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Hexavalent chromium removal in contaminated water using reticulated chitosan micro/nanoparticles from seafood processing wastes

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HIGHLIGHTS

- Chitosan obtained from Argentinian Patagonia shrimp shell wastes was characterized.
- Chitosan micro/nanoparticles (MCH) were obtained by ionotropic gelation with tripolyphosphate.
- Chitosan cross-linking with tripolyphosphate improved Cr(VI) adsorption at pH < 2.5.
- Cr(VI) adsorbed by MCH was reduced to Cr(III) showing a detoxification effect.
- Langmuir isotherm and second order kinetics best fitted experimental data.

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ABSTRACT

Chitosan particles (CH) were obtained from seafood processing wastes (shrimp shells) and physicochemically characterized; deacetylation degree of CH was measured by Infrared Spectroscopy (FTIR) and potentiometric titration; polymer molecular weight was determined by intrinsic viscosity measurements. Reticulated micro/nanoparticles of chitosan (MCH) with an average diameter close to 100 nm were synthesized by ionic gelation of chitosan using tripolyphosphate (TPP), and characterized by SEM, size distribution and Zeta-potential. Detoxification capacities of CH and MCH were tested analyzing the removal of hexavalent chromium Cr(VI) from contaminated water, at different initial chromium concentrations. The effect of pH on adsorption capacity of CH and MCH was experimentally determined and analyzed considering the Cr(VI) stable complexes (anions) formed, the presence of protonated groups in chitosan particles and the addition of the reticulating agent (TPP). Chitosan crosslinking was necessary to adsorb Cr(VI) at pH < 2 due to the instability of CH particles in acid media. Langmuir isotherm described better than Freundlich and Temkin equations the equilibrium adsorption data. Pseudo-second order rate provided the best fitting to the kinetic data in comparison to pseudo-first order and Elovich equations. Chemical analysis to determine the oxidation state of the adsorbed Cr, showed that Cr(VI) was adsorbed on CH particles without further reduction; in contrast Cr(VI) removed from the solution was reduced and bound to the MCH as Cr(III). The reduction of toxic Cr(VI) to the less or nontoxic Cr(III) by the reticulated chitosan micro/nanoparticles can be considered a very efficient detoxification technique for the treatment of Cr(VI) contaminated water.

1. Introduction

In the coastline of Patagonia-Argentina (42–43°S, 64–65°W), seafood processing industry discards large amounts of crustaceans shellfish wastes; exoskeletons are converted in a solid residue, which accumulate in landfills becoming an environmental pollutant. The exoskeleton of the crustaceans represents approximately 50–60% of the total weight in crabs and more than 35% in shrimps. However these residues contain chitin, which is a natural, abundant and non-toxic material. Chitosan is obtained cost-effectively by the derivation of chitin (2-acetamido-2-deoxy-β-D-glucose through β(1–4) linkage) and represents an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity, and excellent chelation behavior (Laus et al., 2010; Wu et al.,

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2010). Chitosan has three types of reactive functional groups, an amino group as well as both primary and secondary hydroxyl groups at the C-2, C-3 and C-6 positions, respectively (Schmuhl et al., 2001; Qi and Xu, 2004). Deacetylation degree and molecular weight are important properties to characterize this biopolymer when it is obtained from natural sources. Chitosan is a well known cationic, biocompatible, biodegradable, non-toxic biopolymer which makes it attractive for numerous applications including waste water treatments.

Water contamination with heavy metals is a critical problem because metals tend to persist and accumulate in the environment. Industrial and mining wastewaters are important sources of pollution of heavy metals. One of the heavy metals that have been a major focus in wastewater treatment is hexavalent chromium (Aydın and Aksoy, 2009; Hena, 2010). The use of chromate and dichromate has many industrial applications such as in textile, electroplating, leather tanning, cement preservations, paints, pigments and metallurgy industries (Aydın and Aksoy, 2009; Bhatnagar and Sillanpää, 2009). Cr(VI) is a toxic metal and must be removed from wastewater before it can be discharged (Hena, 2010). Cr(II), Cr(III) and Cr(VI) are the three oxidation states for chromium in nature, but only the last two are stable (Aydın and Aksoy, 2009). Cr(III) is stable and less toxic or nontoxic, and is considered an essential element for the good health and nutrition of many organisms.

Cr(VI) is 500 times more toxic, mutagenic and carcinogenic than Cr(III) (Dubey and Gopal, 2007). The United States Environmental Protection Agency has laid down the maximum contaminant level for Cr(VI) into inland surface waters as 0.1 mg/L and in domestic water supplies to be 0.05 mg/L (Sivakami et al., 2013).

Different techniques have been used to remove Cr(VI) from the industrial wastewater, such as chemical precipitation, ion exchange, reduction, electrochemical precipitation, solvent extraction, membrane separation, cementation, electrodialysis and adsorption (Sivakami et al., 2013). In the last years very interesting works have been published concerning the removal of hexavalent chromium using adsorbent materials that can reduce Cr(VI) to the less or nontoxic Cr(III) and simultaneously adsorb the reduced Cr(III) (Bellú et al., 2010; Gu et al., 2012; Huang et al., 2013; Park et al., 2008; Qiu et al., 2014a,b,c,d, 2015; Sankararamakrishnan et al., 2006; Sivakami et al., 2013; Xu et al., 2014; Zhang et al., 2010, 2013; Zhu et al., 2012, 2014). These adsorbents not only act as electron donors for the Cr(VI) reduction, but also have active sites for Cr(III) adsorption. Different materials were analyzed and techniques such as X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) were applied to determine the oxidation state of the adsorbed chromium species (Bellú et al., 2010; Park et al., 2008; Qiu et al., 2014a,b, 2015; Xu et al., 2014).

Adsorption using biopolymers, is one of the most recommended processes, due to economical and technical advantages (Bhatnagar and Sillanpää, 2009). The major advantages of biosorption over conventional treatment methods include: low price, high effectiveness, minimization of chemical and/or biological mud, restoration of biosorbent and possibility of metal recovery.

Chitosan, is a natural cationic polyelectrolyte that has been used for remove cationic and anionic metals such as copper (Laus et al., 2010; Yu et al., 2013), mercury and lead (Ng et al., 2003; Qi and Xu, 2004), from aqueous solutions: it combines with metal ions by three forms: ion exchange, adsorption and chelation (Qi and Xu, 2004). The adsorption of a metal ion on chitosan depends strongly on the pH of the solution (Schmuhl et al., 2001). Several authors analyzed the adsorption of Cr(VI) onto chitosan and modified chitosan particles (Hena, 2010; Huang et al., 2013; Sankararamakrishnan et al., 2006; Sivakami et al., 2013; Zhang et al., 2013).

Chitosan is soluble in most dilute mineral acids, (except in sulfuric acid solutions) and in dilute organic acids, such as acetic, propionic, formic and lactic acids (Laus et al., 2010), consequently, its chemical stability needs to be reinforced through treatments using crosslinking agents for its application in acidic media. Chemical and physical cross-linking techniques are usually employed to modify chitosan; crosslinking may be performed by reaction of CH with different agents such as glutaraldehyde, ethylene glycol diglycidyl ether and epichlorohydrin. Tripolyphosphate (TPP) has also been proposed as a possible crosslinking agent (Laus et al., 2010). CH can be chemically cross-linked with glutaraldehyde leading to quite stable matrixes, with strength covalent bonds, however glutaraldehyde is toxic and a strong irritant (López-León et al., 2005; Sano et al., 2005). Chitosan hydrogels can be obtained by ionic gelation, where micro or nanoparticles are formed by means of electrostatic interactions between the positively charged chitosan chains and polyanions employed as physical cross-linkers. Tripolyphosphate can be used as the polyanion for the cross-linking process; it is a condensed non-toxic phosphate suitable for water purification and also used as food additive (Calvo et al., 1997; Laus et al., 2010). The protonated amine groups in chitosan interact with the negatively charged counterions, through an electrostatic interaction creating ionic cross-linked networks. It is important to remark the need to use non-toxic reagents such as TPP for water treatments. The correct interaction between chitosan and TPP leads to the formation of micro and nanoparticles (Calvo et al., 1997); therefore defined proportions of both components must be establish in order to get adequate particle properties related to size distribution and *Z* potential.

The analysis of the pH effect on the performance of CH and MCH particles to remove Cr(VI) from contaminated water is complex because different factors, such as the proportion of Cr(VI) stable complexes (anions) formed, the presence of protonated groups in chitosan particles and the addition of TPP as reticulating agent are interacting; available information on this subject is scarce in literature.

The general objective of the present work was to analyze the use of contaminating crustacean shellfish wastes for water purification, determining the simultaneous effects of pH and ionic crosslinking of chitosan particles on the removal of hexavalent chromium.

The specific objectives are: (a) to obtain chitosan particles (CH) from seafood processing wastes (shrimp shells), determining the de-acetylation degree and the average molecular weight; (b) to synthesize reticulated chitosan micro and nanoparticles (MCH) by ionic cross-linking of non modified chitosan with a non-toxic reagent (TPP, tripolyphosphate) establishing the adequate proportion of both components; (c) to characterize MCH particles by Scanning Electron Microscopy (SEM,) size distribution, Zeta-potential; (d) to analyze the performance of MCH and CH particles, in the adsorption process of hexavalent chromium anions in aqueous solutions at different pH values, initial chromium concentrations and contact times; (e) to determine the oxidation state of the adsorbed chromium on CH and MCH; (f) to model mathematically the equilibrium isotherms and adsorption kinetics in the analyzed systems.

2. Materials and methods

2.1. Chitin and chitosan production

Shrimps shells (*Pleoticus muelleri*) were used for the extraction of chitin and chitosan. The shells were provided by the industry "Madryn Seafood" SRL from Puerto Madryn, Patagonia-Argentina.

2.1.1. Chitin extraction

Shrimp shells were ground using a mill (Moulinex) to obtain a coarse powder (between 0.5 and 1 mm mesh). The powder was treated with 1.5 N HCl solutions 1:10 (w/v) at room temperature for 3 h to remove minerals, then treated with aqueous sodium hydroxide solution (4.5%) at a ratio of 1:15 (w/v) at 80 °C for 3 h to remove protein. The mixture was filtered and washed with deionized water to reach neutrality. The solid thus obtained was discolorated using a solution water/acetone (75/25) at room temperature. Following discoloration, the solid was washed with deionized water to reach neutral pH. Finally the wet mass was dried at 65 °C for 24 h; the product obtained was designated as chitin.

2.1.2. Chitosan production

1 g of chitin was treated with 30 mL of 50% NaOH solution at 120 °C for 120 min. After filtration, washing to neutral pH with deionized water and drying at 65 °C for 24 h, the product obtained was designated as chitosan particles (CH).

2.2. Measurement of the degree of N-deacetylation by potentiometric titration

The N-deacetylation degree (DD%) of shrimp chitosan samples was determined using the potentiometric technique proposed by Broussignac (1968). A sample of 0.5 g of chitosan was mixed with 20 mL of 0.3 M HCl. Potentiometric evaluation was carried out with a 0.1 M NaOH solution, using a Hanna Instrument pH-meter. The equipment was calibrated with buffer solutions at pH 4.0 and 7.0. The potentiometric curves were obtained by measuring the change in pH after each 2 mL addition of base solution; additions were made slowly with continuous stirring. The percentage of N-deacetylation was carried out according to the following expression:

$$\mathrm{DD}(\%) = \left(\frac{203 M_{\mathrm{eq}}}{1 + 42 M_{\mathrm{eq}}}\right) \tag{1}$$

where $M_{\mathrm{eq}} = \frac{N \Delta V}{w}$; ΔV is the volume difference between higher inflection point and lower inflection point, N is the normality of NaOH solution, w is the chitosan mass used; 203 is the molar mass of glucosamine and 42 is the molar mass of acetyl group.

2.3. Measurement of the degree of N-deacetylation by infrared spectroscopy

The degree of N-deacetylation (DD%) of shrimp chitosan, and chitosan microparticles was also determined using Fourier-transform infrared spectra (FTIR, Bruker IFS 66). Samples of 2 mg chitosan were mixed with 100 mg of potassium bromide, and compressed into pellets. The absorbances at 1320 cm^{-1} and 1420 cm^{-1} were used to calculate the DD% according to the following equation proposed by Brugnerotto et al. (2001):

$$\mathrm{DD}(\%) = 100 - \left[31.92 * \left(A_{(1320\mathrm{cm}^{-1})}/A_{(1420\mathrm{cm}^{-1})}\right) - 12.20\right] \tag{2}$$

2.4. Molecular weight

The molecular weight was determined by a viscometric method. The intrinsic viscosity $[\eta]$ of shrimp chitosan was measured by using an Ostwald capillary viscometer.

According to the results reported by Rinaudo (2006), chitosan sample was dissolved in 0.3 M acetic acid 0.2 M sodium acetate buffer, in order to avoid aggregation of molecules and the measurements were performed at 25 °C.

The viscosity average molecular weight of chitosan (Mv) was calculated by measuring the intrinsic viscosity $[\eta]$ according to Mark–Houwink–Kuhn–Sakurada (MHKS) equation:

$$[\eta] = k\,\mathrm{Mv}^{a} \tag{3}$$

Parameters k and a in Eq. (3) depend on the polymer, the solvent system (buffer) used and the temperature. Rinaudo (2006), worked with chitosan of different degrees of acetylation and in several solvents, and reported absolute molecular weight values using size exclusion chromatography with on-line viscometer and light scattering detectors to determine the Mark–Houwink parameters; also the relation between the molecular radius of gyration (Rg) and molecular weight was analyzed. Experimental values of k and a reported by Rinaudo (2006) for chitosan with comparable DD% and in the same solution, were used in the present work to obtain Mv.

2.5. Synthesis and characterization of chitosan reticulated micro/nanoparticles (MCH)

Chitosan reticulated micro/nanoparticles (MCH) were prepared by ionotropic gelation according to Calvo et al. (1997). MCH were obtained by inducing the gelation of a chitosan solution with TPP. CH was dissolved in acetic acid aqueous solutions at various concentrations: 0.5, 0.75, 1.25, 2.5 and 5 g/L. The concentration of acetic acid was in all cases 1.75 times higher than that of CH. TPP was dissolved in purified water at concentrations of 0.25, 0.5, 1.0, 1.5 and 2.5 g/L. Preliminary experiments were done in order to determine the adequate conditions for micro and nanoparticles formation, by combining different volumetric proportions of both solutions. In a first step, samples were visually analyzed and three different systems were identified: clear solution, opalescent suspension, and aggregates. The opalescent suspension corresponded to the presence of very small particles and was further investigated to obtain an adequate MCH size distribution. MCH were separated by centrifugation at 10,000g for 30 min; supernatants were discarded, and MCH were extensively rinsed with distilled water to remove any excess of TPP residues or CH. The MCH suspensions were centrifuged and the sediment (wet mass of nanoparticles) dried in vacuum at 55 °C for 24 h to obtain the dried mass of MCH production yield. Chitosan reticulated particles (MCH) were characterized by the measurement of the size distribution and Zeta potential as a function of the amount of TPP added to the dissolved CH and the pH of the system. A Delsa™Nano C Instrument (Beckman Coulter Delsa(TM) Nano Zeta Potential and Submicron Particle Size Analyzer) was used. The technique for size analysis is based on Photon correlation spectroscopy (PCS), which determines particle size by measuring the rate of fluctuations in laser light intensity scattered by particles as they diffuse through a fluid. In the case of zeta potential determination the technique is based on Electrophoretic light scattering (ELS), which determines electrophoretic movement of charged particles under an applied electric field from the Doppler shift of the scattered light. Scanning electronic microscopy (SEM) (JEOL JSM-6460 LV, USA) was used for visualization of the MCH.

2.6. Adsorption experiments

Adsorption experiments were performed using different conditions of Cr(VI) initial concentration, contact times, and pH values. Analytical grade reagent $K_2Cr_2O_7$, CH from shrimp shells and MCH obtained by the ionic gelation method were used for Cr(VI) adsorption experiments.

The pH of the solutions was maintained by micro-additions of HCl and NaOH. Adsorption experiments were carried out by using

80 mg of CH particles or 40 mg of MCH in 50 mL of Cr(VI) solutions of different initial concentrations ranging from 50 to 400 (mg/L). The selection of these adsorbent dosages was based on previous studies and on literature data (Schmuhl et al., 2001; Qi and Xu, 2004; Aydın and Aksoy, 2009). All the experiments to investigate the adsorption of Cr(VI) ions onto CH or on MCH were carried out in batch tests at 25 °C, under constant stirring (200 rpm). Final concentrations of Cr(VI) were determined by flame atomic absorption spectrometry (FAAS-Instrumental Lab IL457, Instrumental Laboratory Wilmington, MA). The equilibrium adsorption capacity of CH or MCH (Qe) is the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg/g) and was calculated as follows:

$$\mathrm{Qe} = \frac{(\mathrm{Ci} - \mathrm{Ceq})}{w} V \tag{4}$$

where Ci and Ceq are the metal concentrations (mg/L) in the solution initially (time zero) and after equilibrium respectively, V (L) is the volume of the solution and w is the mass (g) of adsorbent used. At each time the adsorption capacity Q (mg/g) was calculated as:

$$\mathrm{Q} = \frac{(\mathrm{Ci} - C)}{w} V \tag{5}$$

where C is the metal concentration in the solution after time t. The percentage of Cr(VI) removal was calculated according to:

$$(\%)\mathrm{Removal} = \left(\frac{\mathrm{Ci} - \mathrm{Ceq}}{\mathrm{Ci}}\right) \times 100 \tag{6}$$

Experiments were replicated twice, using triplicate samples at each tested condition and average values were reported.

The time required for the system to reach equilibrium conditions was established using CH or MCH in 50 mL of Cr(VI) solutions with an initial concentration of 100 mg/L, stirred for 3 h. After pre-established time periods (30 min, 1 h, 1.5 h, 2 h and 3 h), the stirring was halted and the supernatant was removed and diluted to an adequate volume. Concentration was monitored with respect to time for kinetic analysis.

In order to analyze the effect of pH, samples of CH or MCH were placed in a series of flasks containing 50 mL of Cr(VI) metal ion at an initial concentration of 200 mg/L. The solution was buffered within a pH range of 2–6. After 3 h, the sample was filtered from the solution, and quantified by FAAS.

Additional experiments were carried out using different initial concentrations of Cr(VI) ions in a range between 50 to 400 mg/L in contact with 80 mg of CH or 40 mg of MCH. At the end of each mixing period the liquid phase was separated from the solution by filtration and quantified by FAAS.

2.7. Desorption experiments to determine the oxidation state of the adsorbed chromium species

In order to determine the oxidation state of the chromium ions adsorbed onto CH and MCH, desorption experiments at ambient temperature for 2 h, using 0.1 M H_2SO_4 as the desorbent agent were carried out, according to Bhuvaneshwarl et al. (2012).

Cr(VI) concentration in the resulting chromium solution was determined by spectrophotometric analysis of the magenta chromagen which is formed by the reaction of Cr(VI) with 1.5-diphenylcarbazide (DPC) in strongly acidic solution (Clescerl et al., 1999). The colored complex was measured at 540 nm using a Hewlett–Packard HP 8452A Diode Array UV–VIS Spectrophotometer (CA, USA).

The Cr(III) concentration was calculated from the difference between the total Cr and Cr(VI) concentrations. To determine the total Cr concentration [Cr(III) + Cr(VI)], the desorption solution was first oxidized to Cr(VI) by ammonium persulfate $(NH_4)_2S_2O_8$, 98%, in an acidic condition at 100 °C, using $AgNO_3$ saturated solution as catalyst, prior to the 1.5-diphenylcarbazide reaction. The total chromium concentrations were also determined by Flame atomic absorption spectroscopy (FAAS-Instrumental Lab IL457, Instrumental Laboratory Wilmington, MA) to verify the results.

2.8. Equilibrium isotherms and kinetic analysis

Langmuir, Freundlich and Temkin isotherms (Aydın and Aksoy, 2009; Hena, 2010) were used for the mathematical description of the adsorption equilibrium of Cr(VI) ions on CH or MCH adsorbents. The operating parameters were: T = 25 °C, pH = 4, time = 3 h. The kinetic data were analyzed using the pseudo first order, pseudo second order kinetic models and Elovich equation (Sivaraj et al., 2001; Sağ and Aktay, 2002).

2.9. Statistical analysis

Standard deviations, linear and non linear regressions were conducted using the Statistica 8.0 (Statsoft software Inc.).

3. Results and discussion

3.1. Chitin extraction, chitosan production and deacetylation degree determination

Crude shrimp chitin was purified using acid and alkaline treatments. The yield of purified chitin was 24.8 ± 0.4%. This value was into the range reported by different authors (Abdou et al., 2008; Cocoletzi et al., 2009). After N-deacetylation, the yield of shrimp chitosan represented the 76.9 ± 1.1% of the initial crude chitin.

Titration curves were performed to determine the degree of N-deacetylation (DD%) of the obtained chitosan by the potentiometric technique (Fig. 1a); two inflection points were observed and the difference between these points corresponds to the amount of acid required to protonate the amino groups of chitosan (Fig. 1b). The N-deacetylation calculated according to Eq. (1) was 90.2%. Additionally, DD% of chitosan was also determined using Fourier-transform infrared spectra (FTIR).

Fig. 1c shows the spectrum of shrimp chitosan; different characteristic bands can be observed: at 3450 cm^{-1} (N—H and O—H stretching vibrations), 2918 and 2852 cm^{-1} (tension group C—H), 1721 cm^{-1} (C=O carbonyl group), 1618 cm^{-1} (Amine group), 1326 cm^{-1} (Amide III), 1382 cm^{-1} (—CH_3 symmetrical deformation mode (scissoring) in amide group. The bands assigned to the stretching vibrations of C—O—C linkages in the polysaccharide structure are observed at 1151 cm^{-1} (antisymmetric stretching of C—O—C bridge), 1098 cm^{-1} and 1021 cm^{-1} (skeletal stretching vibrations of C—O, characteristic peaks of polysaccharide structure in chitosan). Similar peaks were reported by Sivakami et al. (2013).

The low intensity observed in the band 1100–1000 cm^{-1} of Fig. 1c, could be attributed to the thermal treatment (120 °C) in a strong basic medium, that was applied to the chitin sample to obtain chitosan with a degree of deacetylation of 80%. The application of high temperatures to obtain chitosan can decrease the intensity of the FTIR spectrum corresponding to stretching vibration of the C—O—C bond in the pyranose ring; these results are in agreement with the reports of Pawlak and Mucha (2003).

According to Eq. (2), proposed by Brugnerotto et al. (2001), the degree of deacetylation resulted 86.9%. This value is similar to that obtained by potentiometric titration; therefore, both methods provided a good estimation of DD% that falls into the range of

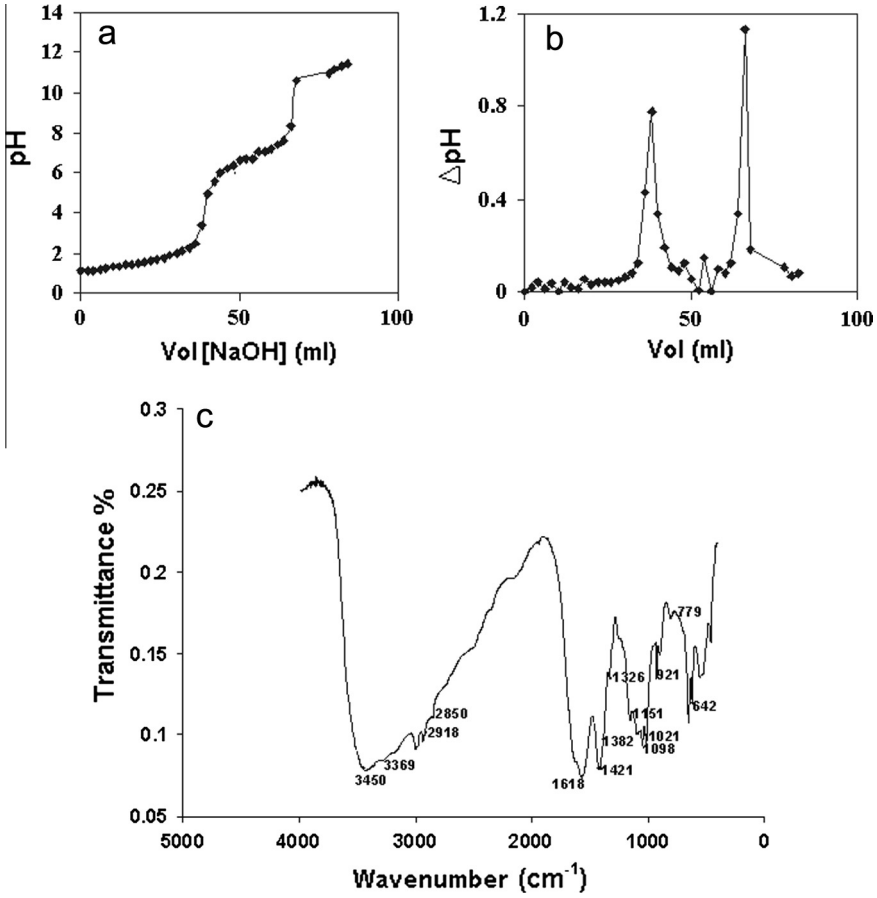

Fig. 1. (a) Potentiometric titration curve for shrimp chitosan. (b) Peaks corresponding to the inflection points of the titration curve shown in (a); (c) infrared spectra of CH obtained from shrimp.

commercial chitosan, because to obtain chitosan DD% must be 65% or higher (Ravi Kumar, 2000; Yen et al., 2008).

3.2. Chitosan molecular weight

The specific viscosity (η_{sp}) is the fractional change in viscosity upon addition of polymer

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} \quad (7)$$

Intrinsic viscosity [η] was determined from $\frac{\eta_{sp}}{c}$ vs. concentration plot extrapolating at zero concentration:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \quad (8)$$

According to Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \quad (9)$$

Intrinsic viscosity [η] = 1002.9 mL/g was obtained by using Eq. (9). The average molecular weight of chitosan (Mv) was determined by using the Mark–Houwink–Kuhn–Sakurada equation (Eq. (3)).

The values of k and a (Eq. (3)) were obtained from Rinaudo (2006) considering a chitosan deacetylation degree (DD%) comparable to that of the sample used in the present work.

For chitosan with 12% degree of acetylation (deacetylation degree DD = 88%) dissolved in a solution 0.3 M acetic acid −0.2 M sodium acetate buffer (at 25 °C), the obtained values were k = 0.074 mL/g and a = 0.80 obtaining an average molecular weight of 1.46×10^5 Da; this value falls into the range reported by other authors, for different chitosan sources (1×10^5–5×10^5 Da) (Ravi Kumar, 2000; Rinaudo, 2006; Yen et al., 2008).

3.3. Physicochemical characterization of the reticulated micro/nanoparticles (MCH)

By changing the proportion of both components (TPP and CH acidic solution) different average diameters of the reticulated particles MCH were observed.

Results of particle size and zeta potential as a function of pH and TPP concentration are shown in Fig. 2. The particle size increased with the amount of TPP (Fig. 2a) and with increasing pH (Fig. 2b); similar results were reported by Yu et al. (2013) with reference to the increase of the size of chitosan nanoparticles with the amount of TPP added.

Fig. 2b shows a significant increase in size at pH > 5 because the reduction of the protonation degree at the surface of the particles decreased electrostatic repulsion between the particles increasing the probability of particle aggregation (Gan et al., 2005).

The zeta potential of MCH decreased with the amount of TPP added (Fig. 2c); a high magnitude of zeta potential denotes stability of particles in suspension. In the case of chitosan the positive values of zeta potential are attributed to the presence of protonated amine groups; when negatively charged TPP reacts with positively charged chitosan, the net zeta potential decreases. Therefore, the higher the zeta potential, the lower the fraction of

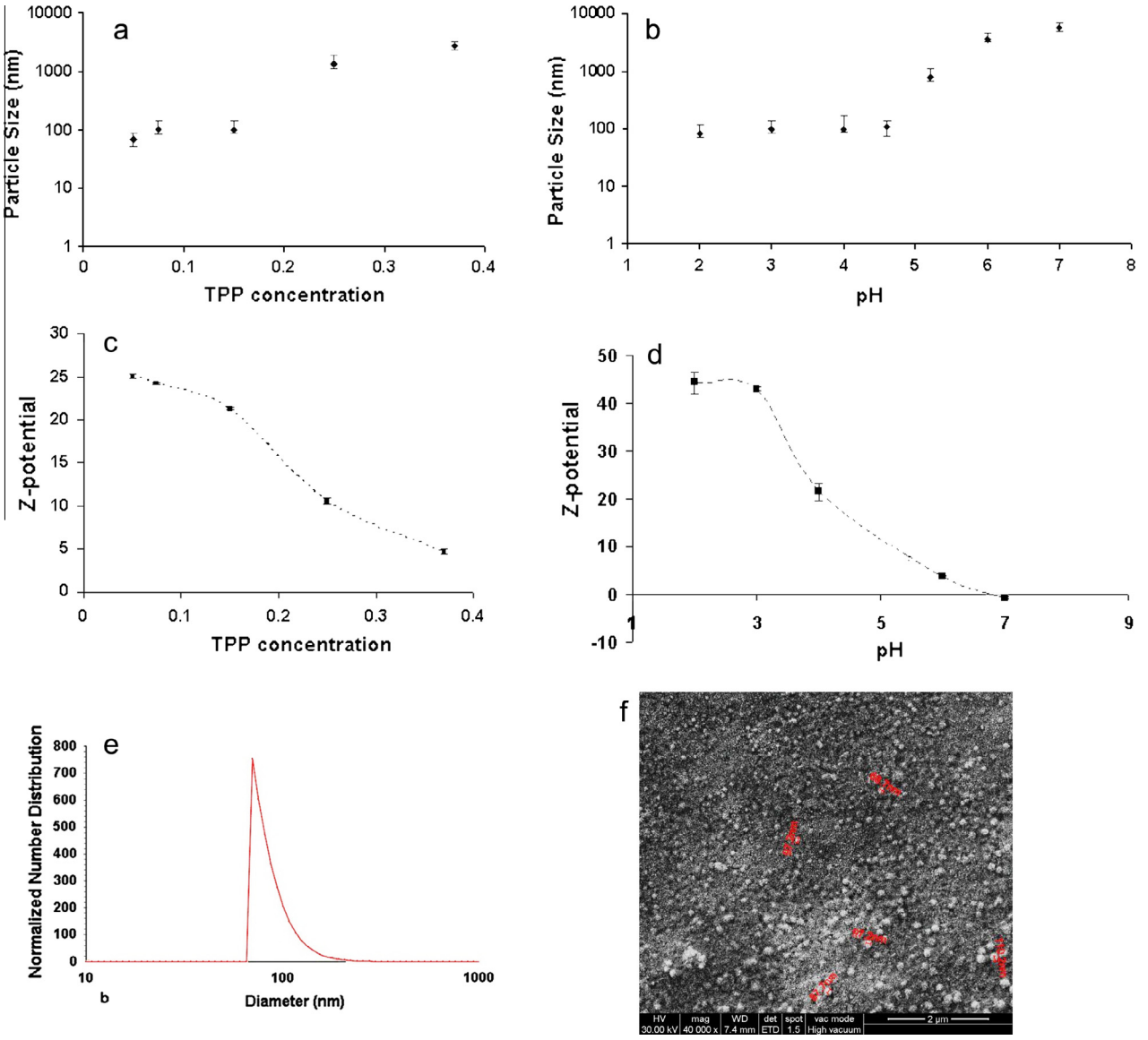

Fig. 2. Size (a and b) and zeta potential (c and d) of the reticulated chitosan micro/nanoparticles (MCH) as a function of TPP concentration and pH. (a and c) Effect of TPP concentration solution added to CH 1.25 g/L acidic solution at pH = 4.0 on: (a) particle size and (c) Zeta potential. (b and d) Effect of pH in the MCH suspension obtained from TPP (1.5 g/L aq. solution) and CH (1.25 g/L acidic solution) combined in a volumetric proportion of 1:3 respectively, on: (b) particle size; (d) Zeta potential; (e and f) particle size distribution of reticulated MCH prepared as described in (b and d) at pH = 4, determined by: (e) Beckman Coulter Equipment and (f) Scanning electron Microscopy SEM.

TPP present in MCH; these findings agree with results reported by Qi and Xu (2004).

The optimum condition to obtain micro/nanoparticles (MCH) was determined; MCH were formed spontaneously upon incorporation of TPP 1.5 g/L aqueous solution to CH 1.25 g/L acidic solution, in a volumetric proportion of 1:3 respectively at pH < 5. For this concentration ratio the zeta potential of MCH decreased with the increase of pH (Fig. 2d). The isoelectric point of CH–TPP reticulated system was around 7.

After adding TPP solution, micro/nanoparticles (MCH) formed immediately through inter and intramolecular linkages created between TPP and CH amino groups; MCH were separated by centrifugation and vacuum dried. For this selected optimum condition the production mass yield of MCH referred to the initial mass of chitosan was 44.8% and the mean size of the MCH was 101 nm (P_{10} = 88 nm; P_{90} = 145 nm) with a monomodal narrow size distribution (polydispersity index < 1). The size of the reticulated MCH determined by the Beckman Coulter Equipment (Fig. 2e) was in agreement with that observed by SEM microscopy (Fig. 2f).

It is interesting to remark that the average diameter of the reticulated MCH obtained under this optimum condition was close to 100 nm therefore these particles could be considered as nanoparticles (Qu et al., 2013). However because the lower limit between micro- and nano-sizing is still a matter of debate, they are designated as micro/nanoparticles in the present work.

Ionic gelation technique presents several advantages over other methods; the nanoparticles are obtained spontaneously under mild control conditions without using high temperatures, organic solvents, or sonication. TPP is a multivalent polyanion, with low toxicity and cost, and it presents no severe constraints of handling and storage (Calvo et al., 1997).

3.4. Cr(VI) batch adsorption studies

3.4.1. Effect of contact time on Cr(VI) removal

The adsorption kinetic curves of Cr(VI) (initial concentration of 100 mg/L and pH = 4) onto CH and MCH are observed in Fig. 3a and b. The curves show that equilibrium was reached after

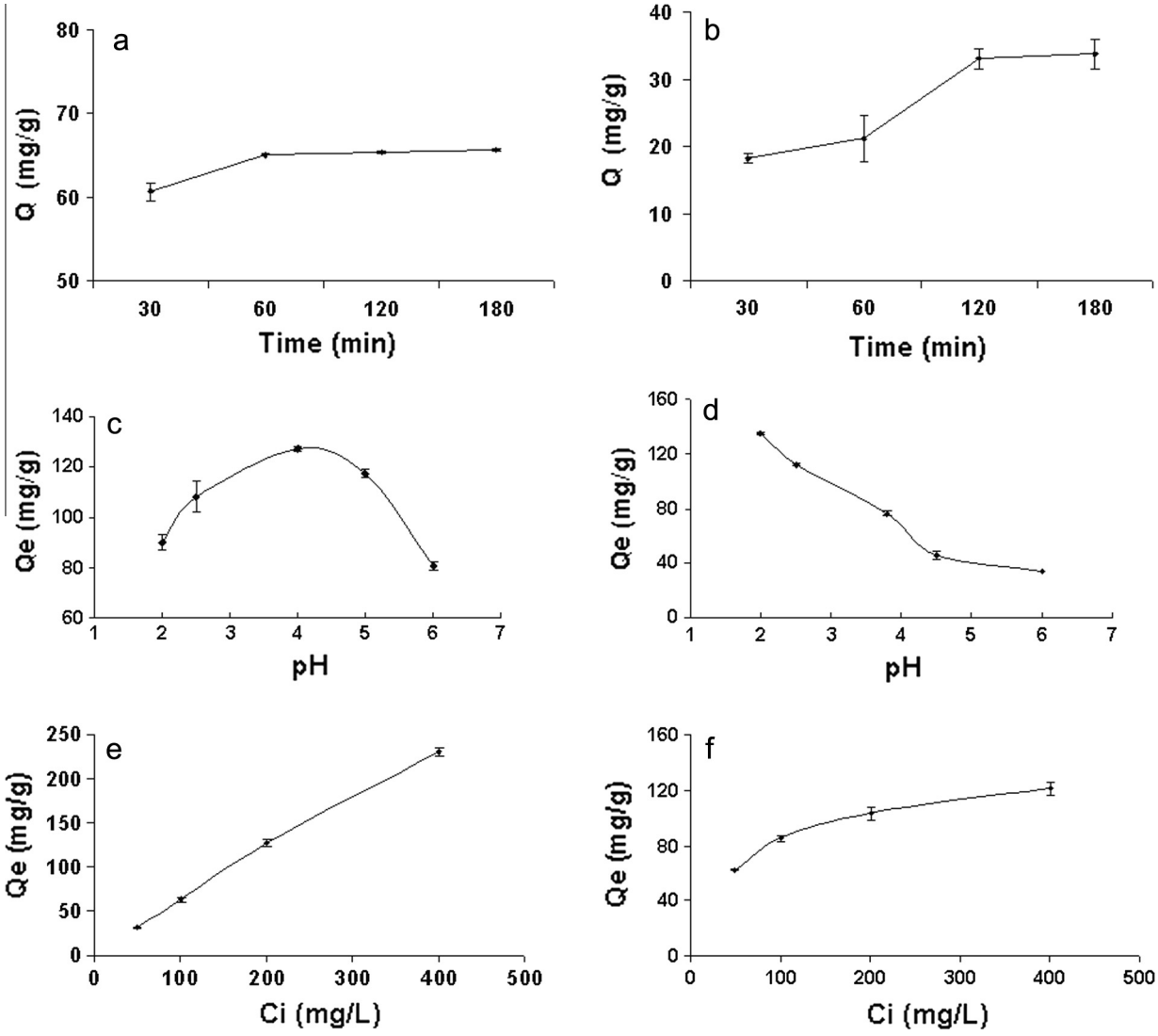

Fig. 3. Adsorption of chromium(VI) on: (a, c and e) chitosan (CH); (b, d and f) reticulated chitosan micro/nanoparticles (MCH). (a and b) Effect of contact time on Adsorption capacity (Q) at Cr(VI) initial concentration = 100 ppm and pH = 4. (c and d) Effect of pH on equilibrium adsorption capacity (Qe) at Cr(VI) initial concentration of 100 ppm. (e and f) Effect of initial Cr(VI) concentration on equilibrium adsorption capacity (Qe). (e) CH at pH = 4; (f) MCH at pH = 2.

approximately 1 h for chitosan particles (Fig. 3a) and after 2 h for MCH (Fig. 3b). The maximum amounts of adsorbed chromium after 3 h contact time led to equilibrium values of 66.9 mg/g for CH and 38.8 mg/g for MCH. After these periods, both systems remained almost unchanged until the end of the experiment.

3.4.2. Effect of pH

Fig. 3c and d shows the effect of pH on the adsorption of Cr(VI) ions onto CH and MCH at Cr(VI) initial concentration = 100 ppm. The removal of Cr(VI) from wastewater by adsorption is highly dependent on the solution pH, which affects the surface charge of the adsorbent, the degree of ionization, and the adsorbate species. Cr(VI) normally exists in the anionic form, as $(Cr_2O_7)^{2-}$, $HCrO_4^-$, $(CrO_4)^{2-}$, and HCr_2O_7; the fraction of any particular species is dependent upon the chromium concentration and pH. The main Cr(VI) species in equilibrium in the acidic pH range in diluted solutions are the anions $HCrO^{4-}$, $CrO4^{2-}$. They interact with the protonated amine functional groups of chitosan. The species such as $Cr_2O_7^{2-}$ and $HCr_2O_7^-$ coexist at high total chromium concentrations, above 1.0 g/L. At pH between 2 and 6, $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions exist in equilibrium, and under alkaline conditions (pH > 8) it exists predominantly as chromate anion (Hena, 2010).

The acid dissociation constant (pK_a) of chitosan is in the range between 6.2 and 6.8, therefore, the extent of protonation is 9%, 50%, 91%, and 99% at pH of 7.3, 6.3, 5.3, and 4.3, respectively (Schmuhl et al., 2001). Below the pK_a value, chitosan is positively charged, while the metal is negatively charged; this leads to an electrostatic interaction (Aydın and Aksoy, 2009; Hena, 2010). Above the pK_a value the sorbent and sorbate are negatively charged and Cr(VI) removal was markedly reduced (Schmuhl et al., 2001). Hamadi et al. (2001) and Schmuhl et al. (2001), reported that the decrease of Cr(VI) removal at a higher pH is attributed to the changes in protonated and unprotonated forms of chitosan.

Chitosan particles are unstable at pH < 2, and dissolves in acidic medium (Qi and Xu, 2004, then they could not be used to adsorb Cr(VI) at this pH range; therefore it is important to improve chitosan stability by using TPP to obtain chitosan micro/nanoparticles (MCH) and to analyze their performance to adsorb Cr(VI). The optimum pH values for the adsorption of Cr(VI) onto CH and MCH were pH = 4 and 2 respectively (Fig. 3c and d). The amount of Cr(VI) adsorbed on the MCH increased 23.2% when pH decreased from 4 to 2.

The values of Qe (equilibrium adsorption capacity) were 127.1 mg/g for CH (pH = 4), and 135.2 mg/g at pH = 2 for MCH.

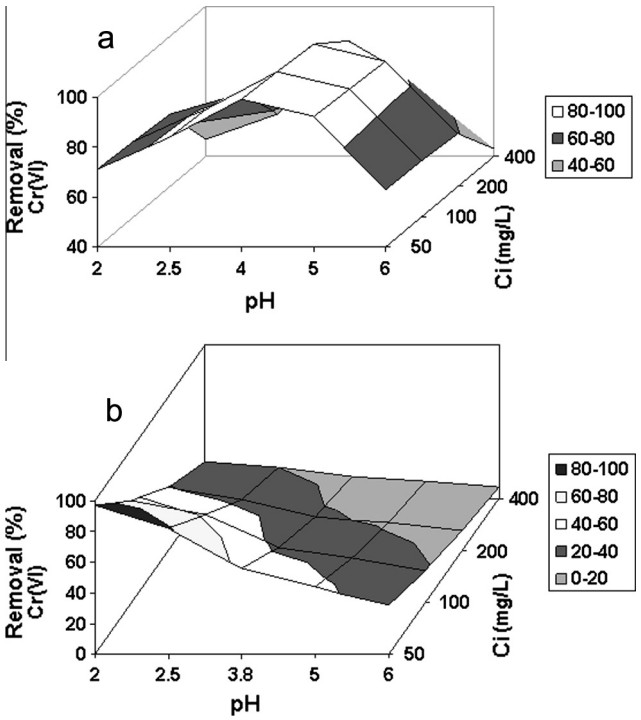

Fig. 4. Effect of chromium(VI) initial concentration and pH on the percentage of Cr (VI) removal using (a) CH; (b) MCH.

The decrease of Qe for CH at pH = 2 is attributed to its instability however, in the case of reticulated particles (MCH), cross-linking improved the removal capacity of Cr(VI) at low pH.

3.4.3. Influence of initial Cr(VI) concentration

Fig. 3e and f shows the adsorption capacities of CH and MCH at different initial Cr(VI) concentrations. The adsorption capacity increased from 31.4 to 230.2 mg/g for CH (Fig. 3e) and from 35.5 to 71.4 mg/g for MCH (Fig. 3f) when the initial Cr(VI) concentration ranged between 50 and 400 mg/L.

Aydın and Aksoy (2009) reported that a chitosan dose of 7 g/L was enough to ensure more than 90% Cr(VI) removal in a solution with a initial concentration of 55 mg/L Cr(VI); Hena (2010) reported a dosage of 6 g/L for CH coated with poly 3-methyl thiophene to remove 98%of Cr(VI) when the concentration was 100 mg/L.

In the present work, at pH = 4, only 1.6 g/L of CH were necessary to remove 99% and 90% of Cr(VI) in solutions containing initial concentrations of 50 mg/L and 400 mg/L respectively showing a very good performance. At pH = 2, only 0.8 g/L of MCH were necessary to remove 98% of Cr(VI) in solutions containing initial concentrations of 50 mg/L.

Fig. 4 shows the simultaneous effect of initial Cr(VI) concentration and pH on the percentage of Cr(VI) removal (Eq. (6)) for CH and MCH respectively.

3.5. Oxidation state of adsorbed chromium

The measurement of the oxidation state of the adsorbed chromium species indicated that when unmodified chitosan particles (CH) were used as the adsorbent material chromium is adsorbed as Cr(VI); in this case when Cr was desorbed from the samples Cr(III) could not be detected.

In contrast, in the case of Cr(VI) removal, using reticulated chitosan micro and nanoparticles (MCH), more than 60% of the adsorbed chromium was reduced to Cr(III). Then MCH reduced Cr(VI) to Cr(III) thus favoring non-toxicity. These results are in agreement with the findings of Sivakami et al. (2013) and are very important from a toxicological point of view.

One of the mechanisms of removal of Cr(VI) by reticulated MCH could be adsorption which proceeds due to the electrostatic attraction between two oppositely charged ions since the chromium(VI) ions in the solution are present in the form of anions and chitosan micro/nanoparticles have an overall positive surface charge. Reticulated MCH used as adsorbents not only act as electron donors for the Cr(VI) reduction to Cr(III), but also act as the active sites for Cr(III) adsorption. The Cr(III) is then adsorbed on the surface of MCH by the attraction of amine groups and the precipitation of Cr(III); a light green color was observed in the MCH. The combination of the reduction of Cr(VI) to Cr(III) and the adsorption of Cr(III) on the adsorbent is expected as an effective approach to remove the Cr(VI) from contaminated wastewater.

3.6. Equilibrium isotherms

The equilibrium adsorption data were analyzed using Langmuir, Freundlich, and Temkin equations (Aydın and Aksoy, 2009; Hena, 2010). Adsorption was evaluated by determining Cr(VI) concentration in solution under equilibrium conditions and pH = 4. The Langmuir isotherm is given by:

$$\frac{Ceq}{Qe} = \frac{Ceq}{Qm} + \frac{1}{K_L Qm} \tag{10}$$

K_L is the Langmuir constant (L/mg) related to the affinity of the binding sites; Qm is the maximum monolayer adsorption capacity (mg/g).

The Freundlich isotherm assumes that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of Cr(VI) at equilibrium. It is expressed as:

$$Qe = K_f Ceq^{1/n} \tag{11}$$

where K_f is the Freundlich constant or capacity factor (mg/g) and $1/n$ is the Freundlich exponent; n is the heterogeneity factor related to adsorption intensity.

The Temkin isotherm in its linear form is given by the equation:

$$Qe = B_t \ln(K_t) + B_t \ln(Ceq) \tag{12}$$

Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy value. The Temkin parameter B_t is related to the heat of adsorption and K_t is the equilibrium binding constant (Ho, 2003).

Fig. 5 shows Langmuir, Freundlich and Temkin linear fittings for Cr(VI) adsorption on CH and MCH at pH = 4 and 25 °C, along with the experimental data. All the isotherms were fitted to experimental data, and the goodness of fit was compared. The parameters obtained from the adsorption equations, for CH at pH = 4 and MCH at both pH values, 4 and 2 are shown in Table1.

The regression values indicate that the adsorption data for chromium removal fitted well to Langmuir and Freundlich isotherms, however the Langmuir isotherm has higher R^2 when compared to the other models. Langmuir isotherm (Eq. (10)) is representative of monolayer adsorption occurring on an energetically uniform surface on which the adsorbed molecules are not interactive. For micro/nanoparticles (MCH), adsorption at pH = 2 was more effective than at pH = 4 (Table 1).

Aydın and Aksoy (2009) and Hena (2010) also reported that Langmuir Isotherm described better C(VI) adsorption onto CH at pH = 4, however Qm and K_L obtained by these authors were

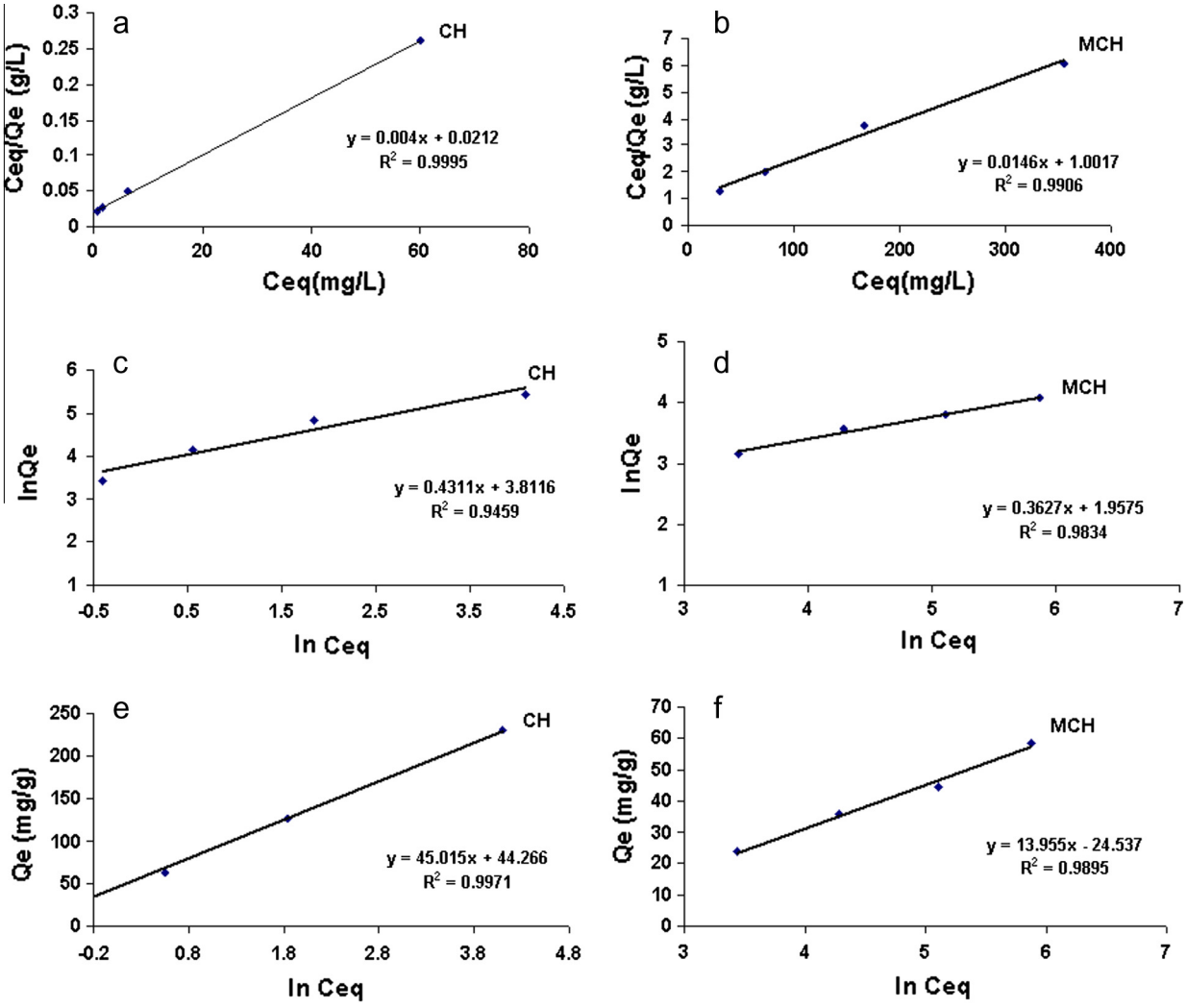

Fig. 5. Equilibrium sorption isotherms for CH (a, c and e) and MCH (b, d and f). Operating conditions: pH = 4, T = 25.5 °C. (a and b) Langmuir equation; (c and d) Freundlich equation; (e and f) Temkin equation.

Table 1
Parameters of the equilibrium isotherms and of the kinetic equations for Cr(VI) adsorption upon chitosan (CH) and chitosan reticulated micro/nanoparticles (MCH).

	Parameters of the equilibrium isotherms								
	Langmuir			Freundlich			Temkin		
	Qm (mg/g)	K_L (l/mg)	R^2	$1/n$	K_f (mg/g)	R^2	B_t	K_t (l/mg)	R^2
Chitosan (CH) pH = 4	250	0.018	0.999	0.43	44.70	0.941	45.01	2.76	0.997
Reticulated Micro/nanoparticles (MCH) pH = 4	68.9	0.014	0.990	0.36	7.02	0.983	13.95	1.76	0.989
Reticulated Micro/nanoparticles (MCH) pH = 2	124	0.086	0.990	0.12	60.42	0.977	22.55	1.46	0.939

	Parameters of the kinetic equations						
	Pseudo-first order		Pseudo-second order		Elovich		
	k_1 (h^{-1})	R^2	k_2 (g/mg h)	R^2	β (g/mg)	α (mg/g h)	R^2
Chitosan (CH) pH = 4	2.71	0.871	0.76	0.999	0.37	6.0×10^{10}	0.750
Reticulated Micro/nanoparticles (MCH) pH = 4	1.94	0.932	0.078	0.946	0.10	116.8	0.877

significantly lower than those obtained in the present work. Schmuhl et al. (2001) obtained a maximum Cr(VI) adsorption capacity of 78 mg/g for chitosan particles and 50 mg/g for cross-linked chitosan with epichlorohydrin.

Sivakami et al. (2013) developed chitosan nanoparticles using TPP and analyzed the adsorption of Cr(VI) on the obtained nanorods. These authors indicated that the adsorption data for chromium removal fitted better to Freundlich isotherm than to Langmuir equation. The values of Langmuir constant (K_L, L/mg), and Freundlich constant (K_f, mg/g) reported by Sivakami et al. (2013) were significantly lower than those obtained in the present work, at pH 2 and 4.

The dimensionless separation factor (RL) was calculated to evaluate the efficiency of the adsorption process.

$$RL = \frac{1}{(1 + K_L Ci)} \quad (13)$$

where Ci is the initial chromium ions concentration (mg/L), and K_L the Langmuir adsorption equilibrium constant (L/mg).

In all cases tested cases the obtained *RL* values for CH and MCH were all in the range 0–1, indicating that Cr(VI) adsorption by CH and MCH is favorable.

3.7. Adsorption kinetics

Kinetic equations corresponding to pseudo-first order, pseudo-second order and Elovich equation were fitted to experimental data (Sivaraj et al., 2001; Sağ and Aktay, 2002; Hena, 2010). The pseudo first order kinetic model of Lagergren has been widely used to predict the metal adsorption kinetics and is given by:

$$dQ/dt = k_1(Qe - Q) \quad (14)$$

where Q is the amount of metal adsorbed at any time (mg/g), Qe is the amount of metal adsorbed at equilibrium time (mg/g) and k_1 is the pseudo first order rate constant (min^{-1}). By integrating Eq. (14) the following is obtained:

$$\ln\left(\frac{Qe}{Qe - Q}\right) = k_1 t \quad (15)$$

The adsorption kinetic data can be further analyzed using the pseudo second order kinetics, which is represented by:

$$dQ/dt = k_2(Qe - Q)^2 \quad (16)$$

where k_2 is the second order rate constant. Integrating Eq. (16) gives:

$$\frac{t}{Q} = \frac{1}{k_2 Qe^2} + \frac{1}{Qe}t \quad (17)$$

The intercept of the linearized pseudo-second order rate equation gives the second order rate constant, k_2.

The Elovich or Roginsky–Zeldovich equation is used in systems with heterogeneous adsorbing surfaces:

$$dQ/dt = \alpha \exp(-\beta Q) \quad (18)$$

where Q is the amount of metal adsorbed at a time *t*, α is the initial adsorption rate ($mg\,g^{-1}\,h^{-1}$), and β is the Elovich constant. To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$, and on applying the initial condition $Q = 0$ at $t = 0$ the equation becomes Sparks (1999):

$$Q = \beta \ln(\alpha\beta) + \beta \ln t \quad (19)$$

Fig. 6 shows pseudo-first order, pseudo-second order kinetic and Elovich model for chromium adsorption on CH and MCH. The parameters obtained by the different tested kinetic equations with the corresponding correlation coefficients are given in Table 1.

For CH, the kinetic studies indicated a rapid removal of chromium from aqueous solutions. The large value of α in Elovich equation for chitosan particles indicates a very high initial adsorption rate in comparison to the MCH.

The kinetic analysis of chromium adsorption showed that pseudo second order kinetic model fitted successfully the experimental data in agreement with findings of Sağ and Aktay (2002), Aydın and Aksoy (2009), Hena (2010) and Sivakami et al. (2013).

4. Conclusions

Chitosan particles were obtained from shrimp shells and were physicochemically characterized; the degree of deacetylation (86–90.1%) was determined by potentiometric titration and FTIR. Molecular weight of chitosan was determined by intrinsic viscosity measurements. Reticulated chitosan micro/nanoparticles (MCH) were synthesized by inducing the gelation of a chitosan solution with tripolyphosphate (TPP), a non-toxic polyanion. Different mean sizes of MCH were obtained by adjusting the ratio of chitosan to tripolyphosphate. MCH were characterized by size distribution and *Z*-potential at different pH and relative proportions of CH and TPP. Specifically for a combination of TPP (1.5 g/L) and chitosan (1.25 g/L) solutions, in a volumetric proportion 1:3, nanoparticles of 100 nm average diameter were obtained.

The adsorption capacity of CH and MCH toward Cr(VI), under different conditions, such as pH, contact time, and initial chromium concentration were analyzed. At pH < 6 the functional groups of chitosan were protonated, resulting in a stronger attraction for a negatively charged chromium ion in the solution, leading to electrostatic interactions. The optimum pH values for the adsorption of Cr(VI) was pH = 4 for CH and pH = 2 for MCH. At high pH values the cross linking with TPP reduced the number of sites for the adsorption of the metal ions onto reticulated chitosan. At

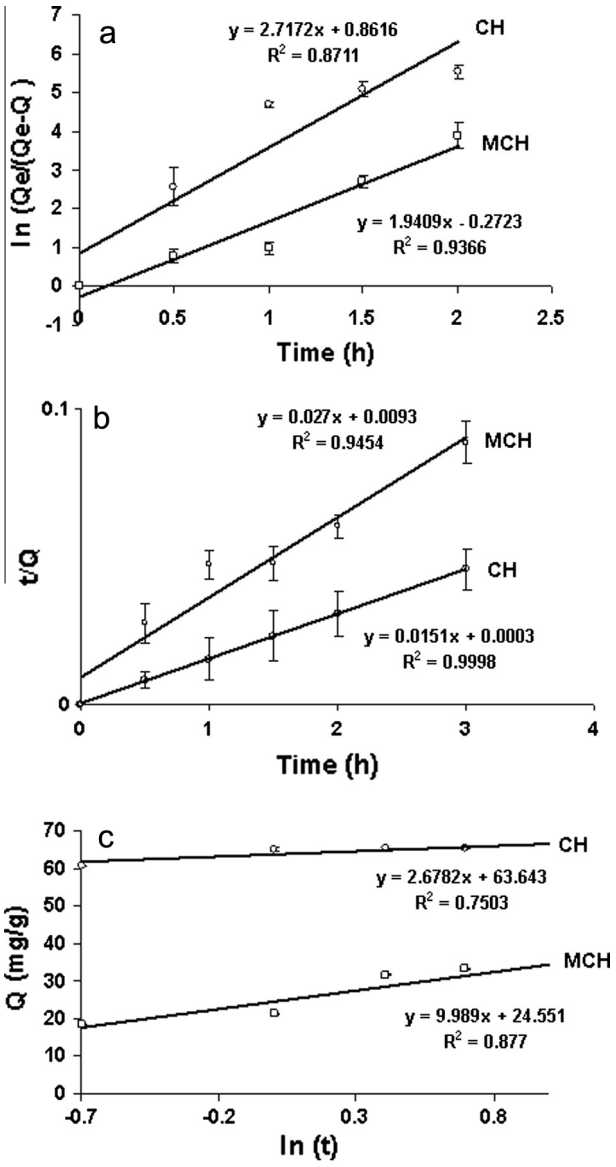

Fig. 6. Kinetic equations for Cr(VI) adsorption on CH and MCH. (a) Pseudo first order; (b) Pseudo second order; (c) Elovich model.

very low pH the adsorption capacities were higher for the reticulated micro/nanoparticles (MCH) because CH is unstable at pH < 2 thus cross-linking with TPP improved the adsorption performance of Cr(VI).

Langmuir, Freundlich and Temkin isotherms were applied for the mathematical description of the adsorption equilibrium curves. Langmuir isotherm provided the best fit to the experimental data. The kinetic analysis was conducted using the pseudo first order, pseudo second order and Elovich models. The pseudo-second order kinetic model provided the best correlation of the experimental data for both, chitosan particles and reticulated chitosan particles.

MCH and CH can be effectively applied for the removal of Cr(VI) from wastewater. Additionally, the present work demonstrated that chitosan crosslinking is clearly needed to adsorb hexavalent chromium at pH < 2.5 due to the dissolution of the non modified CH particles in acid media.

Chemical analyses carried out to determine the oxidation state of the adsorbed chromium, have shown that Cr(VI) was adsorbed on CH particles without further reduction; in contrast Cr(VI) removed from the solution was reduced and bound to the MCH as Cr(III). The reduction of toxic Cr(VI) to the less or nontoxic Cr(III) by the reticulated chitosan micro/nanoparticles (MCH) can be considered a very efficient detoxification technique for the treatment of Cr(VI)-contaminated waters.

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References

Abdou, E.S., Nagy, K.S.A., Elsabee, M.Z., 2008. Extraction and characterization of chitin and chitosan from local sources. Bioresour. Technol. 99, 1359–1367.

Aydın, Y.A., Aksoy, N.D., 2009. Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics. Chem. Eng. J. 151 (1), 188–194.

Bellú, S., Sala, L., González, J., García, S., Frascaroli, M., Blanes, P., García, J., Salas, Peregrin J., Ana, Atria A., Ferrón, J., Harada, M., Cong, C., Niwa, Y., 2010. Thermodynamic and dynamic of chromium biosorption by pectic and lignocellulosic biowastes. J. Water Resour. Prot. 2, 888–897.

Bhatnagar, A., Sillanpää, M., 2009. Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater – a short review. Adv. Colloid Interface 152 (1), 26–38.

BhuvaneshwarI, S., Sruthi, D., Sivasubramanian, V., Kanthimathy, K., 2012. Regeneration of chitosan after heavy metal sorption. J. Sci. Ind. Res., JSIR 71, 266–269.

Broussignac, P., 1968. Chitosan: a natural polymer not well known by the industry. Chim. Ind. Genie. Chim. 99, 1241–1247.

Brugnerotto, J., Lizardi, J., Goycoolea, F.M., Argüelles-Monal, W., Desbrieres, J., Rinaudo, M., 2001. An infrared investigation in relation with chitin and chitosan characterization. Polymer 42 (8), 3569–3580.

Calvo, P., Remuñan-López, C., Vila-Jato, J.L., Alonso, M.J., 1997. Chitosan and chitosan/ethylene oxide-propylene oxide block copolymer microparticles as novel carriers for proteins and vaccines. Pharm. Res. 14 (10), 1431–1436.

Chien, S.H., Clayton, W.R., 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am. J. 44 (2), 265–268.

Clescerl, L.S., Greenberg, A.E., Eaton, A.D., 1999. Standard Methods for the Examination of Water and Wastewater. Method 3500 Chromium Colorimetric Method.

Cocoletzi, H.H., Almanza, E.A., Agustin, O.F., Nava, E.V., Cassellis, E.R., 2009. Obtención y caracterización de quitosano a partir de exoesqueletos de camarón. Surf. Mater. 22 (3), 57–60.

Dubey, S.P., Gopal, K., 2007. Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study. J. Hazard. Mater. 145, 465–470.

Gan, Q., Wang, T., Cochrane, C., McCarron, P., 2005. Modulation of surface charge, particle size and morphological properties of chitosan–TPP nanoparticles intended for gene delivery. Colloids Surf., B 44 (2), 65–73.

Gu, H., Rapole, S.B., Sharma, J., Huang, Y., Cao, D., Colorado, H.A., Luo, Z., Haldolaarachchige, N., Young, D.P., Walters, B., Wei, S., Guo, Z., 2012. Magnetic polyaniline nanocomposites toward toxic hexavalent chromium removal. RSC Adv. 2, 11007–11018.

Hamadi, N.K., Chen, X.D., Farid, M.M., Lu, M.G.Q., 2001. Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. Chem. Eng. J. 84, 95–105.

Hena, S., 2010. Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer. J. Hazard. Mater. 181 (1), 474–479.

Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. Water Res. 37, 2323–2330.

Huang, R., Yang, B., Liu, Q., 2013. Removal of chromium(VI) ions from aqueous solutions with protonated crosslinked chitosan. J. Appl. Polym. Sci. 129 (2), 908–915.

Laus, R., CostaT, G., Szpoganicz, B., Fávere, V.T., 2010. Adsorption and desorption of Cu (II), Cd (II) and Pb (II) ions using chitosan crosslinked with epichlorohydrin–triphosphate as the adsorbent. J. Hazard. Mater. 183 (1), 233–241.

López-León, T., Carvalho, E.L.S., Seijo, B., Ortega-Vinuesa, J.L., Bastos-González, D., 2005. Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior. J. Colloid Interface Sci. 283 (2), 344–351.

Ng, J.C.Y., Cheung, W.H., McKay, G., 2003. Equilibrium studies for the sorption of lead from effluents using chitosan. Chemosphere 52 (6), 1021–1030.

Park, D., Yun, Y.S., Park, J.M., 2008. XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption. J. Colloid Interface Sci. 317 (1), 54–61.

Pawlak, A., Mucha, M., 2003. Thermogravimetric and FTIR studies of chitosan blends. Thermochim. Acta 396 (1), 153–166.

Qi, L., Xu, Z., 2004. Lead sorption from aqueous solutions on chitosan microparticles. Colloids Surf., A 251 (1), 183–190.

Qiu, B., Gu, H., Yan, X., Guo, J., Wang, Y., Sun, D., Wang, Q., Khan, M., Zhang, X., Weeks, B.L., Young, D.P., Guo, Z., Wei, S., 2014a. Cellulose derived magnetic mesoporous carbon nanocomposites with enhanced hexavalent chromium renoval. J. Mater. Chem. A 2 (41), 17451–17462.

Qiu, B., Guo, J., Zhang, X., Sun, D., Gu, H., Wang, Q., Wang, H., Wang, X., Zhang, X., Weeks, B.L., Guo, Z., Wei, S., 2014b. Polyethylenimine facilitated ethyl cellulose for hexavalent chromium removal with a wide pH range. ACS Appl. Mater. Int. 6, 19816–19824.

Qiu, B., Xu, C., Sun, D., Wei, H., Zhang, X., Guo, J., Wang, Q., Rutman, D., Guo, Z., Wei, S., 2014c. Polyaniline coating on carbon fiber fabrics for improved hexavalent chromium removal. RSC Adv. 4, 29855–29865.

Qiu, B., Xu, C., Sun, D., Yi, H., Guo, J., Zhang, X., Qu, H., Guerrero, M., Wang, X., Noel, N., Luo, Z., Guo, Z., Wei, S., 2014d. Polyaniline coated ethyl cellulose with improved hexavalent chromium removal. ACS Sustainable Chem. Eng. 2 (8), 2070–2080.

Qiu, B., Xu, C., Sun, D., Wang, Q., Gu, H., Zhang, X., Weeks, B.L., Hopper, J., Ho, T.C., Guo, Z., Wei, S., 2015. Polyaniline coating with various substrates for hexavalent chromium removal. Appl. Surf. Sci. 334, 7–14.

Qu, X., Alvarez, P.J., Li, Q., 2013. Applications of nanotechnology in water and wastewater treatment. Water Res. 47 (12), 3931–3946.

Ravi Kumar, M.N., 2000. A review of chitin and chitosan applications. React. Funct. Polym. 46 (1), 1–27.

Rinaudo, M., 2006. Chitin and chitosan: properties and applications. Prog. Polym. Sci. 31 (7), 603–632.

Sağ, Y., Aktay, Y., 2002. Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*. Biochem. Eng. J. 12 (2), 143–153.

Sankararamakrishnan, N., Dixit, A., Iyengar, L., Sanghi, R., 2006. Removal of hexavalent chromium using a novel cross linked xanthated chitosan. Bioresour. Technol. 97 (18), 2377–2382.

Sano, L., Krueger, A.M., Landrum, P.F., 2005. Chronic toxicity of glutaraldehyde: differential sensitivity of three freshwater organisms. Aquat. Toxicol. 71 (3), 283–296.

Schmuhl, R., Krieg, H.M., Keizer, K., 2001. Adsorption of Cu(II) and Cr(VI) ions by chitosan: kinetics and equilibrium studies. Water SA 27 (1), 1–8.

Sivakami, M.S., Gomathi, T., Venkatesan, J., Jeong, H.S., Kim, S.K., Sudha, P.N., 2013. Preparation and characterization of nano chitosan for treatment wastewaters. Int. J. Biol. Macromol. 57, 204–212.

Sivaraj, R., Namasivayam, C., Kadirvelu, K., 2001. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solution. Waste Manage. 21, 105–110.

Sparks, D.L. (Ed.), 1999. Soil Physical Chemistry. CRC Press, Boca Raton, FL, pp. 83–145 (Chapter 4).

Wu, F.C., Tseng, R.L., Juang, R.S., 2010. A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals. J. Environ. Manage. 91 (4), 798–806.

Xu, C., Qiu, B., Gu, H., Yang, X., Wei, H., Huang, X., Wang, Y., Rutman, D., Cao, D., Bhana, S., Guo, Z., Wei, S., 2014. Synergistic interactions between activated carbon fabrics and toxic hexavalent chromium. ECS J. Solid State Sci. Technol. 3 (3), M1–M9.

Yen, M.T., Yang, J.H., Mau, J.L., 2008. Antioxidant properties of chitosan from crab shells. Carbohyd. Polym. 74 (4), 840–844.
Yu, K., Ho, J., McCandlish, E., Buckley, B., Patel, R., Li, Z., Shapley, N.C., 2013. Copper ion adsorption by chitosan nanoparticles and alginate microparticles for water purification applications. Colloids Surf., A 425, 31–41.
Zhang, D., Wei, S., Kaila, C., Su, X., Wu, J., Karki, A.B., Young, D.P., Guo, Z., 2010. Carbon-stabilized iron nanoparticles for environmental remediation. Nanoscale 2, 917–919.
Zhang, H., Wang, F., Jin, X., Zhu, Y., Li, X., Zhou, H., 2013. Chromium removal with cross-linked chitosan adsorption and base-precipitation combination. Water Sci. Technol. 67 (12), 2768–2775.
Zhu, J., Wei, S., Gu, H., Rapole, S.B., Wang, Q., Luo, Z., Haldolaarachchige, N., Young, D.P., Guo, Z., 2012. One-pot synthesis of magnetic graphene nanocomposites decorated with core@double-shell nanoparticles for fast chromium removal. Environ. Sci. Technol. 46 (2), 977–985.
Zhu, J., Gu, H., Guo, J., Chen, M., Wei, H., Luo, Z., Colorado, H.A., Yerra, N., Ding, D., Ho, T.C., Haldolaarachchige, N., Hopper, J., Young, D.P., Guo, Z., Wei, S., 2014. Mesoporous magnetic carbon nanocomposite fabrics for highly efficient Cr(VI) removal. J. Mater. Chem. A 2, 2256–2265.