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PREPARATION AND EVALUATION OF MAGNETIC CHITOSAN PARTICLES MODIFIED WITH ETHYLENEDIAMINE AND Fe(III) FOR THE REMOVAL OF Cr(VI) FROM AQUEOUS SOLUTIONS

Thiago V. Toledo[a], Carlos R. Bellato[a,*], Carlos H. Ferreira de Souza[a], Junielly T. Domingues[a], Danilo de C. Silva[a], César Reis[a] and Maurício P. Ferreira Fontes[b]
[a]Departamento de Química, Universidade Federal de Viçosa, Campus Universitário, s/n, 36570-000 Viçosa – MG, Brasil
[b]Departamento de Solos, Universidade Federal de Viçosa, Campus Universitário, s/n, 36570-000 Viçosa – MG, Brasil

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The adsorption of Cr(VI) in aqueous solution by magnetic particles of crosslinked chitosan-ethylenediamine-Fe(III) (MPCh-EDA-FeCL) was studied in a batch system. Fe^{3+} in the MPCh-EDA-FeCL permitted that adsorption of Cr(VI) occurred with maximum efficiency between pH 3 and 11. The maximum adsorption capacity at pH 7.0 was 81.04 mg g^{-1} at 25 °C. The adsorption kinetic process was described by the pseudo-second-order model. Thermodynamic parameters indicated spontaneous, exothermic and chemical adsorption nature. The adsorbent was successively regenerated using a 0.1 mol L^{-1} NaOH solution. Results were satisfactory for treatment of wastewater from the electroplating industry.

Keywords: magnetic chitosan; adsorption; chromium(VI).

INTRODUCTION

Heavy metal pollution is one of the most important environmental problems of today. Among the various heavy metals, chromium (Cr) is a cause of great concern because of the serious problems it generates in ecosystems.[1] In aqueous solutions this element exists in two stable oxidation states, referred to as Cr(III) and Cr(VI).[2] Although trivalent chromium is an essential micronutrient associated with the metabolism of lipids and carbohydrates, and whose absence is related to diabetes and cardiovascular disease, Cr(VI) is considered dangerous to public health due to its mutagenic and carcinogenic properties.[3] In humans, it is known that chromium(VI) is also capable of causing lung, liver and kidney cancer, severe gastric damage and other health problems.[4]

Hexavalent chromium is present in effluents from various industrial processes such as electroplating, leather tanning, wood protection, manufacturing of electrical equipment and electronics, metalworking and others.[1,5] As a function of the pH and concentration of this element in the aqueous solution, it may be in the form of highly soluble anionic species such as chromate (CrO_4^{2-}), hydrogenchromate ($HCrO_4^-$) or dichromate ($Cr_2O_7^{2-}$).[5] Thus, chromium(VI) should be removed from wastewater before discharge into the environment because its high solubility makes it easily transported in water resources.[4]

Some of the most common methods applied for the removal and recovery of Cr(VI) from aqueous solutions include reduction and precipitation, solvent extraction, adsorption, ion exchange using resins, reverse osmosis, electrolysis and others.[1,4] Among these, adsorption is identified as one of the most efficient and low cost.[5] The low cost of the adsorption process is mainly due to the recent use of various natural materials and wastes as adsorbents.[5] Some of the highlighted materials include those of biological origin (biosorbents) which are obtained from fungi, algae, biopolymers etc.[6] Some biopolymers such as chitosan-based nanofibers, lignocellulose, chitosan, chitin, cellulose and lignin are known for their good capacity to adsorb metal ions from aqueous solutions.[7]

Chitosan is obtained from the deacetylation of chitin, a polysaccharide consisting predominantly of unbranched chains of β-(1→4)-2-acetamido-2-deoxy-D-glucose present in the exoskeleton of insects, crustaceans and certain fungi. During recent decades many scientific studies have reported the potential application of chitosan and some of its important properties have been highlighted, such as biodegradability, non-toxicity, high hydrophilicity, structural flexibility, high chemical reactivity of their functional groups, etc.[8-11]

Chitosan, the second most abundant biopolymer in nature, is a good adsorbent of metal ions due to the functional amino ($-NH_2$) and hydroxyl (-OH) groups presents in its structure. Moreover, its adsorption capacity can be improved by chemical methods such as crosslinking for addition of various other functional groups.[6,8] Functional groups such as acetamide, hydroxyl, carboxyl, quaternary ammonium, ethylenediamine, and others have been incorporated to the structure of adsorbents to increase versatility of their application.[12,13] According to literature, the complexation of chitosan with Fe(III) ions in the insoluble form also increases its adsorption capacity of oxyanions, for example, phosphate and chromate.[14]

The classical methods for separating the adsorbent from the aqueous solution mainly include filtration, sedimentation and centrifugation. However, these methods are time consuming and uneconomical. In this context, magnetic separation technology has recently emerged as an efficient, fast and low cost method. Magnetic chitosan can be prepared by the combination of chitosan and magnetic particles and is easily removed from the reaction medium by applying an external magnetic field.[8]

In the present study the adsorption properties of chitosan were combined with the magnetic properties of iron oxide to produce a magnetic adsorbent that can be easily removed from the aqueous solution after adsorption by applying an external magnetic field. By reacting with ethylenediamine, amino groups were also added to this material, which provide it with greater adsorption power (MPCh-EDA). This material was further complexed with Fe^{3+} to obtain the final adsorbent referred to as magnetic particles of crosslinked chitosan-ethylenediamine-Fe(III) (MPCh-EDA-FeCL).

Various metal ions are preferably adsorbed in acid medium; however, chitosan can be easily solubilized by dilute mineral acids and therefore its chemical stability is enhanced by treatment with crosslinking agents.[15,16] In this study epichlorohydrin was used in synthesis of the adsorbent, because it can bind to both the oxygen of hydroxyls

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*e-mail: bellato@ufv.br

(-OH) and to the nitrogen of amine groups ($-NH_2$) present in chitosan. When binding to oxygen, it is able to promote crosslinking by uniting the side chains of chitosan and when binding to nitrogen can act as a support for the insertion of molecules such as ethylenediamine.[15-19] As reported in literature,[12,16,20,21] the surface of chitosan or chitosan modified with ethylenediamine becomes less positive with increasing pH due to deprotonation which occurs in the amine groups ($-NH_2$), and in pH values greater than the pH_{pcz} (6.3) its surface charge becomes negative so as to repel anionic species, which drastically reduces its adsorption capacity in neutral and/or slightly basic pH. However, the incorporation of Fe(III) to the structure of MPCh-EDA-FeCL permits that this adsorbent maintains a positive surface charge in a wide pH range (3 to 11) and a high affinity for anionic species of Cr(VI), which makes it a promising material for the treatment of contaminated waters.

In the present work the MPCh-EDA-FeCL were used for the removal of Cr(VI) in a batch system. The optimum conditions, equilibrium data, isotherms and the effect of temperature and adsorption kinetics were obtained. A Langmuir and Freundlich isotherm was fitted to the equilibrium adsorption data. Peseudo-first-order and pseudo-second-order equations were adopted to test the experimental kinetic data. Reusability of the adsorbent was also demonstrated. Finally, the MPCh-EDA-FeCl were used to remove Cr(VI) from the effluent sample obtained from the electroplating industry.

EXPERIMENTAL

Preparation of MPCh-EDA-FeCL

The preparation of the MPCh-EDA-FeCL was performed according to the following steps:

Step 1: 2.0 g of chitosan (low molecular weight, 75-85% deacetylated, Sigma Aldrich) were added to 50 mL of acetic acid 5% (w/v). The gel formed was stirred for 24 hours until complete dissolution of the polymer; after this period, 0.3 g of magnetic iron oxide was added to the mixture which was allowed to stir for another 60 minutes to complete homogenization. Then, the gel was dripped (2 mL min^{-1}), using a Masterflex ® peristaltic pump, in a 0.5 mol L^{-1} NaOH solution where magnetic particles formed based on the contact of gel drops with the alkaline solution by the principle of coacervation. These particles remained in contact with the NaOH solution after dripping for 30 minutes. After this time the beads were washed with deionized water until the wash water presented pH 7.0.[20-22]

Step 2: The particles obtained in the previous step were suspended in 300 mL of a mixture of ethanol and deionized water (1:1 v/v) and 6 mL of epichlorohydrin. The mixture was stirred at 60 °C for 16 hours and then cooled. Subsequently, particles were washed three times with a mixture of distilled water and ethanol to remove the excess unreacted epichlorohydrin.[12]

Step 3: The particles obtained in step 2 were suspended in 300 mL of a mixture of ethanol and deionized water (1:1 v/v) and 5.0 mL of ethylenediamine. The system remained under agitation for 24 hours at 60 °C, and subsequently washed three times with a mixture of water and ethanol.[12]

Step 4: To complete the synthesis of MPCh-EDA-FeCL, the material obtained in step 3 was complexed with Fe^{3+} ions by means of adaptation of the model proposed in literature.[20] For this, the still moist particles were maintained in contact for 40 minutes under stirring with 500 mL of a 0.109 mol L^{-1} $FeCl_3.6H_2O$ solution. Then, the particles were washed with deionized water to remove excess uncomplexed Fe(III) and left in an oven for 18 hours at 45 °C. Finally, the material obtained was ground and passed through a 150 mesh sieve (acquisition of particles with diameter smaller than 0.106 mm) and stored in a desiccator to be used for adsorption of Cr(VI). After preparation, the MPCh-EDA-FeCL showed magnetic properties when tested with a 0.3 T magnet, where all material was attracted by the magnet. In all stages of acquiring experimental adsorption data a magnet was used to attract and agglomerate the suspended adsorbent material, thus allowing for removal of supernatant aliquots without loss and/or interference of the adsorbent.

Proposal of the mechanism of interaction between chitosan and the employed reagents in synthesis of MPCh-EDA-FeCL, as well as interaction of the adsorbent with Cr(VI), is shown in Figure 1.

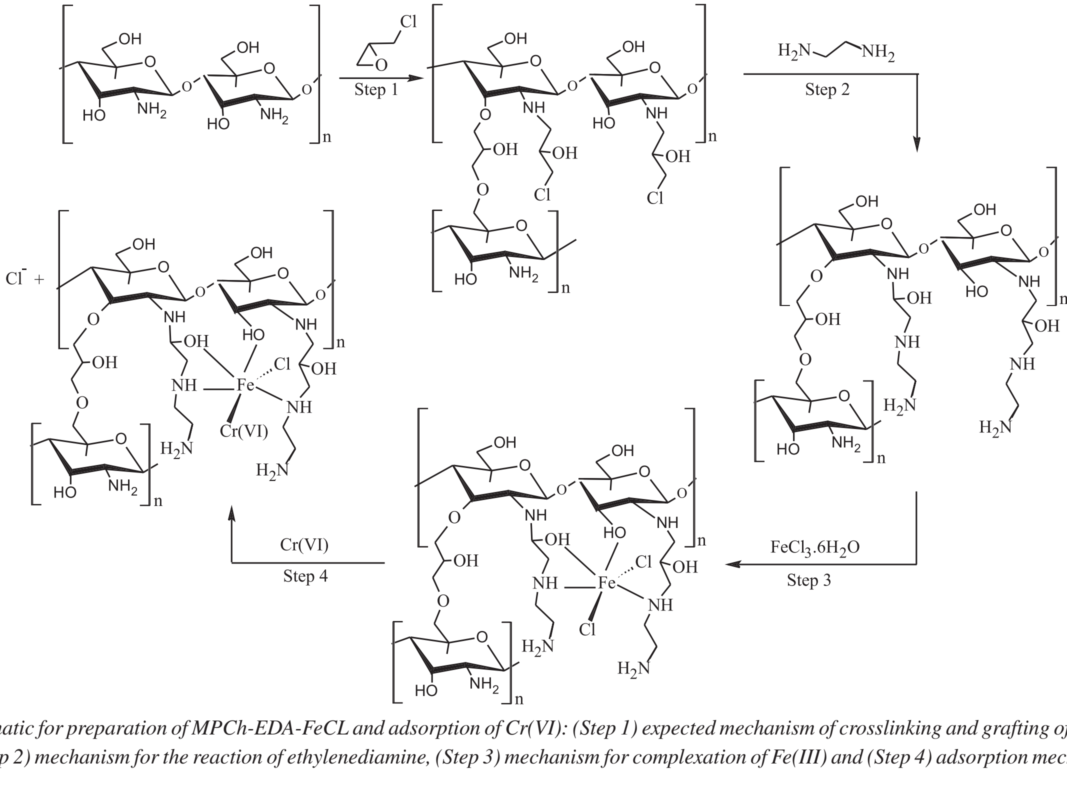

Figure 1. Schematic for preparation of MPCh-EDA-FeCL and adsorption of Cr(VI): (Step 1) expected mechanism of crosslinking and grafting of epichlorohydrin in chitosan, (Step 2) mechanism for the reaction of ethylenediamine, (Step 3) mechanism for complexation of Fe(III) and (Step 4) adsorption mechanism of Cr(VI)

Characterization of the MPCh-EDA-FeCL

The MPCh-EDA-FeCL was characterized by elemental analysis (CHN), X-ray diffraction (XRD) and infrared spectroscopy (IR).

Analysis of carbon, hydrogen and nitrogen concentrations was performed using the Elemental Analyzer 2400 CHN Perkin Elmer. Mass of the sample used for each analysis was around 2 mg. The XRD was performed with a diffractometer X-ray Diffraction System model X' Pert PRO (PANalytical) using a Ni filter and Co-Kα radiation (λ = 1.78890 Å) and angular variation of 5-70° (2θ). The IR analysis was carried out in the region of 400 to 4000 cm^{-1} on a VARIAN 660-IR spectrophotometer with attenuated reflectance accessory PIKE GladiATR.

Batch adsorption experiments

Study of Cr(VI) adsorption by different materials

In this study, the adsorption efficiency of Cr(VI) by different materials: crosslinked-chitosan (ChCL), ethylenediamine-crosslinked chitosan (Ch-EDACL), magnetic particles of crosslinked chitosan (MPChCL) and magnetic particles of ethylenediamine crosslinked chitosan (MPCh-EDACL), was compared to the efficiency of MPCh-EDA-FeCL. For this, 50 mg of each of these materials were individually added to 20 mL of a 100 mg L^{-1} Cr(VI) solution adjusted to pH 7. The system was then maintained for 240 min in a thermostatic bath with stirring at a controlled temperature of 25 °C. Subsequently, the analyte concentration was determined by Atomic Absorption Spectroscopy (AAS).

Effect of initial pH

In order to optimize the pH for maximum Cr(VI) removal efficiency by MPCh-EDA-FeCL, solutions of 100 mg L^{-1} of Cr(VI) had their pH values adjusted in the range from 1 to 12. Thus, 50 mg samples of MPCh-EDA-FeCL were added to 20 ml of Cr(VI) 100 mg L^{-1} at different pH values, and the system maintained for 60 min in a thermostatic bath with controlled agitation at a temperature of 25 °C. Subsequently, concentration of the analyte was determined by AAS.

Adsorption kinetics

In this study, 50 mg of MPCh-EDA-FeCL were added to 20 mL Cr(VI) solutions of 100, 150 and 200 mg L^{-1} at pH 7.0. The system was stirred at 25 °C in a thermostatic bath (QUIMIS®). Each sample was removed at a determined time, in the order of 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 min. The concentration of Cr(VI) in the supernatant was determined by AAS.

Isotherms and the effect of temperature

These studies were also performed in batch using Cr(VI) solutions with concentrations between 20 and 200 mg L^{-1} and pH 7.0. Solution volumes of 20 mL were added to 50 mg of MPCh-EDA-FeCL and the system maintained under constant stirring in a temperature controlled system for a period of 60 min. This procedure was performed at temperatures of 25, 30, 35, 40 and 45 °C. The concentration of Cr(VI) was then determined by AAS.

Adsorption thermodynamics

The adsorption thermodynamic parameters were calculated using equations 1 and 2:

$$\ln(K_d) = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \tag{1}$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{2}$$

where K_d is the distribution coefficient at different temperatures (298, 303, 308, 313 and 318 K) and is equal to the amount adsorbed at equilibrium (q_e in mg g^{-1}) divided by the equilibrium concentration (C_e in mg L^{-1}) at different temperatures ($K_d = q_e/C_e$) and R is the molar gas constant (8.314 J mol^{-1} K^{-1}), ΔH_{ads} is the heat of adsorption determined at constant adsorbate contents and is known as the isosteric heat of adsoprtion.[23]

The values of ΔH_{ads} and ΔS_{ads} were respectively obtained from the angular and linear coefficients obtained in by linear regression when plotting $\ln(K_d)$ versus (1/T). Equation 2 was applied to calculate the standard Gibbs free energy (ΔG_{ads}) at each temperature.[23]

RESULTS AND DISCUSSION

Characterization of MPCh-EDA-FeCL

Elemental analysis of carbon, hydrogen and nitrogen was performed for the materials obtained in steps 2 (MPCh-CL) and 3 (MPCh-EDACL) of the synthesis described above. The percentage contents of C, H and N obtained were, respectively, 37.74, 7.53 and 4.96% for MPChCL and 37.42, 7.46 and 7.14% for MPCh-EDACL. The increase in nitrogen content by 1.4 times for the product of step 3 proves that incorporation of amino groups on the chitosan structure was successful. This value corresponded to a yield of ethylenediamine incorporation equal to 40%. Incorporation of these groups represents a great advantage in adsorption processes, since they act as good sites for adsorption of metallic ions.[6] Figure 1S (Supplementary Material) shows the infrared spectra for pure chitosan, MPCh-EDA-FeCL and this material after adsorption of Cr(VI).

The spectrum presented in Figure 1S (A), referring to pure chitosan, showed the same characteristic absorption bands as material reported in literature,[12] which also deal with low molecular weight chitosan. The spectra shown in (B) and (C) differ little from that shown by the original chitosan, indicating no significant structural change or degradation of the material after incorporation of iron oxide with magnetic properties, nor changes to Cr(VI) adsorption. The main change in (B) compared to the starting material is the appearance of absorption bands below 600 cm^{-1} and disappearance of the absorption band at ~ 2725 cm^{-1}. The absorption bands below 600 cm^{-1} are attributed to stretching of the Fe-N and Fe-O bonds, signifying that the incorporation of Fe(III) to the base material was sucessful.[20] The band at ~ 2725 cm^{-1} referred to stretching of the C-H bond and was eliminated by overlapping of magnetic oxide particles which resulted in a lower degree of freedom for this bond.[12] Adsorption of Cr(VI) in biopolymer arrays often causes shifting of absorption bands in the infrared region and the major ligand groups to hexavalent chromium are carboxyl, amine, alkane and amide.[24,25] Thus, in Figure 1S (C) the adsorption band at ~ 3154 cm^{-1} may be attributed to the axial stretching of OH^- when superimposed on the amino group during the stretching required for hydrogen bonding between chitosan molecules. The spectrum also shows bands at ~ 2196 cm^{-1} for stretching of the C-H bond, at ~ 2013 cm^{-1} related to vibration of the C-H bond of the amino group, at ~ 1868 cm^{-1} referring to the vibration of the C-N bond of the tertiary amine, at ~ 1483 cm^{-1} for stretching of the C=O bond in the secondary amide, at ~ 1224 and 1174 cm^{-1} referring to C-H vibration, and at ~ 1003 cm^{-1} indicating the C-N bond.[12] Bands at ~ 878 and ~ 745 may be attributed to Cr=O and Cr-O bonds, respectively.[26]

Analyses were performed using the X -ray diffraction for samples of: chitosan, iron oxide, MPCh-EDACL and MPCh-EDA-FeCL. Diffractograms are presented in Figure 2.

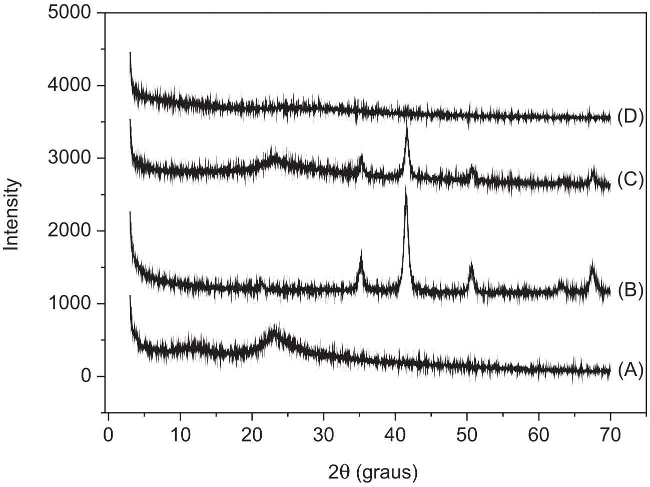

Figure 2. *X-ray diffractograms: pure chitosan (A), iron oxide with magnetic properties (B), the MPCh-EDACL (C) and MPCh-EDA-FeCL (D)*

According to Figure 2, for pure chitosan (A) two characteristic peaks at values of 2θ near 10 and 25° are observed. Peaks between 9 and 13° refer to the structure of the amorphous portion of chitosan, which is due to the random presence of amino groups (NH_2). The peaks between 15 and 25º refer to the crystalline portion of the biopolymer structure, which result from the packing of polymer chains as well as their interactions.[20]

The iron oxide diffractogram in Figure 2 (B), synthesized individually, and the MPCh-EDACL, Figure 2 (C), indicated that there was no significant structural change due to the incorporation of chitosan iron oxide since most of the peaks are overlapped, showing that there was only the deposition of iron oxide on its surface.

The diffractogram of MPCh-EDA-FeCL, Figure 2 (D), presented a crystallinity index less than the previous ones. This is due to the fact that interactions between biopolymers, such as chitosan and metal ions including Cr(VI), Ni(II), Fe(II) and Fe(III) affect crystallinity, resulting in the formation new crystalline phases based on new covalent bonds between the biopolymer and these ions.[20]

Study of Cr(VI) adsorption by different materials

The comparative study of Cr(VI) adsorption by different materials, obtained by modification or alteration of the MPCh-EDA-FeCL preparation stages, is shown in Figure 3.

Literature reports various materials that are used as magnetic cores in the synthesis of adsorbents, where iron oxides are most commonly used due to their biocompatibility, strong magnetic properties, low toxicity and ease of synthesis.[27] In this study the synthesized iron oxide is composed of goethite and maghemite, where only maghemite exhibits magnetic properties.[3] Maghemite and goethite present point of zero charge (PZC) equal to 7.50 and 7.85, respectively.[28,29] When the pH of the medium is lower than the PZC, the iron oxide (maghemite and goethite) presents a positive charge, contributing to increase the adsorption capacity of the Cr(VI) ion by chitosan, as shown in Figure 3. It is also observed from Figure 3 that the incorporation of iron oxide, ethylenediamine and Fe^{3+} to the chitosan matrix (MPCh-EDA-FeCL) resulted in a considerable gain in the adsorption capacity of Cr(VI). The MPCh-EDA-FeCL showed greatest removal (91.3%) among the materials analyzed, i.e., a gain of 77.1% compared to the original chitosan (ChCL), which make them promising for the treatment contaminated water. Thus, the MPCh-EDA-FeCL were selected for further studies.

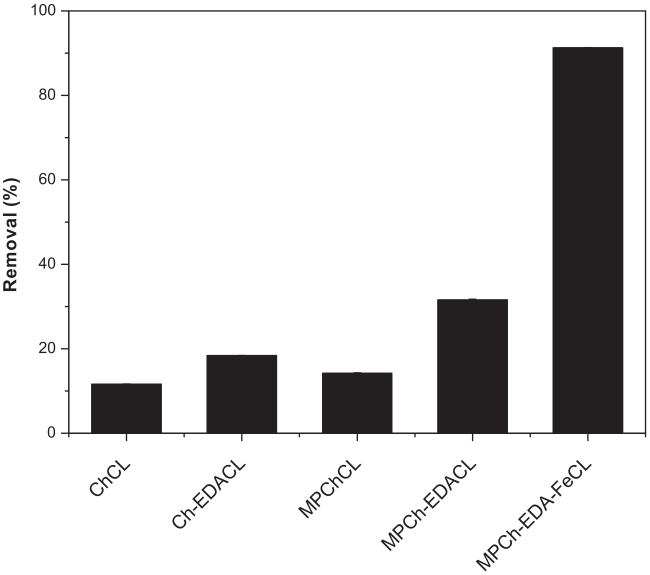

Figure 3. *Evaluation of the adsorption efficiency of Cr (VI) by different materials*

Effect of initial pH

Evaluation of the initial pH for the aqueous solution is an important factor to be considered in an adsorption process because it generally regulates the surface charge and the degree of ionization of the sorbent, and also the concentration and distribution of different adsorbate species in the medium.[1,23,30] Figure 4 shows the adsorption percentage of Cr(VI) by the MPCh-EDA-FeCL for each of the pH values studied.

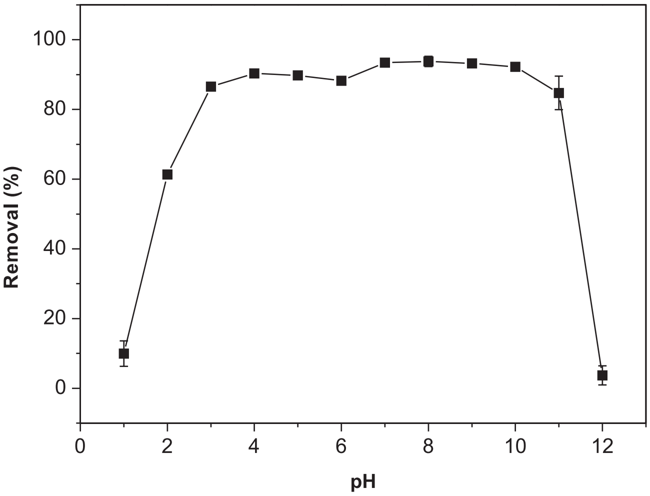

Figure 4. *Effect of the initial solution pH on adsorption of Cr(VI) by the MPCh-EDA-FeCL*

According to Figure 4 the lower adsorption efficiencies of Cr(VI) presented by MPCh-EDA-FeCL were found for the extreme pH values studied (1 and 12). At pH 1, only 9.9% of Cr(VI) was removed from the original solution while at pH 12, only 3.7%. The reduction in adsorption capacity at pH values lower than 2 is due to competition between protons (H^+) from the aqueous medium and the Cr(VI) species for the adsorption sites of MPCh-EDA-FeCL. In this case, H_2CrO_4 is the predominant species and because it does not present a charge does not favor adsorption.[21] At pH 12, the high concentration of hydroxyl ions (OH^-) in aqueous medium associated with complete deprotonation of the amino groups were responsible for making the surface charge of MPCh-EDA-FeCL negative, which directly affected the attraction of ions such as CrO_4^{2-}, and consequently resulted in a marked decrease in the adsorption of Cr(VI).[24,31] Moreover, at pH > 10, the adsorption of Cr(VI) is also favored due to little competition between hydroxyls of the medium and the predominate Cr(VI) species, CrO_4^{2-}.[20,21]

The highest adsorption capacities were observed in the pH range between 3 and 11, where there was a plateau in the percentage Cr(VI) removal. For this pH range the adsorption was between 84.7% and 93.8%. These results indicated that MPCh-EDA-FeCL can be used in conditions ranging from slightly acidic to slightly basic without loss of efficiency.

Chitosan has a point of zero charge (pH_{pzc}) at pH 6,3 and maghemite and goethite present point of zero charge (PZC) equal to 7.50 and 7.85, respectively.[20,28,29] With the increase in pH, the charge of the adsorvent without iron (MPCh-EDA-CL) become less positive. At $pH > pH_{pcz}$, it surface becomes negatively charged, so that it repels the anionic species.[20] Thus, it can be concluded that as pH increases, there occurs formation of oxyanions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) which are adsorbed by the positive adsorption site generated by iron complexed in the MPCh-EDA-FeCL.[20] The high removal percentages are mainly related to the presence of Fe(III) in the structure of the adsorbent (Figure 1) and how this interacts with the main species of Cr(VI) in the aqueous medium.[3,14,20,21,31]

Considering that one of the objectives of this work is to use the adsorbent MPCh-EDA-FeCL for the removal of Cr(VI) from wastewater of electroplating processes already at conditions to be discharged in water bodies, all further studies were conducted at pH 7.

Adsorption kinetics

The relationship between the amount of Cr(VI) adsorbed versus time for different concentrations (100, 150 and 200 mg L^{-1}) is shown in Figure 2S (supplementary material). In Figure 2S it is observed that the Cr(VI) adsorption rate is very fast in the first 10 minutes. The maximum quantity of the metal adsorbed is obtained at 10, 30 and 60 minutes for the concentrations of 100, 150 and 200 mg L^{-1}, respectively. Adsorption is rapid in the early stages because the adsorption rate is directly related to the concentration gradient, which decreases as saturation of the adsorption sites occurs.[5,22] In the first 10 minutes adsorption reached values equal to 34.02, 43.35 and 48.38 mg g^{-1} for concentrations of 100, 150 and 200 mg L^{-1}, respectively. As of 10 minutes until the equilibrium time there was no significant increase in adsorption, i.e., there occurred an increase of only 6.01 and 13.2 mg g^{-1}, respectively, at the concentrations of 150 and 200 mg L^{-1}. In literature, many papers report different times obtained for the adsorption of Cr (VI) on modified chitosan matrices. For example, Hu *et al.,*[21] obtained a time of about 10 minutes for adsorption on ethylenediamine-modified crosslinked magnetic chitosan resin (EMCMR). Nthumbi *et al.,*[32] found at time of 20 minutes when using chitosan/polyacrylamide nanofibres and Yavuz *et al.,*[33] obtained 240 minutes when adsorption was on alkyl-substituted polyaniline/chitosan (sPANIs/Ch-HCl).

Results obtained in the kinetic study of Cr(VI) adsorption by MPCh-EDA-FeCL were also treated in the form of two kinetic models: pseudo-first order and pseudo-second order.

The pseudo-first order model is given by equation 3, where K_1 (min^{-1}) is the first order adsorption constant:[34]

$$\log(qe - qt) = \log q_e - \frac{K_1}{2,303} t \tag{3}$$

The pseudo-second order model is represented by equation 4, where K_2 is the second-order constant (g mg^{-1} min^{-1}):[21]

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 q_e^{\,2}} \tag{4}$$

In both models, qt and qe (mg g^{-1}) are, respectively, the quantities of Cr(VI) adsorbed per unit mass at time t and at equilibrium; the variables K_1 and K_2 were obtained by linear regression and are shown in Table 1.

In Table 1 it was observed from the high coefficients of determination ($R^2 > 0.991$) that the pseudo-second order model is the most appropriate to describe Cr(VI) adsorption by MPCh-EDA-FeCL. Moreover, it was found that the estimated values of adsorption capacity (qe) for this model are very similar to the values obtained experimentally (qe exp). Fit of this model indicated that chemisorption is involved in controlling the speed of adsorption.[35] For this model it was found that K_2 increases as the concentration of Cr(VI) decreases, which confirms the inverse relationship between these two quantities.[36]

Isotherms and the effect of temperature

The equilibrium data of Cr(VI) adsorption was explored using the Langmuir and Freundlich isotherm model in order to determine the correlation between the mass of the solid phase and equilibrium concentration in the aqueous phase. The adsorption capacity according to the Langmuir model is given by equation 5:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_{max} (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants related to the adsorption capacity and energy, q_e is the amount of the metal ion adsorbed (mg g^{-1}) and C_e is the equilibrium concentration, in mg L^{-1}. This model assumes that monolayer adsorption occurs, there is no interaction between the ions adsorbed and the adsorption sites are identical.[37]

The experimental graph was obtained by plotting q_e versus C_e (supplementary material – Figure 3S) and values of the Langmuir constants (q_{max} and K_L) were obtained by the non-linear regression method and are shown in Table 2.

Table 1. Kinetic parameters for adsorption of Cr(VI) by the MPCh-EDA-FeCL

C_o (mg L^{-1})	qe exp (mg g^{-1})	Pseudo-first order			Pseudo-second order		
		K_1 (min^{-1})	qe (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	qe (mg g^{-1})	R^2
100	37.32	1.42 x 10^{-2}	3.10	0.979	1.23 x 10^{-2}	37.64	0.999
150	48.62	1.11 x 10^{-2}	6.15	0.969	5.42 x 10^{-3}	49.36	0.999
200	60.44	6.75 x 10^{-3}	23.84	0.982	1.64 x 10^{-3}	61.58	0.991

Table 2. Parameters of the Langmuir and Freundlich isotherms for adsorption of Cr(VI) by MPCh-EDA-FeCL

Isotherm model		Temperature (°C)				
		25	30	35	40	45
Langmuir	q_{max} (mg g^{-1})	81.04	68.28	59.12	67.48	62.59
	K_L (L mg^{-1})	0.15	0.13	0.13	0.13	0.07
	R_L	0.026	0.031	0.031	0.031	0.053
	R^2	0.981	0.988	0.993	0.995	0.996
Freundlich	k_F ((L g^{-1})	18.71	16.16	15.29	16.06	10.32
	n	2.6225	2.9499	2.9674	2.9674	2.5063
	R^2	0.998	0.996	0.991	0.996	0.987

The parameter R_L (Equation 6) is a dimensionless constant called the equilibrium parameter, which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where C_0 is the highest concentration (mg L^{-1}) and K_L is the Langmuir constant. Values of $R_L > 1$ indicate that the process is unfavorable, $R_L = 1$ indicates a linear isotherm, $0 < R_L < 1$ indicates favorable adsorption and $R_L = 0$ indicates that the process is irriversible.[22,38]

The Freundlich isotherm is an empirical equation that assumes that the adsorption process occurs in multilayers on heterogeneous surfaces and the adsorption capacity is related to the concentration of Cr(VI) in equilibrium.[3] The Freundlich equation is given by equation 7:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where q_e and C_e are, respectively, the amount adsorbed (mg g^{-1}) and the equilibrium concentration of the adsorbate (mg L^{-1}); K_F and n are the constants related to the Freundlich adsorption capacity and intensity, respectively.

The experimental graph was obtained by plotting q_e versus C_e and values of the Freundlich constants (K_F and n) were obtained by the non-linear regression method, as shown in Table 2.

As shown in Table 2, data of the Cr(VI) adsorption equilibrium by MPCh-EDA-FeCL fit to the two models studied, since the coefficient of determination (R^2) approached one in both cases. Values of q_{max} obtained from the Langmuir model were between 81.04 and 59.12 mg g^{-1}, where the highest value was obtained for the temperature of 25 °C, indicating that adsorbing Cr(VI) on MPCh-EDA-FeCL is more favorable at lower temperatures. These maximum adsorption capacities demonstrate the great efficiency of the adsorbent material compared to other others chitosan materials also applied for removal of Cr(VI), such as magnetic chitosan resin modified with ethylenediamine (51.813 mg g^{-1}),[21] chitosan flakes (22.09 mg g^{-1}),[6] high molecular weight chitosan (35.6 mg g^{-1}),[39] chitosan quaternary salt (30.2 mg g^{-1}),[40] chitosan-polyacrylamide nanofibers (0.26 mg g^{-1}),[32] protonated crosslinked chitosan beads (7.518 mg g^{-1}),[40] carboxylated crosslinked chitosan beads (8.264 mg g^{-1})[41] and grafted crosslinked chitosan beads (9.340 mg g^{-1}),[41] poly(2-ethylaniline)/chitosan (P2EANI/Ch-HCl) (2.83 mmol g^{-1})[33] and graphene oxide functionalized with magnetic cyclodextrin–chitosan (67.66 mg g^{-1}).[42]

The values of $0 < R_L < 1$ also showed that adsorption is favorable for the temperature and concentration range evaluated. Because the constant related to the solute-surface binding energy of the adsorbent (b) was virtually unchanged, it was concluded that the binding energy is little dependent on temperature.

For the Freundlich model, K_F values ranged from 18.71 to 10.32 L g^{-1} and the magnitude of this constant also showed a tendency to increase with decreasing temperature. Because the values of n were greater than one, the adsorption process was also favorable for this model.[25]

The experimental data for Cr(VI) adsorption by MPCh-EDA-FeCL at different temperatures was used to calculate the thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). These results are presented in Table 3.

Table 3. Thermodynamic parameters of Cr(VI) adsorption by MPCh-EDA-FeCL

Temperature/K	ΔG° /kJ mol^{-1}	ΔH° /kJ mol^{-1}	ΔS° /kJ mol^{-1}K^{-1}
298	- 14.22	- 39.85	- 0.086
303	- 13.79		
308	- 13.36		
313	- 12.93		
318	- 12.50		

As shown in Table 3, negative values of ΔG° indicate that Cr(VI) adsorption by MPCh-EDA-FeCL is favorable, spontaneous and that there is a high affinity of metal ions on the adsorbent surface. The negative value of ΔH° indicates that the adsorption process presents exothermic nature, which is evidenced by decreased adsorption with increasing temperature.[21,43,44] Magnitude of the ΔH° may also confirm the nature of adsorption, i.e. between 2.1 and 20.9 kJ mol^{-1} suggests that the adsorption process is physical and between 20.9 and 418.4 kJ mol^{-1} is chemical.[25] Thus, the value of ΔH° found (-39.85) indicates that adsorption of Cr(VI) occurs by chemisorption, confirming the information obtained by the pseudo-second order kinetic model. The negative value of ΔS° is related to the decrease in disorder at the solid-liquid interface.[3]

Desorption

Reuse of the MPCh-EDA-FeCL was investigated via adsorption/desorption cycles using a 0.1 mol L^{-1} NaOH solution as the desorbent. Thus, MPCh-EDA-FeCL were previously saturated with Cr(VI) and subsequently left in contact with 5 mL of the desorbent solution. After five consecutive adsorption/desorption cycles the material still showed good Cr(VI) adsorption capacity, i.e., 95.3, 85.2, 79.2, 70.4 and 62.3%, respectively, from the first to fifth cycle. These results indicate that MPCh-EDA-FeCL may be successfully regenerated and reused several times in the adsorption of Cr(VI) without the need to be substituted with new material.

Application of the MPCh-EDA-FeCL in electroplating effluent

To evaluate the Cr(VI) removal efficiency by MPCh-EDA-FeCL in a real sample, an effluent sample from the electroplating industry was collected. Speciation of Cr(III) and Cr(VI) in the effluent sample was performed according to the method proposed in literature.[45] Evaluation of the efficiency of MPCh-EDA-FeCL on Cr(VI) adsorption in the effluent was performed by obtaining an adsorption isotherm at 25 °C. The isotherm was constructed employing concentrations in the range of 5 to 250 mg L^{-1}, obtained from dilutions of the effluent sample. The effluent used had concentrations, in g L^{-1}, of total Cr, Cr(VI) and Cr(III), respectively, equal to 24.152, 18.132 and 6.020. The value of q_{max} (66.18 mg g^{-1}) was low when compared to the values shown in Table 2, which is probably due to the presence of other anionic species in the effluent sample which compete for adsorption sites. For the effluent sample used, the concentrations of PO_4^{3-}, NO_3^-, Cl^- and SO_4^{2-} were 0.20, 2.040, 450 and 1.22 mg L^{-1}, respectively. The adsorbent showed to be adequate and promising, since when applied in this effluent sample it was able to remove Cr(VI) to levels below those allowed for the discharge of effluents into water bodies (0.1 mg L^{-1}),[46] in cases where the initial Cr(VI) concentrations were below 60 mg L^{-1}.

CONCLUSIONS

The present study shows that the MPCh-EDA-FeCL can be used as an effective adsorbent for the removal of Cr(VI) in aqueous solutions. Fe^{3+} in the MPCh-EDA-FeCL permitted that adsorption of Cr(VI) occurred with maximal efficiency in the pH range of 3 to 11. These results indicated that the MPCh-EDA-FeCL can be used in conditions ranging from slightly acidic to slightly basic without efficiency loss. The MPCh-EDA-FeCL showed a rapid removal of Cr(VI), where the maximum amount removed was obtained after 10, 30 and 60 minutes for the concentrations of 100, 150 and 200 mg L^{-1}, respectively. Fit of the experimental data to the pseudo-second--order model indicated that adsorption occurs by chemisorption. Equilibrium adsorption values fit well to the Langmuir and Freundlich models. The maximum adsorption capacities calculated from the Langmuir model were 81.04, 68.28, 59.12, 67.48 and 62.59 mg g^{-1}, respectively, for the temperatures of 25, 30, 35, 40 and 45 °C. The thermodynamic parameters were determined and indicated the spontaneous, exothermic and chemical nature of adsorption. Results of the adsorption-desorption cycles showed that the adsorbent can be easily regenerated with a 0.1 mol L^{-1} NaOH solution and removed from the aqueous solution by a magnetic field, which makes it economically viable in practical applications. The results were also satisfactory when the MPCh-EDA-FeCL were employed in removal of Cr(VI) from the electroplating effluent.

SUPPLEMENTARY MATERIAL

Figures 1S, 2S and 3S are available at http://quimicanova.sbq.org.br, in the form of a PDF file with free access.

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PREPARATION AND EVALUATION OF MAGNETIC CHITOSAN PARTICLES MODIFIED WITH ETHYLENEDIAMINE AND Fe(III) FOR THE REMOVAL OF Cr(VI) FROM AQUEOUS SOLUTIONS

Thiago V. Toledo[a], Carlos R. Bellato[a,*], Carlos H. Ferreira de Souza[a], Junielly T. Domingues[a], Danilo de C. Silva[a], César Reis[a] e Maurício P. Ferreira Fontes[b]
[a]Departamento de Química, Universidade Federal de Viçosa, Campus Universitário, s/n, 36570-000 Viçosa – MG, Brasil
[b]Departamento de Solos, Universidade Federal de Viçosa, Campus Universitário, s/n, 36570-000 Viçosa – MG, Brasil

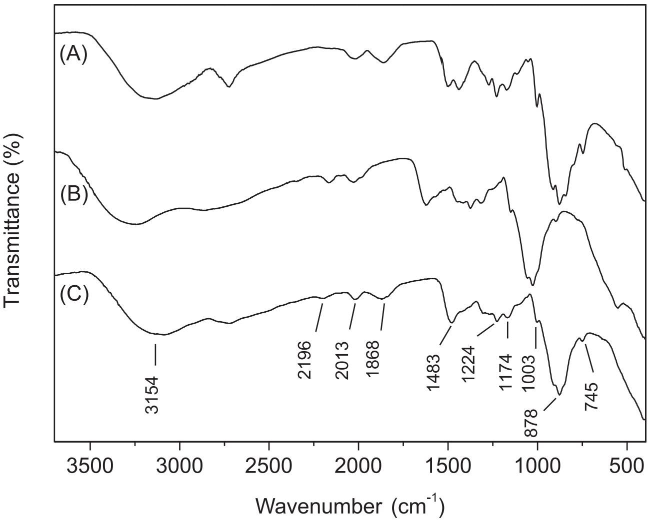

Figure 1S. *Infrared spectra obtained for pure chitosan (A), MPCh-EDA-FeCL (B) and MPCh-EDA-FeCL after absorption of Cr(VI) (C)*

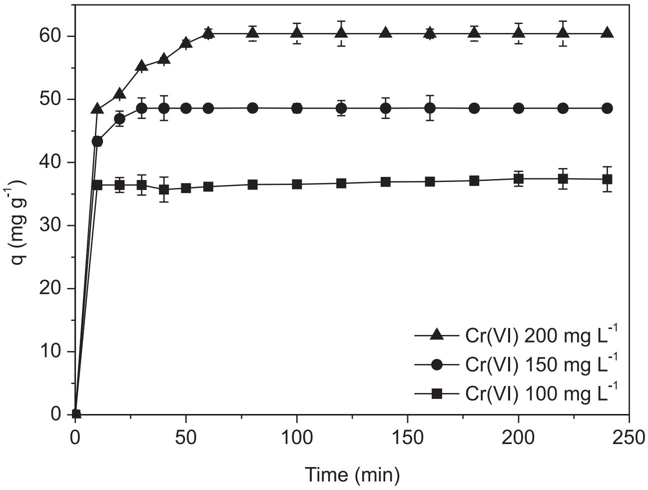

Figure 2S. *Effect of the contact time on adsorption of Cr(VI) by MPCh-EDA-FeCL for initial concentrations of 100 (■), 150 (●) and 200 mg L^{-1} (▲) of the adsorbate*

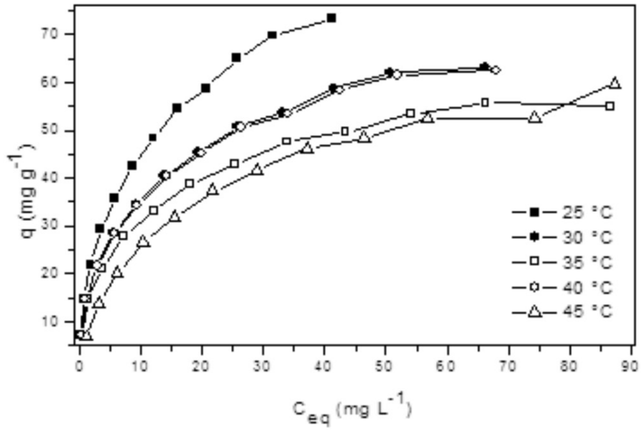

Figure 3S. *Experimental adsorption isotherms of Cr(VI) by MPCh-EDA-FeCL for different temperatures*

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*e-mail: bellato@ufv.br