

TEOS as an Improved Alternative for Chitosan Beads Cross-Linking: A Comparative Adsorption Study

Guillermo J. Copello, María E. Villanueva, Joaquín A. González, Sofía López Egües, Luis E. Diaz

Cátedra de Química Analítica Instrumental, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires (UBA), IQUIMEFA (UBA-CONICET), Junín 956, C1113AAD Buenos Aires, Argentina

Correspondence to: L. E. Diaz (E-mail: ldiaz@ffyb.uba.ar) or G. J. Copello (E-mail: gcopello@ffyb.uba.ar)

ABSTRACT: In this work the use of tetraethoxysilane (TEOS) for cross-linking of chitosan hydrogel beads was studied at the level of 1 mmol TEOS per gram of chitosan. They were compared with glutaraldehyde and epichlorohydrin cross-linked beads. The hydrogels were characterized by FTIR, SEM, water content, nitrogen content, and their point of zero charge. The performance of the anionic dye Remazol Black (RB) and the cationic Cd(II) adsorptions was assessed in order to characterize the sorbate–sorbent interaction. Adsorption experimental data were analyzed using two- and three-parameter isotherm models along with the evaluation of mean adsorption energy and standard free energy. The adsorption was observed to be pH dependent. The uptake rate of RB and Cd(II) showed that the three type of beads followed a similar kinetic behavior. For both sorbates the TEOS cross-linked beads showed the higher maximum adsorption capacity, followed by epichlorohydrin and glutaraldehyde cross-linked beads. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41005.

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INTRODUCTION

Chitosan hydrogels and its derivatives have been thoroughly studied in the past decade for its application in adsorption processes. The pursuit of improving chitosan-derived materials is based on the advantages of this polysaccharide regarding costs, biodegradability and innocuousness to humans and the environment.^{1–4} Chitosan (β -(1→4)-2-amino-2-deoxy-D-glucose) is a by-product of food industry obtained from deacetylation of chitin. Chitin is a polysaccharide whose structure consists predominantly of unbranched chains of β -(1→4)-2-acetoamido-2-deoxy-D-glucose. It can be extracted from shrimp, crab shell, fungi, and other crustaceans.⁵

In regard to its application as a biosorbent polymer, chitosan has gained particular attention because of its low cost and an adsorption capacity comparable to traditional adsorbents, such as activated carbon and ion exchange resins.^{2,6} However, chitosan is commercially obtained in the form of flakes or powder. This is disadvantageous for its use as adsorbent in engineering and biotechnological applications, both in batch or column systems, because of its low surface area, low porosity, and compressibility at operating pressure.⁷ The development of films or hydrogel beads are alternatives to overcome these issues but

they still do not solve the drawback of chitosan solubility in acidic media. Chemical cross-linking has been investigated not only to minimize solubility but also to endow hydrogel beads with desirable mechanical and adsorptive properties.^{8–10} The amine group of this polysaccharide is involved in the adsorption mechanism of most of the target sorbates. Thus, with the aim of preserving chitosan full adsorption capacity, the cross-linking process should avoid the interaction among the cross-linker molecule and the amine groups. Literature shows glutaraldehyde (Glu) as the most widely used cross-linker molecule for this biopolymer.^{11–14} Paradoxically, Glu interaction with chitosan requires the consumption of two glucosamine units to form the corresponding Schiff bases, which leads to a loss of adsorption sites.¹² Moreover, polymerization of Glu also occurs forming a greater cross-linking chain which diminishes adsorption capacity in terms of sorbate-mass : sorbent-mass ratio.¹⁵ Another widespread used cross-linker is epichlorohydrin (Epi). As Glu, Epi is a bifunctional molecule that reacts at alkaline media with both the -OH and -NH₂ groups in chitosan structure. The reaction of Epi with the amino groups forms a secondary amine, maintaining the basic characteristic of chitosan. This implies that the loss of adsorption sites is lower than when using Glu, which has been demonstrated by different studies.^{16,17}

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Other disadvantage of Glu and Epi, as well as other cross-linkers such as ethylene glycol diglycidyl ether (EGDE) or glyoxal, is that they are toxic and nonenvironmentally friendly.² In order to cope with these drawbacks, water soluble and safer cross-linkers have been proposed. Polyphosphate, citric acid, and genipin could be mentioned among them.^{2,4,18}

In a different approach, silicon oxide polymeric precursors have been used for immobilization of chitosan, such as tetraethoxysilane (TEOS), sodium silicates, aminopropyltriethoxysilane and glycidoxypropyltrimethoxysiloxane among others.^{19,20} Most silicon oxide precursors form interpenetrated polymers with chitosan after polymerization. Hence, the active sites of the polysaccharide remain intact while its solubility is diminished and its adsorption capacity is maintained.²¹ Nevertheless, most of these approaches involve the obtaining of a hybrid material whose main component is SiO₂; therefore the overall adsorption capacity of these materials is lower than that of pure chitosan.²²

From the above mention arises the interest in finding nontoxic cross-linking conditions that do not diminish the adsorption capacity of the sorbent. The aim of this work is to study and characterize the behavior of chitosan hydrogel beads cross-linked using a TEOS : chitosan ratio of 1 mmol/g. At this ratio chitosan is in excess compared to TEOS, which contrasts with the developments described in literature where the alcoxysilane is the main component of the composite. The adsorption performance of TEOS, Epi, and Glu cross-linked beads were compared. The azo dye Remazol Black 5 (RB) was chosen as an anionic sorbate model (bearing four -SO₃⁻ groups). Cd(II) was chosen as a cationic sorbate model. Conditions regarding batch optimum pHs, adsorption kinetic and capacities were compared. The differences of sorbate-sorbent interactions among the cross-linkers used were characterized. With this aim, an extensive analysis of adsorption kinetic and equilibrium behavior was performed.

EXPERIMENTAL

Reagents and Materials

TEOS and Epichlorohydrin were purchased from Fluka (Switzerland, Germany and Israel, respectively). Glutaraldehyde (25%) was from J.T. Baker (Phillipsburg, NJ, USA). Remazol Black B (RB, Reactive black 5) and chitosan (calculated degree of acetylation, DA: 41%) were purchased from Sigma (St. Louis, MO, USA and Japan, respectively). Cd(NO₃)₂ was acquired from Merck (Darmstadt, Germany). All metal working solutions were made by dilution of the stock solution. Cadmium concentration was verified against the appropriate dilution of Titrisol Cadmium Standards 1000 mg/L (Merck). All other reagents were of analytical grade.

Preparation of Chitosan Beads

The solution of chitosan was prepared by dissolution of 2 g of chitosan in 100 mL of acetic acid aqueous solution (2% v/v). The solution was added drop-wise to the gelling medium (2 mol/L NaOH) with constant stirring. The chitosan hydrogel beads were incubated in the gelling medium during 24 h at room temperature. Then the beads were washed with distilled water until solution reached pH 7.

Beads Cross-Linking

Three types of beads were obtained taking into account the cross-linker used: (1) Chitosan-Epichlorohydrin (named Chi-Epi), (2) Chitosan-Glutaraldehyde (Chi-Glu), and (3) Chitosan-TEOS (Chi-TEOS). The cross-linked beads were prepared using a cross-linker : NH₂ molar ratio of 1 : 2. The cross-linker:NH₂ molar ratio was calculated considering the molarity of cross-linker to be used and the calculated molar amount of nitrogen per gram of chitosan.

Epichlorohydrin Cross-Linking

Chitosan beads (10 g) were immersed in 100 mL of distilled water. The solution was adjusted to pH 10 using 0.1 mol/L NaOH and then 0.078 mL of Epichlorohydrin was added. The mixture was incubated over night at 60°C with constant stirring. Then the beads were thoroughly washed with distilled water in order to eliminate residual reagents and by-products.

Glutaraldehyde Cross-Linking

Chitosan beads (10 g) were immersed in 100 mL of 0.2 mol/L phosphate buffer (pH 7.5). Then 0.4 mL of 25 % glutaraldehyde was added. The mixture was incubated over night in a caramel color flask with constant stirring. Then the beads were thoroughly washed with distilled water in order to eliminate residual reagents and by-products.

TEOS Cross-Linking

A TEOS sol was prepared by sonicating (35 kHz, Transsonic TI-H-5, Elma, Germany) a mixture of 1 mL TEOS, 0.06 mL of 0.05 mol/L HCl and 0.2 mL of water for 30 min at 25°C. Chitosan beads (10 g) were immersed in 100 mL of 0.02M phosphate buffer (pH 6). Then 0.28 mL of the TEOS sol was added. The mixture was gently stirred for 10 min at room temperature and filtered. After that the beads were immersed in 100 mL of 0.2 mol/L phosphate buffer (pH 7). The mixture was incubated over night with constant stirring. Then the beads were thoroughly washed with distilled water in order to eliminate residual reagents.

Characterization

Matrices water content was determined with a moisture analyzer at constant temperature (80°C) (MX-50, A&D Company, Tokyo, Japan). FTIR transmission spectra were acquired in the range of 4000–450 cm⁻¹ using a Fourier Transform Infrared Spectrometer (FTIR) (Nicolet 360). All samples were previously dried for 24 h at 60°C to avoid water related bands interference. The degree of acetylation (DA) was determined by the method proposed by Brugnerotto et al., which is based on the relationship between a reference band at 1420 cm⁻¹ and the amide III band at 1320 cm⁻¹ by applying the following equation: $A_{1320}/A_{1420} = 0.3822 + 0.03133DA$.²³ Scanning Electron Microscopy (SEM) images of freeze-dried and gold-coated samples were taken using a FEI Quanta 200 microscope. Nitrogen content determination was performed using the micro-Kjeldahl method. The point of zero charge (pH_{pzc}) of the cross-linked beads was determined by the drift method.²⁴ Briefly, a solution of 0.01 mol/L NaCl, was boiled to remove dissolved carbon dioxide and used to prepare several solutions with an initial pH ranging from 4 to 9. Then, 0.05 g of beads were added to 10 mL of each solution and incubated at room temperature for

Table I. Water Content, Nitrogen Content and Point of Zero Charge of the Chitosan and Cross-Linked Beads

Matrix	Water content (%)	Nitrogen content (%)	pH _{pzc}
Chitosan	96.59 ± 0.09 ^a	8.3 ± 0.3	N.T. ^b
Chi-Epi	96.65 ± 0.08	6.3 ± 0.3	6.75
Chi-Glu	95.32 ± 0.09	4.1 ± 0.2	6.6
Chi-TEOS	93.7 ± 0.7	5.7 ± 0.2	5.75

^a Mean ± Std deviation.^b Not Tested.

48 h. The final pH was measured and plotted against the initial pH. The pH point at which the curve of the final pH crosses the pH_{initial} = pH_{final} line is the pH_{pzc}.

Adsorption Experiments

Adsorption experiments were carried out by a batch method at room temperature (25°C) with constant stirring (120 rpm). A weighted mass of cross-linked beads (0.05 g) was added to an aqueous solution (5 mL) of RB or Cd(II), ranging from 0.1 to 20 mmol/L or 1 to 200 μmol/L respectively. The effect of the media pH, interaction times and adsorption isotherms were determined by sorbate decay in the solution supernatant. RB determinations were carried out at the characteristic absorption peak (595 nm) using an UV-Vis Spectrophotometer (Cecil CE 3021, Cambridge, England). Cadmium determinations were done with a Buck Scientific VGP 210 Atomic Absorption Spectrophotometer (E. Norwalk, CT, USA) by the electrothermal atomization method using pyrolytic graphite tubes. Potassium phosphate (10 mmol/L, pH 7) was used as matrix modifier.

All adsorption assays were carried out in plastic vessels. Blank experiments were conducted in order to verify the absence of sorbate precipitation and/or adsorption to the walls of the vessels. All experiments and their corresponding measurements were conducted in triplicate under identical conditions and statistically analyzed by one-way ANOVA and by Tukey Multiple comparison post test if ANOVA $P < 0.05$. R language and environment was used for statistical computing and graphics.²⁵

RESULTS AND DISCUSSION

Beads Characterization

Homogeneous beads were obtained by all the cross-linking treatments. These beads were insoluble even at pH 4, condition that solubilizes the non-cross-linked chitosan beads. Supporting Information 1 shows SEM images of chitosan beads and the cross-linked beads. As can be seen, the topography of the cross-linked is not only different among treatments but also different to the non-cross-linked beads. These images show that every cross-linking treatment results in a modification of the primary chitosan bead structure. This is also evidenced in the water content, nitrogen content and pH_{pzc} of the cross-linked beads (Table I). Although, the water content of the Chi-Glu and Chi-Epi beads is similar to the chitosan beads, Chi-TEOS beads showed lower water contents. This was evidenced as a slight reduction of the beads size (as can be seen in SEM images at

Supporting Information 2). This reduction could be expected. Proximal Si-OH groups in a silicon oxide network tend to dehydrate, forming new Si-O-Si bondings during the syneresis process, which implies the contraction of the network.²⁶ The pH_{pzc} of Chi-Glu and Chi-Epi beads was found to be slightly higher than that of chitosan (6.3–6.6).²⁷ On the other hand, Chi-TEOS beads showed a pH_{pzc} one pH unit lower than the other two cross-linking treatments. This was also expected because of the own pH_{pzc} of the silicon oxide structure, which is around pH 2.5 for most of the SiO₂ materials.²⁶ Thus, the overall pH_{pzc} of the Chi-TEOS beads would be the result of a contribution of the pH_{pzc} of chitosan and the SiO₂ network.

The beads were also analyzed by means of the nitrogen content. The cross-linker : NH₂ molar ratio for all treatments was fixed at 1 : 2. Hence, it was expected that the lower nitrogen content, by addition of the cross-linker mass, would be in the beads treated with the highest molecular weight cross-linkers, in this case TEOS and epichlorohydrin. Nevertheless, the lowest nitrogen content was found for the Chi-Glu beads which implies a higher efficiency of cross-linking, probably because of the selectivity of glutaraldehyde carbonyl groups towards chitosan amino groups.

The IR spectra of the beads in the range of 2000–400 cm⁻¹ and in the range of 4000–400 cm⁻¹ are shown in Figure 1 and Supporting Information 3, respectively. In all the spectra the bands corresponding to the chitosan structure could be observed with no additional bands corresponding to the cross-linking agents. The latter absence is probably in relation with the amount of cross-linking agent used, which is near 1 mmol per gram of chitosan. In all spectra it can be observed the typical chitosan bands at 1557 cm⁻¹ (amide II, N-H bending), 1418 cm⁻¹ (CH₂ bending), 1383 cm⁻¹ (CH bending), 1319 cm⁻¹ (amide III and CH₂ wagging) and the polysaccharide related bands at 1155 cm⁻¹ (symmetric bridge oxygen stretching), 1068 and

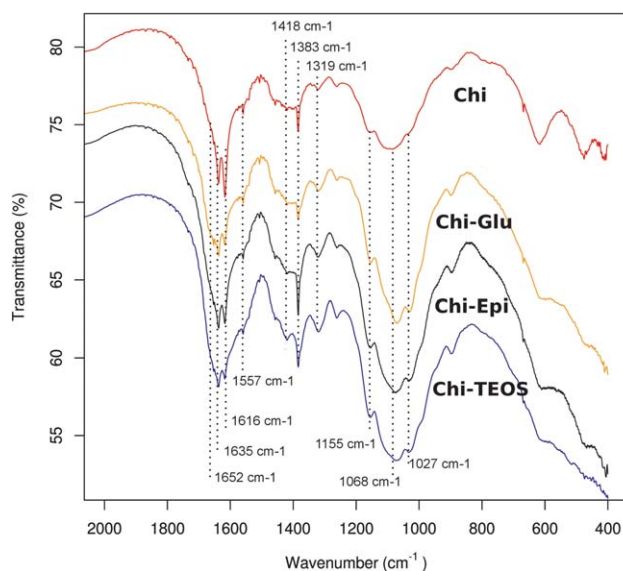


Figure 1. FTIR spectra of the chitosan beads and the cross-linked chitosan beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

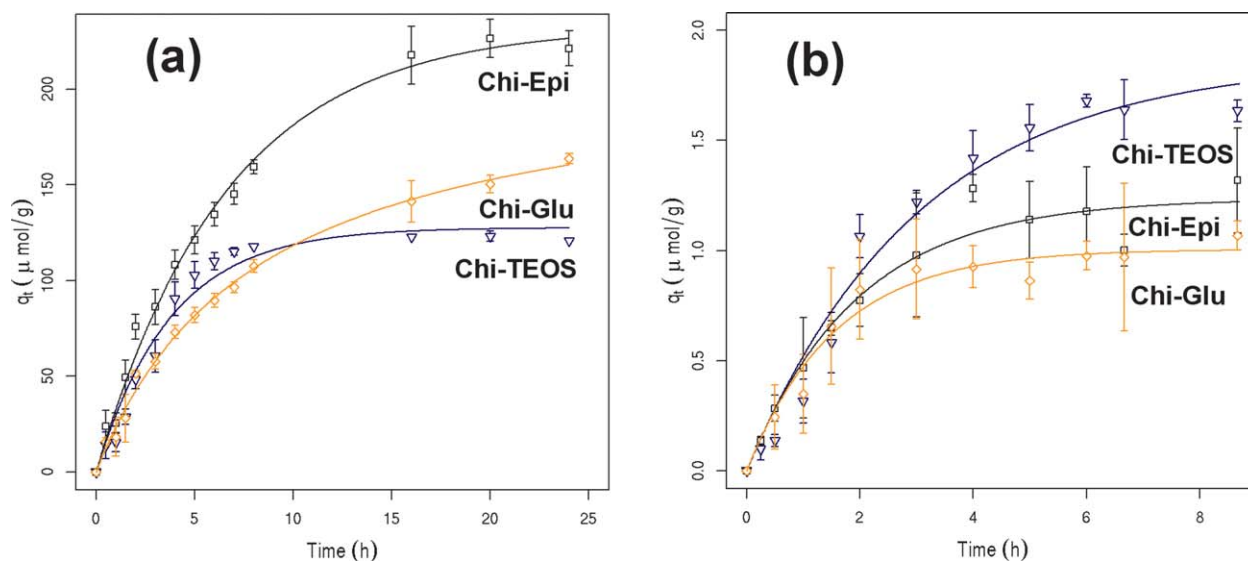


Figure 2. Pollutants adsorption over time at (a) pH 4 for RB and (b) pH 7 for Cd(II). For RB adsorption on Chi-Glu beads pseudo-second-order plot is presented, for all other cases pseudo-first-order plot is presented. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1027 cm^{-1} (both from C-O stretching).^{23,28} The main differences between the spectra of chitosan and the cross-linked beads could be seen respecting the amide I band, where there is an inversion of the relative intensities of the doublet observed at 1635 and 1616 cm^{-1} (C=O and C-N stretching, respectively). In addition, in all spectra of cross-linked beads, it could be observed the widening of this doublet together with the insinuation of an additional band at 1652 cm^{-1} . Other researchers have assigned the latter band to the formation of an imine bond (C=N) when chitosan is cross-linked with glutaraldehyde and the formation of a Schiff base occurs.¹⁵ Thus, the 1652 cm^{-1} band in the Chi-Glu spectrum could be explained by the presence of the imine bond. On the other hand, this bond could not be expected for the other two treatments. We propose that the widening and the inversion of the amide I doublet could probably be related to intramolecular rearrangements in the chitosan chains. Therefore, its vibration behavior would be altered specially in the acetoamide groups of the acetylated moiety of chitosan. These groups are more likely to suffer conformational changes than the glucopyranose rest because of their spacial mobility.²⁹

As TEOS polymerization was carried at room temperature probably there is no covalent bonding between the SiO_2 network and polysaccharides. The stabilization of the chitosan beads by TEOS would involve the formation of an interpenetrated network with the polysaccharide, as has been previously reported.^{20,22} As has been pointed out by other researchers working on chitosan and chitin- SiO_2 based materials, the lack of any visible changes in the measured spectra indicates that there are no strong interactions among the components but weak interactions, such as hydrogen bonds, could be expected.^{30,31}

Effect of pH on Adsorption Behavior

The effect of media pH on the adsorption behavior was analyzed in the pH range 4–8 (Supporting Information 4). None of

the cross-linking treatments affected the expected adsorption behavior. For all the cases, the adsorption of RB was higher at low pHs where the dye is negatively charged and the chitosan amino groups are positively charged. For the case of the Cd(II) the higher adsorption for all beads were at pH 7 where the amino groups are deprotonated and can interact with the cation Cd^{2+} . On the other hand, it was observed for Chi-TEOS beads that as media pH shifts from the optimum condition the decrease in adsorption is more abrupt than for the Chi-Epi and Chi-Glu beads. Moreover, only for Chi-TEOS beads, RB and Cd(II) adsorptions at the optimum pH were significantly different ($P < 0.05$, Tukey post-test) from the nearest pH value. Kinetic and equilibrium assays were carried out at the optimum adsorption pH (pH 4 for RB and pH 7 for Cd(II)).

Adsorption Kinetics

Adsorption kinetic experimental results are shown in Figure 2. These plots show adsorption over time at pH 4 for RB and pH 7 for Cd(II). In order to characterize the differences among the adsorption behaviors of the beads, an extensive kinetic modeling analysis was performed using the pseudo-first-order, pseudo-second-order, Elovich and the modified Freundlich equations in their nonlinear forms.^{27,32,33} Table II summarizes the kinetic parameters for the models that fitted best the RB and Cd(II) adsorption. Supporting Information summarizes in Tables SM 5 and SM 6 the kinetic parameters for all the evaluated models. The mathematical models are also presented in Supporting Information.

The adequacy of the nonlinear models adjustment was compared by two selection criteria, the Root-mean-square-errors (RMSE) and the Akaike's information criteria (AIC).³⁴ Smaller RMSE and AICc values represent better curve fittings.³⁴

Aside from RB adsorption uptake rate onto Chi-Glu beads, AICc and RMSE values indicate that all treatments showed a better adjustment to the pseudo-first order model followed by

Table II. Kinetic Parameters for RB Adsorption

Sorbate	Bead type	Pseudo 1st order			Pseudo 2nd order		
		q_e ($\mu\text{mol/g}$)	k_1 (h^{-1})	AICc	q_e ($\mu\text{mol/g}$)	k_2 ($\text{g}/\mu\text{mol h}$)	AICc
RB	Chi-Epi	232 ± 4	0.151 ± 0.006	296.7	302 ± 8	$(4.5 \pm 0.4) \times 10^{-4}$	297
	Chi-Glu	163 ± 4	0.139 ± 0.007	273	215 ± 7	$(5.7 \pm 0.5) \times 10^{-4}$	265
	Chi-TEOS	128 ± 3	0.27 ± 0.02	296	154 ± 7	$(1.8 \pm 0.3) \times 10^{-3}$	320
Cd(II)	Chi-Epi	1.23 ± 0.06	0.51 ± 0.08	-25	1.6 ± 0.1	0.31 ± 0.09	-23
	Chi-Glu	1.00 ± 0.06	0.6 ± 0.1	-16	1.2 ± 0.1	0.5 ± 0.2	-14
	Chi-TEOS	1.86 ± 0.09	0.33 ± 0.04	-31	2.6 ± 0.2	0.10 ± 0.03	-24

the pseudo-second order, Elovich and Modified Freundlich model, in that order. This could imply that the chitosan kinetic adsorption behavior is not influenced by the cross-linking treatments, at least at the amount used for these assays. Also, when the pseudo-first order and pseudo-second order models are compared for the same sorbate/sorbent system, the closeness of the goodness-of-fit values would indicate that the latter model is also appropriate for the description of these system kinetics. Several reports demonstrated that biosorption is better described by the pseudo-second order model.³⁵ This was attributed to the poor adjustment of the pseudo-first order model to sorption processes which suffer from a time lag. This can be caused by the presence of a boundary layer or an external resistance controlling the beginning of the sorption process.³⁶ It is possible that these factors are negligible in these systems because of the high hydration and porosity of the chitosan beads. Also, the pseudo-1st order model has been used before in the adjustment of reversible reactions with an equilibrium being established between liquid and solid phases.¹⁷ When the adjustment to Modified Freundlich model is analyzed, it can be seen that the m parameter is close to a value of 2 in almost all the cases. As this model can describe kinetics controlled by intra-particle diffusion when m approaches a value of 2, the obtained values

would indicate that the intra-particle diffusion process plays an important role in the adsorption kinetics of the treated beads.³⁷

Adsorption Isotherms

Adsorption equilibrium data were obtained after equilibrium time was achieved, at pH 4 and 7 for RB and Cd(II), respectively (Figure 3). Adsorption capacities (q_{eq}) are expressed as the moles of sorbate per mass unit of sorbent (mmol/g) and determined as follows: $q_{eq} = (C_0 - C_{eq})V/m$

where C_0 and C_{eq} are the initial and the equilibrium sorbate concentrations of the incubation solution respectively (mmol/L), V is volume of solution (L), and m is the sorbate mass (g). In order to thoroughly assess the adsorption process, two and three parameters isotherm models were analyzed. The two parameter models analyzed were Langmuir, Freundlich, and Dubinin-Radushkevich models and the three parameter models were Redlich-Peterson, Toth and Sips models.^{32,38-41} Tables III and IV summarize the equilibrium parameters for the models that better fitted RB and Cd(II) adsorption. Supporting Information summarizes in Tables SM 7 and SM 8 the equilibrium parameters for all the evaluated models. The mathematical models are also presented in Supporting Information.

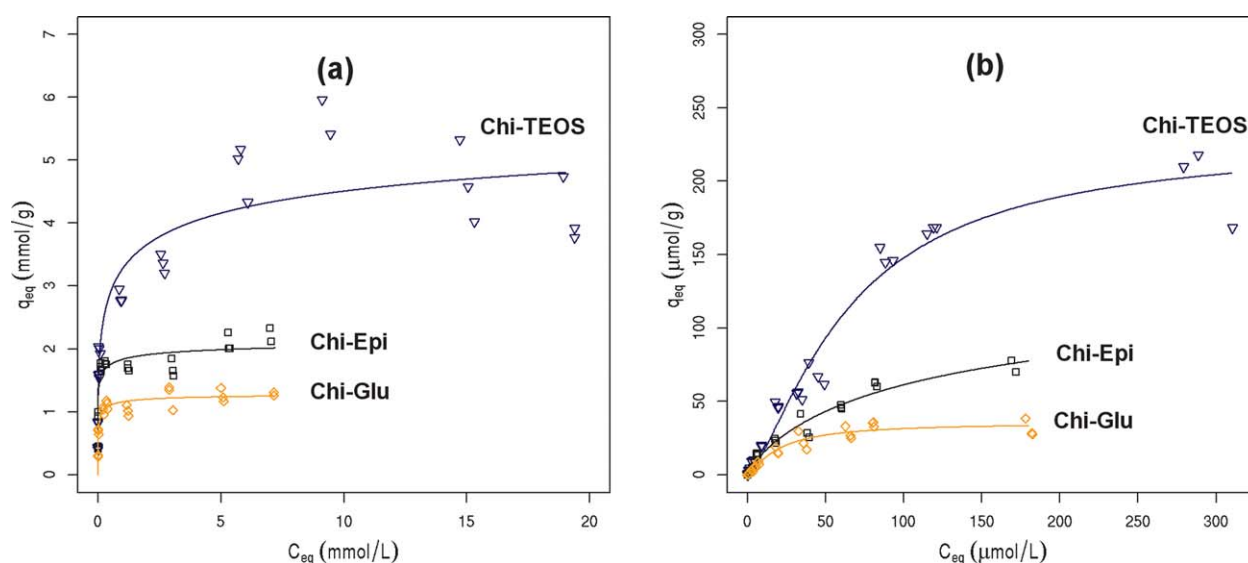


Figure 3. Adsorption isotherms at (a) pH 4 for RB and (b) pH 7 for Cd(II). Sips plot is presented for all the cases. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Isotherm Model Parameters for RB Adsorption

	Best model			AICc	Sips			
	Model	Parameters			q_{mS} (mmol/g)	K_S (L/mmol)	n_S	AICc
Chi-Epi	D-R	q_{DR} (mmol/g) 2.4 ± 0.1	K_{DR} (mol ² /kJ ²) $(9 \pm 1) \times 10^{-4}$	-3.3	2.3 ± 0.3	87 ± 83	0.33 ± 0.09	-2.1
Chi-Glu	R-P	K_{RP} (L/mmol) 117 ± 40	α_{RP} ((L/mmol) ^{n_{RP}}) 102 ± 36	-25.8	1.3 ± 0.08	41 ± 16	0.7 ± 0.1	-24.5
Chi-TEOS	D-R	q_{DR} (mmol/g) 5.9 ± 0.3	K_{DR} (mol ² /kJ ²) $(2.0 \pm 0.2) \times 10^{-3}$	56.5	6 ± 2	1 ± 2	0.34 ± 0.09	58.5

The adjustments to the models do not show a distinctive behavior in terms of homogeneity–heterogeneity of the adsorption process. In fact, the classical models that better describe these behaviors, Langmuir and Freundlich, in none of the cases showed the best fitting. Moreover, if the heterogeneity parameters of the R-P, Sips and Toth models show a trend, it would be indicative of a homogeneous ($n \approx 1$) or a heterogeneous adsorption process ($n \neq 1$).^{41,42} In these systems, when the heterogeneity parameter of these models are compared, there was not a strong tendency towards a particular value. Remarkably, in all the cases the second best fitting was obtained using the Sips model, which combines Langmuir and Freundlich models. D-R showed to be the better model for describing RB and Cd(II) adsorption on Chi-Epi beads as well as for RB adsorption on Chi-TEOS beads. Toth model was the better fitting model for Cd(II) adsorption on Chi-Glu and Chi-TEOS beads. R-P showed the best agreement for the RB adsorption on Chi-Glu beads.

For the case of both sorbents, the maximum adsorption capacity of the Langmuir, D-R, Sips, and Toth models showed higher values for the Chi-TEOS beads followed by the Chi-Epi and the Chi-Glu beads in that order. A higher q_m for the use of epichlorohydrin compared with glutaraldehyde was also reported by other researchers.^{16,17} The nitrogen content of the Chi-Glu beads was observed to be the lowest among the treatments. Thus, considering amine groups as the main adsorption sites, glutaraldehyde cross-linking not only decreased the amount of adsorption sites in terms of capacity but also in terms of sites per mass of sorbent, which agrees with previous reports.¹⁵ This was not the case of Chi-TEOS and Chi-Epi which showed a similar amount of nitrogen per mass of bead. The differences in their q_m are probably because of a lesser drop

in active activation sites when the chitosan beads are cross-linked with TEOS. This reinforces the theory of the formation of interpenetrated networks between the silicon oxide and chitosan that stabilizes the biopolymer with a minimum interaction with its amine groups. In fact, if during the bead cross-linking Si-OH groups interact with chitosan amine groups by hydrogen bonding, this interaction could be displaced when it is exposed to high amounts of sorbate. Therefore, it is proposed that the interaction between Chi-TEOS beads and the adsorbates would mainly be the same as in pristine chitosan. This would imply an electrostatic interaction between: (1) one or more amine groups for cationic sorbates and (2) one or more protonated amine groups for anionic sorbates.

Evaluation of Adsorption Energy and Standard Free Energy

If the adsorbent surface is heterogeneous and homogeneous subregions are considered, an average free energy value could be calculated using D-R equation:⁴³ $E_{DR} = (2K_{DR})^{-1/2}$, where E_{DR} is the mean free energy of adsorption (kJ/mol). The standard free energy (ΔG^0) of the process is related to the adsorption equilibrium constant (K_a), from Langmuir equation, by the following equation:⁴⁴ $\Delta G^0 = -RT \ln K_a$

E_{DR} and ΔG^0 values are summarized in Tables SM 7 and SM 8. The mean free energy of adsorption can be indicative of the type of adsorption interaction. In an adsorption process where chemisorption prevails, the magnitude of E_{DR} is in the range of 8–16 kJ/mol.⁴³ Lower values are related to physisorption processes and larger values have been reported for coordination or chemical reactions.⁴³ For the three treatments the E_{DR} values for Cd(II) adsorption are between 7 and 9 kJ/mol, which makes it difficult to determine if the adsorption of a Cd²⁺ ion onto a deprotonated amine group of chitosan proceeds strictly by a

Table IV. Isotherm Model Parameters for Cd(II) Adsorption

	Best model			AICc	Sips				
	Model	Parameters			q_{mS} (μ mol/g)	K_S (L/ μ mol)	n_S	AICc	
Chi-Epi	D-R	q_{DR} (μ mol/g) 177 ± 13	K_{DR} (mol ² /kJ ²) $(8.6 \pm 0.5) \times 10^{-3}$	177.7	133 ± 32	$(8 \pm 5) \times 10^{-3}$	0.8 ± 0.1	179.5	
Chi-Glu	Toth	q_{mT} (μ mol/g) 34 ± 3	b_T (L/ μ mol) $(31 \pm 5) \times 10^{-3}$	n_T 1.8 ± 0.7	169.4	35 ± 3	$(50 \pm 10) \times 10^{-3}$	1.3 ± 0.2	170.1
Chi-TEOS	Toth	q_{mT} (μ mol/g) 199 ± 6	b_T (L/ μ mol) 8.8 ± 0.5	n_T 4 ± 1	280	228 ± 15	$(15 \pm 2) \times 10^{-3}$	1.4 ± 0.1	293

chemisorption process. Chi-Glu and Chi-Epi E_{DR} values for RB adsorption were 19 and 23 kJ/mol, respectively. This would indicate that after the adsorption of one of the four $-SO_3^-$ groups in RB onto a $-NH_3^+$ in chitosan, the repositioning of the dye could facilitate the generation of at least one additional interaction. On the other hand, the rigid inorganic structure of the silicon oxide network of Chi-TEOS beads (E_{DR} slightly below 16 kJ/mol) would impede the reorganization of chitosan chains hindering the multi-interaction between one RB molecule and several $-NH_3^+$. This scenario would also help to understand the higher adsorption capacity of Chi-TEOS beads for RB. In this sense, one RB molecule would consume only one adsorption site from the Chi-TEOS beads. On the other hand, in the other type of beads more than one site would be consumed per one molecule of dye. The negative values obtained for the standard free energy shows the spontaneity of the process at these conditions.

CONCLUSIONS

In this work chitosan hydrogel beads modified by three different cross-linking treatments were studied in terms of their physico-chemical properties and pollutants adsorption behavior. Glutaraldehyde and epichlorohydrin were compared to TEOS, whose use has only been previously described in literature as the main component of chitosan hybrids. The TEOS cross-linking lead to a safer and environmentally friendly chitosan hydrogel bead stable in acidic media and with desirable adsorption characteristics.

It was demonstrated that none of the treatments affected the expected adsorption tendency in regard of media pH. Also, the uptake rate of RB and Cd(II) showed that the three type of beads followed a similar kinetic behavior. The pseudo-first-order model fitted the best for almost all cases, followed by pseudo-second-order model. The equilibrium assays showed dissimilar isotherm model adjustments for each sorbate-sorbent system. The model which showed to have a good fitting for all systems was the Sips model. For RB and Cd(II) adsorption, Chi-TEOS beads showed the higher maximum adsorption capacity, followed by Chi-Epi and Chi-Glu beads.

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