 rpm.

Chitosan has been used for the adsorption of many substrates in solutions and the analysis of the obtained data has frequently been interpreted by the Langmuir mathematical model (ADAMSON, 1976), although other models, such as Freundlich, Dubinin-Radushkevich (D-R), are extant.

Current study reveals that adsorption curves are very close to the proposed models by Langmuir, D-R and in some cases, Freundlich. They are in fact analyzed by those models. The simplest way to determine the adsorption parameters is putting them in their linear form.

As Table 1 shows, in the case of iodide, bromide and chloride ions, the adsorption rates have the best fitting by D-R mathematical models, with E rates varying between 0.807 and 1.202 kg mol⁻¹, suggesting physisorption (WAN NGAH; HANAFIAH, 2008).

Table 1 shows higher rates of R^2 for D-R and Langmuir model in the case of bromide adsorption and suggests that the adsorption of the ion occurs as a physisorption in monolayer. In this case and according to the rates from Langmuir linear model, the bromide adsorption shows maximum capacity of adsorption (Q_m) rates around 1.95 mmol g^{-1} .

Table 1. Linearization by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) mathematical models for the adsorption of chloride, bromide, iodide and phosphate ions.

Ion	Langmuir parameters		Freundlich parameters		D-R parameters	
	Q_m (mmol g^{-1})	R^2	K_f (L^{-1}mmol)	n	E (kJ mol^{-1})	R^2
Chloride	3.132	0.91	0.472	0.439	1.202	0.98
Bromide	1.950	0.98	0.078	0.381	0.611	0.99
Iodide	0.008	0.88	0.002	0.570	0.807	0.97
Phosphate	0.819	0.98	0.364	1.975	1.259	0.93

Q_m : maximum capacity of adsorption; K_f : constant related to the interaction forces adsorbent/adsorbate; R^2 : coefficient of determination; K_f : related to the adsorption capacity; n : related to solid heterogeneity; E : mean sorption energy.

Likewise, the phosphate adsorption presented best fitting for Langmuir and Freundlich models and suggested monolayer and multilayer adsorption, simultaneously. In this case, the values of n , from the Langmuir model, show mean rate 1.975 and indicate highly energetic sites (SODRÉ et al., 2001).

Recovery and reuse of the chitosan microspheres

After undertaking the ions adsorption experiments previously described, some microspheres were once again converted into $\text{RNH}_3^+\text{NO}_3^-$ form to see whether their recovery and posterior reuse would be possible.

The recovered exchanger was put in contact with increasing concentrations of KH_2PO_4 solutions at constant pH. Later, they were transferred to a mechanic agitator for a period of three hours, at 150 rpm. After the adsorption balance was attained, the phosphate amount was determined following the previously described methodology. Figure 8 shows the adsorption isotherm of the phosphate ion by the recovered microspheres.

The maximum adsorption capacity (Q_m) of the microspheres after their regeneration was $0.832 \text{ mmol g}^{-1}$. The above rate is very close to its theoretical exchange capacity at $0.908 \text{ mmol g}^{-1}$ (Figure 4).

When the exchange capacity after the microspheres recovery, $0.832 \text{ mmol g}^{-1}$, is compared with $0.819 \text{ mmol g}^{-1}$, the exchange capacity obtained in its first use (Table 2), an increase trend may be detected in the exchange capacity due to the activation of the exchange sites of the exchanger. The above confirms the possibility of recovery and reuse of the chitosan microspheres as an anion exchanger.

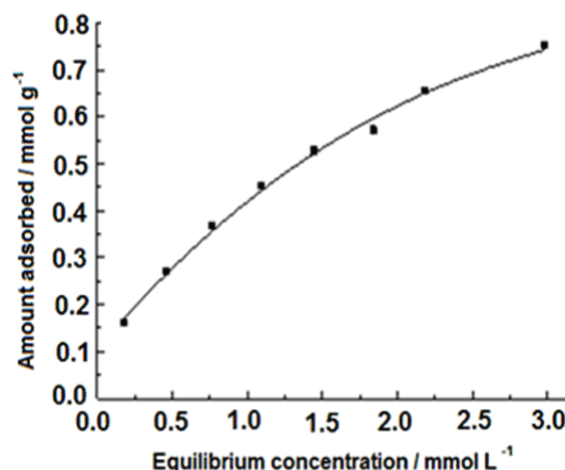


Figure 8. Adsorption isotherm of phosphate ions with recovered chitosan microspheres.

A small reduction is observed (Table 2) in n rates by Freundlich model, with a small reduction of the highly energetic sites of adsorption, or rather, 1.975 when the chitosan was first used (Table 1) and 1.813 when the material was reused. However, when K_f results were compared, an increase in the adsorption capacity by Freundlich model was shown to have occurred (Tables 1 and 2).

The mathematical model of D-R showed low R^2 rates for the observed data and the model is not applied in discussion on chitosan regeneration in the phosphate adsorption process.

Table 2. Linearization by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) mathematical models for the adsorption of phosphate ions after chitosan regeneration

Ion	Langmuir parameters		Freundlich parameters		D-R parameters	
	Q_m (mmol g^{-1})	R^2	K_f (L mmol^{-1})	n	E (kJ mol^{-1})	R^2
Phosphate	0.832	0.97	0.419	1.813	0.99	0.90

Q_m : maximum capacity of adsorption; K_f : constant related to the interaction forces adsorbent/adsorbate; R^2 : coefficient of determination; K_f : related to the adsorption capacity; n : related to the solid heterogeneity; E : mean sorption energy.

Conclusion

The theoretical capacity of chitosan ion exchanger was $0.908 \text{ mmol NH}_3^+$ per microsphere gram.

The dependence of adsorption processes due to pH showed that optimum pH interval ranged approximately between 2.7 and 3.0.

Tests with the recovered exchanger for phosphate ion adsorption showed that the exchange capacity was maintained, confirming that the exchanger may be reused in ion exchange studies.

It may be concluded that chitosan produced from shrimp shells has high viability for use as anion exchanger and provides a sustainable feedstock in the production of this material.

References

- ADAMSON, A. W. **Physical chemistry of surfaces**. 3rd ed. New York: John Wiley and Sons, 1976.
- AGUIAR, M. A. S.; BERBIGÃO, P. N.; MORI, V. Amperometric determination of iodide in oral expectorants solutions with flow injection analysis using the reaction iodide/nitrite. **Eclética Química**, v. 31, n. 2, p. 63-68, 2006.
- ALVES, M.; FONTENELE, R. M. M.; CAVALCANTE, D. H.; SEGUNDO, J. N. O.; SÁ, M. V. C. Domestic sludge and fish pond effluents in the municipality of Pentecoste, Ceará State, Brazil. **Acta Scientiarum. Technology**, v. 34, n. 4, p. 405-412, 2012.
- BECKER, T.; SCHLAAK, M.; STRASDEIT, H. Adsorption of nickel (II) and cadmium (II) by new chitosan derivatives. **Reactive and Functional Polymers**, v. 44, n. 1, p. 289-298, 2000.
- BROUSSIGNAC, J. Un haut polymère naturel peu connu dans l'industrie le chitosane. **Chimie et Industrie Genie Chimique**, v. 99, n. 9, p. 1241-1247, 1970.
- COELHO, T. C.; LAUS, R.; MANGRICH, A. S.; FÁVERE, V. T.; LARANJEIRA, M. C. M. Effect of heparin coating on epichlorohydrin cross-linked chitosan microspheres on the adsorption of copper (II) ions. **Reactive and Functional Polymers**, v. 67, n. 5, p. 468-475, 2007.
- DEBBAUDT, A. L.; FERREIRA, M. L.; GSCHAUER, M. E. Theoretical and experimental study of Mn^{2+} adsorption on biopolymers. III. Comparative kinetic pattern of Pb, Hg and Cd. **Carbohydrate Polymers**, v. 56, n. 3, p. 32-332, 2004.
- DOMSZY, J. G.; ROBERTS, A. F. Evaluation of infrared spectroscopic technique for analyzing chitosan. **Macromolecular Chemistry and Physics**, v. 186, n. 8, p. 1671-1677, 1985.
- GACÉN, J.; GACÉN, I. Quitina y quitosano: nuevos materiales textiles. **Boletín Intexter**, v. 110, n. 1, p. 67-71, 1996.
- GARCÍA, P. L.; GOMES, F. P.; SANTORO, M. I. R. M.; KEDOR-HACKMANN, E. R. M.; QUERO, J. L. V.; MONTÓN, A. N.; MONTOYA, G. C.; CABRERA, M. A. Determination of vecuronium bromide in pharmaceuticals: development, validation and comparative study of HPLC and CZE analytical methods. **Chromatographia**, v. 73, n. 7-8, p. 799-805, 2011.
- GONÇALVES, M. E. P.; CAMÕES, M. F.; PAIVA, J. M.; BENOLIEL, M. J.; CARNEIRO, R. N. Validation of simultaneous determination of bromides and bromates by ion chromatography in drinking water. **Química Nova**, v. 27, n. 3, p. 503-507, 2004.
- GONÇALVES JUNIOR, A. C.; NACKE, H.; FÁVERE, V. T.; GOMES, G. D. Comparison between an anionic exchanger of chitosan quaternary ammonium salt and a commercial exchanger in the extraction of available phosphorus in soils. **Química Nova**, v. 33, n. 5, p. 1047-1052, 2010.
- HACKMAN, R. H. Studies on chitin. **Australian Journal of Biological Sciences**, v. 7, n. 2, p. 168-178, 1953.
- HERNÁNDEZ, R. B.; YOLA, O. R.; MERCÊ, A. L. R. Chemical equilibrium in the complexation of first transition series divalent cations Cu^{2+} , Mn^{2+} and Zn^{2+} with chitosan. **Journal of Brazilian Chemical Society**, v. 18, n. 7, p. 1388-1396, 2007.
- HIRAI, A.; HORII, F.; KITAMURU, R. CP/MAS ^{13}C NMR study of never-dried cotton fibers. **Journal of Polymer Science**, v. 28, n. 12, p. 357-361, 1990.
- JUSTI, K. C.; FÁVERE, V. T.; LARANJEIRA, M. C. M.; NEVES, A.; PERALTA, R. A. Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol. **Journal of Colloid and Interface Science**, v. 291, n. 2, p. 369-374, 2005.
- KIMURA, I. Y.; GONÇALVES JR., A. C.; STOLBERG, J.; LARANJEIRA, M. C. M.; FÁVERE, V. T. Effect of pH and contact time in adsorption of reactive dyes by chitosan microspheres. **Polímeros**, v. 9, n. 2, p. 51-57, 1999.
- KIMURA, I. Y.; LARANJEIRA, M. C. M.; FÁVERE, V. T.; FURLAN, L. The interaction between reactive dye containing vinylsulfone group and chitosan microspheres. **International Journal of Polymeric Materials**, v. 51, n. 8, p. 759-768, 2002.
- LARANJEIRA, M. C. M.; FÁVERE, V. T. Chitosan: functional biopolymer with biomedical industrial potential. **Química Nova**, v. 32, n. 3, p. 672-678, 2009.
- LINDINO, C. A.; MEOTTI, M. L.; MEOTTI, P. M.; GONÇALVES JUNIOR, A. C. Chitosan modified electrodes for phosphate determination. **Acta Scientiarum. Technology**, v. 33, n. 3, p. 323-329, 2011.
- MARHOL, M.; **Ion exchangers in analytical chemistry**: their properties and use in inorganic chemistry. New York: Elsevier, 1982.
- MATHUR, N. K.; NARANG, C. K. Chitin and chitosan, versatile polysaccharides from marine animals. **Journal of Chemical Education**, v. 67, n. 11, p. 938-942, 1990.
- MCKAY, G. Use of adsorbents for the removal of pollutants from wastewaters. Boca Raton: CRC Press, 1996.
- MUZZARELLI, R. A. A. **Chitin**. Oxford: Pergamon Press, 1978.
- NGAH, W. S. W.; KAMARI, A.; KOAY, Y. J. Equilibrium and kinetics studies of adsorption of copper(II) on chitosan and chitosan/PVA beads. **International Journal of Biological Macromolecules**, v. 34, n. 2, p. 155-161, 2004.
- OLIVEIRA, I. R. W. Z.; VIEIRA, I. C. Construction and analytical applications of biosensors using different immobilization procedures of vegetable peroxidase on chitosan matrix. **Química Nova**, v. 29, n. 5, p. 932-939, 2006.
- PERLIN, A. S.; HAMER, G. K. **Characterization of carbohydrate polymers by carbon-13 NMR spectroscopy**. In: PASIKA, W. M. (Ed.). Carbon-13 NMR in Polymer Science. Washington, D.C.: American Chemical Society, 1979. p. 57-71.
- PRIOR, M.; SMANHOTTO, A.; SAMPAIO, S. C.; NOBREGA, L. H.; OPAZO, M. A. U.; DIETER, J. Percolation and accumulation of phosphorus in the soil due to the application of swine wastewater in maize (*Zea*

- mays L.). **Pesquisa Aplicada and Agrotecnologia**, v. 2, n. 1, p. 89-96, 2009.
- RAO, K. S. V. K.; CHUNG, I.; HA, C. Synthesis and characterization of poly(acrylamidoglycolic acid) grafted onto chitosan and its polyelectrolyte complexes with hydroxyapatite. **Reactive and Functional Polymers**, v. 68, n. 5, p. 943-953, 2008.
- RAIJ, B. V.; ANDRADE, J. C.; CANTARELLA, H.; QUAGGIO, J. A. **Chemical analysis for evaluation of the fertility of tropical soils**. Campinas: Instituto Agrônômico, 2001.
- RAYMOND, L.; FREDERICK, G. M.; MARCHESSAULT, R. H. Degree of deacetylation of chitosan using conductometric titration and solid-state NMR. **Carbohydrate Research**, v. 246, n. 19, p. 331-336, 1993.
- RORRER, G. L.; HSIEN, T. Y. Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water. **Industrial and Engineering Chemistry Research**, v. 32, n. 9, p. 2170-2178, 1993.
- SALAMI, F. H.; BONIFÁCIO, V. G.; FATIBELLO-FILHO, O.; MARCOLINO-JR., L. H. Spectrophotometric flow determination of chlorine in water using a long path-length optic cell and multicommutation. **Química Nova**, v. 32, n. 1, p. 112-115, 2009.
- SOUZA-MACHADO, A.; VALVERDE, J. G.; SANTANA-JUNIOR, J. S.; BARRETO, L. G.; NONATO, G. S.; HAGENBECK, K. F.; XAVIER, D. V.; BRASIL, J. M. Toxic effects attributed to benzalkonium chloride on nasal mucosa and mucociliar activity. **Revista Brasileira de Imunopatologia**, v. 31, n. 1, p. 2-9, 2008.
- SPINELLI, V. A.; LARANJEIRA, M. C. M.; FÁVERE, V. T.; KIMURA, I. Y. Kinetics and equilibrium of adsorption of oxyanions Cr(VI), Mo(VI), and Se(VI) by quaternary ammonium chitosan salt. **Polímeros**, v. 15, n. 3, p. 218-223, 2005.
- SPINELLI, V. A.; LARANJEIRA, M. C. M.; FÁVERE, V. T. Preparation and characterization of quaternary chitosan salt: adsorption equilibrium of chromium(VI) ion. **Reactive and Functional Polymers**, v. 6, n. 2, p. 347-352, 2004.
- SODRÉ, F. F.; LENZI, E.; COSTA, A. C. Applicability of adsorption models to the study of copper behavior in clayey soils. **Química Nova**, v. 24, n. 3, p. 324-330, 2001.
- STURGEON, R. E.; BERMAN, S. S.; WILLIE, S. N. Pre-concentration of trace elements from seawater with silica immobilized 8-hydroxyquinoline. **Analytical Chemistry**, v. 53, n. 14, p. 2337-2344, 1981.
- VITALI, L.; LARANJEIRA, M. C. M.; GONÇALVES, N. S.; FÁVERE, V. T. Spray-dried chitosan microspheres containing 8-hydroxyquinoline-5-sulphonic acid as a new adsorbent for Cd(II) and Zn(II) ions. **International Journal of Biological Macromolecules**, v. 42, n. 2, p. 152-157, 2008.
- WAN NGAH, W. S. W.; HANAFIAH, M. A. K. M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. **Bioresource Technology**, v. 99, n. 10, p. 3935-3948, 2008.
- WESKA, R. F.; MOURA, J. M.; BATISTA, L. M.; RIZZI, J.; PINTO, L. A. A. Optimization of deacetylation in the production of chitosan from shrimp wastes: use of response surface methodology. **Journal of Food Engineering**, v. 80, n. 3, p. 749-753, 2007.

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