



Bionanocomposites based on layered silicates and cationic starch as eco-friendly adsorbents for hexavalent chromium removal

Journal:	<i>Dalton Transactions</i>
Manuscript ID:	DT-ART-01-2014-000330.R1
Article Type:	Paper
Date Submitted by the Author:	21-Feb-2014
Complete List of Authors:	Koriche, Yamina; Université Khemis Miliana, Darder, Margarita; Instituto de Ciencia de Materiales de Madrid, Department of Porous Materials and Intercalation Compounds Aranda, Pilar; CSIC, Instituto De Ciencia De Materiales De Madrid Semsari, Saida; University of Blida, Ruiz-Hitzky, Eduardo; Instituto de Ciencia de Materiales de Madrid, CSIC, Instituto de Ciencia de

ARTICLE

Bionanocomposites based on layered silicates and cationic starch as eco-friendly adsorbents for hexavalent chromium removal

Cite this: DOI: 10.1039/x0xx00000x

Yamina Koriche,^{a,b,c} Margarita Darder,^a Pilar Aranda,^a Saida Semsari,^b and Eduardo Ruiz-Hitzky^aReceived 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Functional bionanocomposites based on two layered silicates, the commercial montmorillonite known as Cloisite[®] and a natural bentonite from Algeria, were prepared by intercalation of cationic starch, synthesized with two different degrees of substitution, 0.85 and 0.55. After characterization of the prepared bionanocomposites by XRD and zeta potential measurements, batch studies were conducted to evaluate the adsorption capacity of hexavalent chromium anions from aqueous solution. The adsorption isotherms, adsorption kinetics, and the effect of pH on the process were studied. The removal efficiency was evaluated in the presence of competing anions such as NO₃⁻, ClO₄⁻, SO₄²⁻ and Cl⁻. In order to regenerate the adsorbent for its repeated use, the regeneration process was studied in two different extractant solutions, 0.1 M NaCl at pH 10 and 0.28 M Na₂CO₃ at pH 12.

1. Introduction

Bionanocomposites represent an emerging group of advanced materials resulting from the assembly of biopolymers and diverse inorganic solids, most commonly layered silicates belonging to the clay minerals group. These materials show improved structural and functional properties similarly to conventional nanocomposites, and also offer non-toxicity, biocompatibility and biodegradability associated with the biopolymer counterpart.¹⁻⁴ The use of clay minerals of natural origin also contributes to these non-toxic and biocompatible characteristics of the resulting materials. Layered silicates of the smectite family are the most commonly used inorganic solids in the preparation of hybrid and biohybrid materials, including the groups of organoclays and bionanocomposites,

based on the intercalation of molecular or polymeric (bio)organic species.^{5,6} Smectites are 2:1 phyllosilicates comprising two sheets of Si tetrahedral sheets sandwiching one octahedral sheet that contains Al or Mg ions, and showing swelling ability in water as well as cationic exchange capacity due to the negative charge of the silicate layers.⁷ Among many other applications of hybrid materials derived from clays, organoclays and bionanocomposites are receiving application as adsorbents for environmental remediation.⁸ Some recent examples are the application of chitosan-montmorillonite bionanocomposites to efficiently adsorb a wide diversity of pollutants like herbicides,⁹ dyes¹⁰ or As(V) and Cr(VI) anions,¹¹ or the cationic starch/clay bionanocomposite reported previously as an effective low-cost and ecofriendly adsorbent for organic anionic pollutants such as the Congo red dye and the 2,4-D herbicide.¹² In fact, abundant and low-cost neutral polymers like starch, commonly used to prepare green nanocomposites, can be easily modified by covalently grafting of functional groups with the aim of improving the adsorption capacity of this biopolymer.^{13,14} Its functionalization with quaternary ammonium groups introduces anion-exchange properties and it is also helpful to facilitate the biopolymer assembling with charged clay minerals in order to produce more stable adsorbents, favoring the intercalation of the polysaccharide chains in the interlayer space of layered silicates (Scheme 1) compared to the neutral starch.^{12,15} The presence of the silicate layers within the bionanocomposite material

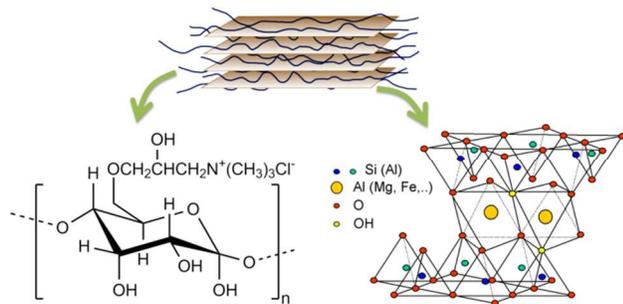
^aInstituto de Ciencia de Materiales de Madrid, CSIC, C/Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain. E-mail: eduardo@icmm.csic.es

^bLaboratoire de Génie Chimique, Département de Chimie Industrielle, Université Saad Dahleb, 09000 Blida, Algeria

^cUniversité de Khemis Miliana, Route de Theneit Alhad, 44225 Khemis Miliana, Algeria.

† Electronic Supplementary Information (ESI) available: EDX spectra of CST1/CL bionanocomposites before and after adsorption of chromate anions; fitting of kinetics data to the pseudo-first order and pseudo-second order models; mole fraction of Cr(VI) species as a function of pH; mole fraction of phosphate species as a function of pH. See DOI: 10.1039/b000000x/

contributes to increase the stability in water of the cationic starch and to allow its easy recovery from the aqueous solution after the adsorption process.



Scheme 1 Bionanocomposite based on the intercalation of cationic starch functionalized with quaternary ammonium groups in the layered silicate montmorillonite.

Chromium is one of the most dangerous harmful heavy metals. Its most stable oxidation states in the environment are Cr(III) and Cr(VI). While Cr(III) is an essential element for living beings and plays an important role in carbohydrate metabolism,¹⁶ Cr(VI) is a strong oxidant irritating plant and animal tissues and it is also carcinogenic and mutagenic.¹⁷ It has a great mobility in the chromate form (CrO_4^{2-}), which is extensively used in industrial processes such as electroplating, leather tanning, wood preservations, manufacturing of dye, paint and paper.¹⁸ The maximum permissible limit of Cr(VI) for discharge into inland surface water is 0.1 mg/L. Thus, it becomes imperative to remove chromium from industrial wastes before discharging them into water or onto land. At present, several treatment technologies have been developed to remove chromium from water and waste water. Common methods include chemical precipitation, reverse osmosis, ion exchange, electrolysis, and adsorption.¹⁹ Among them, adsorption is one of the most economically favorable and technically and easily feasible method for removing Cr(VI) from wastewater. A wide variety of adsorbents has been reported,²⁰ including metal oxides,^{21,22} clay minerals,²³ layered double hydroxides,²⁴ biomass,²⁵⁻²⁷ industrial wastes,²⁸ and activated carbon²⁹⁻³¹ among others. Recently, diverse polymer-based nanocomposites including magnetic nanoparticles or clays like the polypyrrole/magnetite³² and the polypyrrole/palygorskite³³ materials have been tested as adsorbents for chromium removal, as well as the so-called bionanocomposites based on naturally occurring polymers, such as the abovementioned chitosan-montmorillonite material.¹¹

The aim of the present work is the preparation of functional bionanocomposites based on two layered silicates, the commercial montmorillonite known as Cloisite[®] and a natural bentonite from Algeria. Two cationic starch biopolymers with different degrees of substitution, 0.85 and 0.55, have been assembled to those clays for their application as adsorbents in the removal of chromate oxyanions (CrO_4^{2-}) from aqueous

solution. The efficiency of the adsorption process was studied in the presence of competing anions, such as NO_3^- , ClO_4^- , SO_4^{2-} and Cl^- , and the possibility of regenerating the adsorbent was also evaluated with two different extracting solutions in order to allow its repeated use.

2. Experimental section

2.1. Materials

Potato starch (ST) and glycidyltrimethylammonium chloride ((2,3-epoxypropyl) trimethyl ammonium chloride, GTAC) were supplied by Sigma-Aldrich. Sodium hydroxide was obtained from Fluka and absolute ethanol from J.T. Baker. Commercial Cloisite[®]Na (CL) was obtained from Southern Clay Products and the sodium bentonite (Bnt) was prepared from a natural bentonite (Maghnia deposit, Algeria) supplied by the Société des Bentonites d'Algérie (BENTAL) company. The purification and preparation of homoionic Na bentonite (Bnt) sample (< 2 μm fraction) have been done as described elsewhere.^{34,35} The chromate solutions were prepared with K_2CrO_4 obtained from Merck. Other reagents used in this work were all of analytical grade and the solutions were prepared with bidistilled water (resistivity of 18.2 $\text{M}\Omega\text{ cm}$) obtained with a Maxima Ultrapure Water system from Elga.

2.2. Preparation of cationic starch

Cationic starch (CST) with two different degrees of substitution, 0.85 and 0.55, was prepared according to previously reported methods.³⁶ Briefly, CST with DS 0.85 (CST1) was prepared by thoroughly mixing a 35% (w/v) suspension of native potato starch (non-gelatinized) with 10 mL of GTAC and 10 mL of an aqueous solution of 1.25 M NaOH. After magnetic stirring for 24 h at 70 °C under reflux, the reaction mixture was cooled down to room temperature and then the CST was collected by precipitation in absolute ethanol with stirring. The resulting product was washed thoroughly with absolute ethanol to eliminate the non-reacted GTAC and by-products, and finally the CST was filtered and dried at 40 °C for 24 h. The same procedure was followed for the preparation of the CST with DS 0.55 (CST2), but using 2.5 mL of GTAC. The nitrogen content in both CST was estimated by elemental analysis with a PerkinElmer 2400 series II CHNS/O elemental analyzer, and the degree of substitution DS was calculated according to the nitrogen content (N%) using equation 1, where N is the nitrogen amount estimated by chemical analysis (%), 162 the molecular weight of anhydroglucose unit and 151.5 is the molecular weight of GTAC.³⁶⁻³⁸

$$\text{DS} = \frac{162\text{N}}{(1400-151.5\text{N})} \quad (1)$$

2.3. Preparation and characterization of CST/clay bionanocomposites

The adsorption of CST on both smectites for the preparation of CST/clay bionanocomposites was carried out following the

procedure described in our previous work.¹² Briefly, bionanocomposites with initial 1:1 CST:CL or CST/Bnt mass ratio were prepared by mixing 150 mg of clay (Bnt or CL) suspended in 25 mL of bidistilled water with 25 ml of aqueous solutions containing 150 mg of CST. The mixtures were placed for 48 h in a thermostatic bath at 30 °C (± 2 °C) and the resulting hybrid materials were recovered by centrifugation, washed with bidistilled water to eliminate the excess of CST, and finally freeze-dried and later used in the chromate adsorption studies. The CST content was determined by CHN chemical analysis using the PerkinElmer 2400 series II CHNS/O elemental analyzer). The X-ray diffraction (XRD) patterns of the bionanocomposites were collected in a Bruker D8 T2T Advance diffractometer using a Cu-K α source, with a scan step of 2°/min between 2–70° 2 θ values. Zeta potential measurements were carried out using a Malvern Instruments Zetasizer Nano ZS. CST and CST/clay bionanocomposite suspensions (1.25 wt.%) were prepared in 0.1 M NaCl solutions with the desired pH in the range of 2–12 adjusted with 0.1 M HCl or 0.1 M NaOH and shaken for 24 h to attain stable suspensions.

2.4. Adsorption of hexavalent chromium anions

A solution of 3.83 mmol/L of K₂CrO₄ was prepared by dissolving the required amount of K₂CrO₄. Solutions of lower concentration were prepared by dilution. The adsorption isotherms were determined by batch equilibration of 25 mg of the adsorbent with 10 mL of chromate aqueous solution of initial concentration (C_0) between 0.076 and 0.766 mmol/L at pH around 7.5, the experiments were carried out in a thermostated bath with horizontal shaking at 25 °C for 24 h, centrifuged and the supernatant was analyzed for chromate concentration with UV–Vis spectrophotometer (Shimadzu UV-2401) at the appropriate wavelength corresponding to the maximum absorption of chromate (372 nm), after adjusting the pH value at 7.5. The amount of adsorption Q was calculated by the following equation:

$$Q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 is the initial chromate concentration and C_e is the concentration at equilibrium in the solution.

For the study of the adsorption kinetics, the mixture of 20 mL of 0.383 mmol/L chromate solution with 50 mg of the adsorbent was shaken in the bath shaker at 25 °C, varying the contact time from 5 to 240 min. The effect of pH on the adsorbed amount of CrO₄²⁻ was investigated by varying the pH of the 0.383 mmol/L solution using 0.1 M NaOH or 0.1 M HCl between pH 3.0 and pH 11 at 25 °C, using a dispersion of adsorbent of 2.5 g/L. The characteristic changes in the vibrational frequency of both bionanocomposites and the recovered bionanocomposite after adsorption of chromates were recorded using an attenuated total reflectance infrared (ATR-IR) spectrometer (Shimadzu, GladiATR10). The presence of chromium in the bionanocomposite after adsorption

was confirmed semi-quantitatively by energy-dispersive X-ray spectroscopy (EDX) with an EDAX detector TypeSDD Apollo 10 mounted on the FE-SEM equipment FEI-NOVA NanoSEM 230.

2.5. Effect of competing anions on the adsorbed amount of chromate anions

In order to study the competing effect of similar anions, the adsorption of chromate was measured in the presence of various inorganic anions commonly present in the industrial effluents at similar initial concentration. A series of 1:1 molar ratio chromate/competing anion solutions with a concentration of 0.383 mmol/L for each anion was prepared using sodium salts of H₂PO₄⁻, NO₃⁻, ClO₄⁻, SO₄²⁻ and Cl⁻, and the pH values of each solution was adjusted to 7.5. An amount (25 mg) of the adsorbent was added to 20 mL of each solution and the samples were kept at the same adsorption conditions mentioned above. Finally, the adsorbent was separated by centrifugation and the supernatant was analyzed for determining the CrO₄²⁻ concentration.

2.6. Regeneration/re-use experiment

For regeneration testing, 100 mg of the bionanocomposite exposed to 0.383 mmol/L chromate solution for 2 h were recovered and directly treated with 10 mL of two different extracting solutions, 0.1 M NaCl at pH 10 and 0.28 M Na₂CO₃ at pH 12, and shaken for 1 h at 25 °C. The solid sorbents were then separated and the desorbed chromate determined in order to evaluate the removal efficiency of each extracting solution. The solids treated with 0.28 M Na₂CO₃ at pH 12 were exposed to 1 mM HCl in order to eliminate the carbonate anions, then the solids were dried at 40 °C for 24 h and finally reused in successive adsorption-desorption cycles.

3. Results and discussion

3.1. Assembling of cationic starch to layered clays

The two cationic starch (CST) polysaccharides used in this study present a degree of substitution of 0.85 and 0.55 and are denoted as CST1 and CST2, respectively, which corresponds to 85 and 55 quaternary ammonium groups per 100 glucose units, as determined from the nitrogen content in each CST measured by CHN elemental analysis. This same technique allowed to estimate the final amounts of CST present in the bionanocomposites prepared from 1:1 CST/CL initial ratio, which were 32.8% and 44.8% for CST1/CL and CST2/CL, respectively, as well as in those materials prepared from 1:1 CST/Bnt initial ratio, yielding values of 30.2 % and 43.6% for CST1/Bnt and CST2/Bnt, respectively. In all cases, the specific surface area of the resulting bionanocomposites is close to 20 m²/g.

The XRD patterns of both CST/clay bionanocomposites (Fig. 1a, b) show higher values of the basal spacing (d_{001}) in the materials prepared with CST2 (2.74 nm for CST2/CL and 2.72

nm for CST2/Bnt) than in those prepared with CST1 (2.00 nm for CST1/CL and 1.94 nm for CST1/Bnt). This fact could be attributed to the smaller amount of positive charges in the CST2 chains, requiring the intercalation of large quantities of biopolymer in order to compensate the negatively charged sites of the silicate layers, as determined from the chemical analysis results. These large amounts of intercalated biopolymer would be responsible for the increased distance between the silicate layers observed in the CST2/clay materials. FESEM images of these bionanocomposites are shown in Fig. S1.

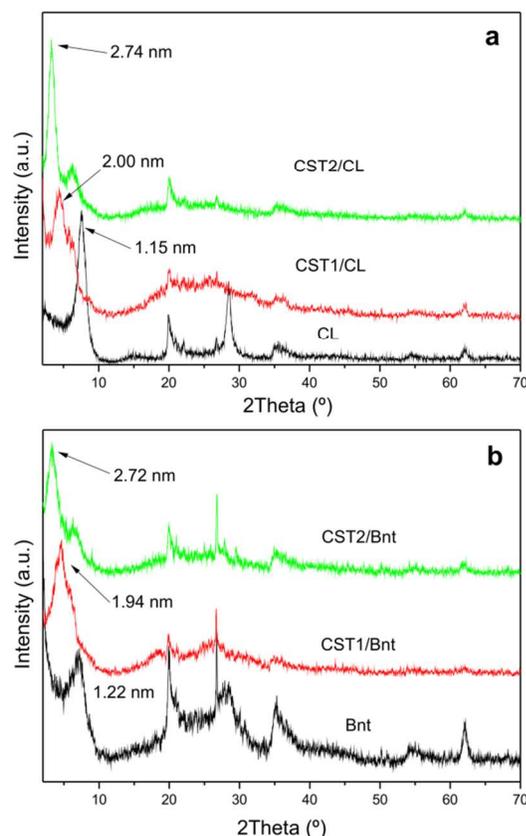


Fig. 1 XRD patterns of CL and CST/CL bionanocomposites (a), as well as of Bnt and CST/Bnt bionanocomposites (b).

3.2. Zeta potential characterization

Zeta potential curves as a function of pH for CST1 and CST2 are shown in Fig. 2a. The zeta potential values of all the samples were positive and ranged between 3.56 and 23.6 mV. As expected, CST1 showed the slightly superior values of the apparent zeta potentials than CST2, in accordance with the higher DS of CST1 in comparison to CST2. The zeta potential curves of Cloisite® (CL) and its bionanocomposites with CST1 and CST2 are shown in Fig. 2b. The negative zeta potential value of Cloisite® over the entire pH-range confirms the high anionic surface charge of this clay, which shows a high cationic exchange capacity (92 meq/100 g). Previous studies reported a similar result for the zeta potential of montmorillonite at the

same conditions.^{39,40} In the acidic medium (pH = 2), the zeta potential value of Cloisite® is less negative than at higher pH values and the reason may be due to the neutralization of a part of the anionic sites in the silicate layers with the protons present in the medium. Actually, Al³⁺ and Mg²⁺ ions located in the octahedral sheet can be lixiviated at this low pH conditions, modifying the clay structure and so affecting its surface charge.

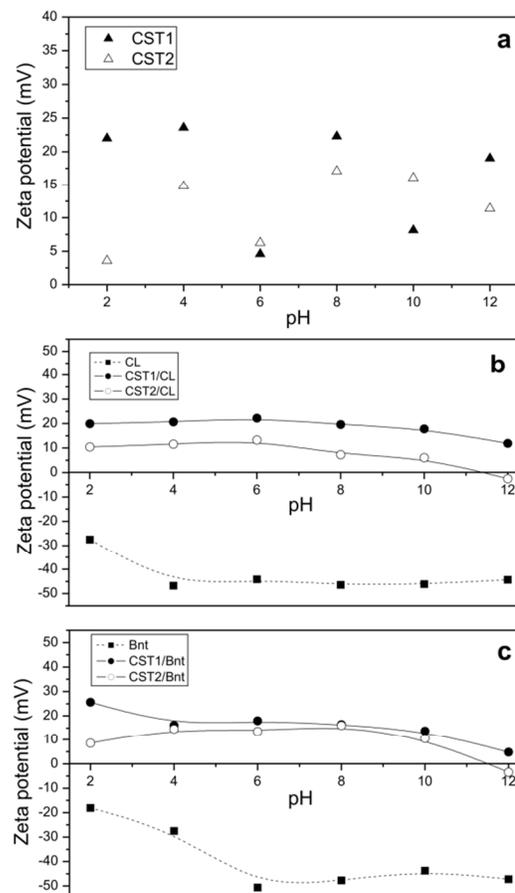


Fig. 2 Zeta potential as a function of pH for the CST1 and CST2 polysaccharides (a), for CL and the CST1/CL and CST2/CL bionanocomposites (b), as well as for Bnt and the CST1/Bnt and CST2/Bnt bionanocomposites (c).

The CST1/CL bionanocomposite exhibits a net positive charge in all the pH range due to the excess of a positive charge resulting from the high DS of CST1. The zeta potential values in the basic medium were slightly inferior to those in the acidic medium in all cases. The curve corresponding to the CST2/CL bionanocomposite presents the same tendency, and in addition this biohybrid material presents an isoelectric point at pH around 11.4, which can be due to the smaller excess of cationic groups in comparison to the material prepared from CST1. In the case of bionanocomposites based on Bnt (Fig. 2c), which shows also cationic exchange ability (72 meq/100 g), the variation of zeta potential as a function of pH presents the same behavior than that observed for the CST/CL bionanocomposites.

3.3. Adsorption of hexavalent chromium anions

The functionalization of layered clays with modified starch bearing cationic quaternary ammonium groups increases their degree of interaction with anionic pollutants and other negatively charged compounds, as previously reported.¹² Adsorption of CrO_4^{2-} anions onto CST/CL bionanocomposite was confirmed by means of FTIR and SEM-EDX analysis. Fig. 3 shows the FTIR spectra of CST1/CL bionanocomposite before and after adsorption of CrO_4^{2-} anions. In both cases, the spectra show the combination of the characteristic absorption bands due to the cationic starch and the clay:¹² $\nu_{\text{C-H}}(\text{CH}_2)$ at 2933 cm^{-1} and $\nu_{\text{C-H}}(-\text{N}(\text{CH}_3)_3)$ at 1477 cm^{-1} characteristic of the polysaccharide, as well as $\nu_{\text{H-O}}(\text{Si-OH})$ at 3620 cm^{-1} and $\nu_{\text{Si-O}}$ at 995 cm^{-1} due to the silicate. After contact with chromate anions, the spectrum of the bionanocomposite shows clearly the appearance of a new band around to 878 cm^{-1} corresponding to the asymmetric stretching vibration mode of the $\text{Cr}=\text{O}$ bond,⁴¹ due to the electrostatic interaction of the chromate oxyanions and the cationic charges present in the bionanocomposite.

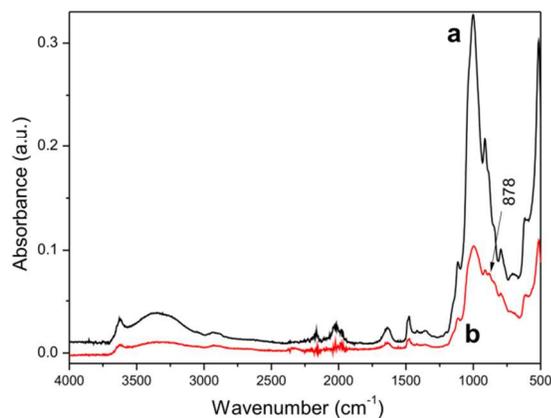


Fig. 3 ATR-IR spectra of CST1/CL adsorbent (a) before and (b) after the adsorption of chromate anions.

The energy-dispersive X-ray analysis (EDX) of the CST/clay samples (Fig. S2) also confirms the adsorption of chromate on the CST/CL adsorbent, as the presence of chromium is pointed out by the peak between 5 and 6 keV (Fig. S2b).^{42,43} The peak observed at around 2.6 keV, attributed to chloride ions, in the spectrum of the bionanocomposites before chromate adsorption (Fig. S2a) disappears after the adsorption process, appearing the new signal at 5-6 keV due to chromate anions (Fig. S2b). This fact confirms that the mechanism of the adsorption process is due to an anion exchange of the chloride anions by the chromate oxyanions in the cationic starch chains located at the surface and/or in the interlayer space of the clay.

3.3.1. ADSORPTION ISOTHERMS

A higher DS of CST in the bionanocomposites is expected to lead to a higher amount of cationic groups, and consequently to increase the adsorption capacity towards anionic molecules.

Thus, the adsorption of chromate oxyanion (CrO_4^{2-}) was studied on CST/clay bionanocomposites prepared from CST with DS 0.85 and 0.55. The adsorption isotherms of chromate by these materials are plotted in Fig. 4.

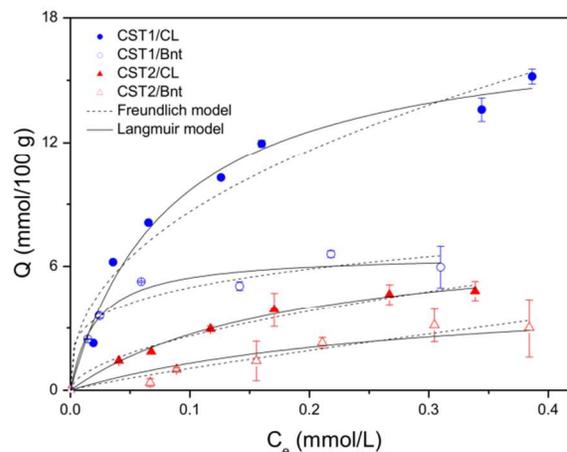


Fig. 4 Adsorption isotherms of chromate anions on CST/CL and CST/Bnt bionanocomposites at 25 °C.

The adsorption isotherms reveal the specific relation between the concentration of adsorbate and the adsorption capacity of an adsorbent at a constant temperature. In this study, two important adsorption models are selected, that is, Langmuir and Freundlich models.

The Langmuir isotherm assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is the most commonly used model for monolayer adsorption process, as represented by the following equation:⁴⁴

$$Q_e = \frac{Q_{\text{Max}} b C_e}{1 + b C_e} \quad (3)$$

where Q_e is the equilibrium adsorption capacity of CrO_4^{2-} on adsorbent (mmol/100g), C_e is the equilibrium CrO_4^{2-} concentration (mmol/L), Q_{Max} is the monolayer adsorption capacity of the adsorbent (mmol/100g) and b is the Langmuir adsorption constant (L/mmol).

The Freundlich isotherm equation, the most important adsorption isotherm for heterogeneous surfaces, is described by the following equation:⁴⁵

$$Q_e = K C_e^{1/n} \quad (4)$$

where Q_e is the equilibrium adsorption capacity of CrO_4^{2-} on adsorbent (mmol/100g), C_e is the equilibrium CrO_4^{2-} concentration (mmol/L), K is a constant related to the adsorption capacity and $1/n$ is an empirical parameter related to the adsorption intensity.

In this study, the experimental data were fitted to both models by non-linear regression and the resulting fitting parameters are summarized in Table 1 together with the correlation coefficient (R^2). The fitting curves from the two isotherms are also illustrated in Fig. 4.

Table 1 Parameters resulting from data fitting to Langmuir and Freundlich isotherms

	Freundlich			Langmuir		
	K_F	$1/n$	R^2	b (L/mmol)	Q_{Max} (mmol/100 g)	R^2
CST1/CL	23.11	0.427	0.948	11.87	17.80	0.984
CST2/CL	9.30	0.552	0.977	5.37	7.70	0.992
CST1/Bnt	8.63	0.240	0.923	47.09	6.60	0.960
CST2/Bnt	7.66	0.863	0.933	3.533	4.98	0.909

The correlation coefficients for the Langmuir model are closer to 1 than those obtained for the Freundlich model. In addition, the Q_{Max} values for the adsorption of CrO_4^{2-} onto the bionanocomposites calculated from the Langmuir model are very close to the experimental data. Obviously, the Langmuir model is much better to describe the adsorption of CrO_4^{2-} onto CTS/clays bionanocomposites than the Freundlich model, indicating the homogeneity of the adsorption sites in both CST/clays bionanocomposites. It can be also observed that the maximum adsorption capacity toward anionic species increased with the increase of the DS of CST, rather than with a higher amount of intercalated cationic polysaccharide. This behavior can be also related to the higher positive zeta potential values of the CST1/clay bionanocomposite in comparison to those of the CST2/clay material in all the pH range.

The effectiveness of CST/clay bionanocomposite adsorbent was compared in terms of the adsorption capacity with some reported eco-friendly adsorbents. For instance, the maximum adsorbed amounts of chromate onto chitosan with different deacetylation degrees,⁴⁶ chitosan cross-linked with epichlorohydrin,⁴⁷ carboxymethylcellulose,⁴⁸ and biopolymer beads of cross-linked alginate and gelatin⁴⁹ were 97.4 mg/g, 11.3 mg/g, 5.1 mg/g and 0.8 mg/g, respectively. These results indicated that the adsorption capacity of the CST/clay adsorbents proposed in this study (20.6 mg/g) is lower than pure chitosan but compares favorably with the other reported biopolymer-based materials. Anyway, the presence of the layered solid in the bionanocomposites is advantageous in order to afford an easier recovery of the biosorbent from the aqueous solution.

3.3.2. KINETICS STUDY

In order to investigate the mechanism controlling the adsorption process of CrO_4^{2-} on CTS/clay bionanocomposites, the pseudo-first order and the pseudo-second order kinetic models⁵⁰ were applied to evaluate the experimental data obtained from batch CrO_4^{2-} removal experiments (Fig. 5). Pseudo-first order or Lagergren's kinetics equation is based on the assumption that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time, and the linear form of the equation is given as:

$$\log(Q_e - Q_t) = \log(Q_e) - (K_1/2.303) t \quad (5)$$

where Q_e and Q_t are the amounts of adsorbed CrO_4^{2-} (mmol/100 g) at equilibrium and at a predetermined time (t), respectively, and K_1 (min^{-1}) is the rate constant of this equation. The fittings of the experimental data to the linear form of the pseudo-first order model are shown in Fig. S3a, and the values of the pseudo-first-order rate constants, K_1 and Q_e values for CST/clay bionanocomposites are listed in Table 2.

The linear form of the pseudo-second-order rate equation represented by Ho and McKay⁵⁰ is given as:

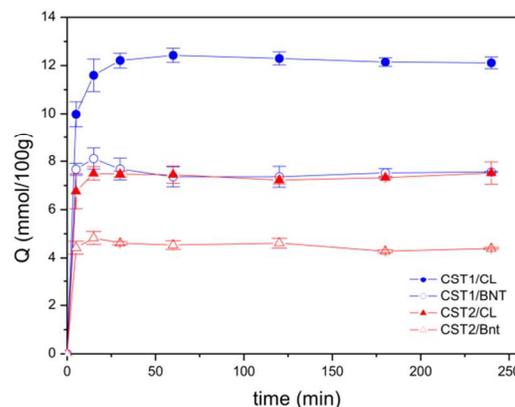
$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (6)$$

where Q_e and Q_t are the amounts of adsorbed CrO_4^{2-} (mmol/100 g) at equilibrium and at a predetermined time (t), respectively, and K_2 (g/mmol.min) is the pseudo-second order rate constant. The fittings of the experimental data to this form of the pseudo-second order model are shown in Fig. S3b, and the values of Q_e , K_2 and R obtained from this rate model are given in Table 2.

Table 2 Kinetic parameters for chromate adsorption

	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	K_1 (min^{-1})	Q_e (mmol/100 g)	R	K_2 (g/mmol.min)	Q_e (mmol/100 g)	R
CST1/CL	0.043	3.37	0.97	-310.4	12.16	0.99994
CST2/CL	0.0198	2.28	0.88	0.193	7.44	0.9998
CST1/Bnt	0.0273	3.60	0.92	0.87	7.52	0.9999
CST2/Bnt	0.0045	0.54	0.32	-0.13	4.34	0.9994

The correlation coefficients for the pseudo-second-order are better than those obtained with the pseudo-first-order kinetic model, suggesting that adsorption of chromate anions on these adsorbents follows a pseudo-second order model in all cases. Although it is difficult to corroborate a possible mechanism of interaction, it could be considered that the adsorption of CrO_4^{2-} takes place probably via surface exchange reactions until the surface functional sites are fully occupied, and thereafter CrO_4^{2-} anions could diffuse into the CST/clay layers for further interactions and/or reactions such as ion-exchange.

**Fig. 5** Kinetics of chromate adsorption by the CST/clay bionanocomposites.

3.3.3. EFFECT OF PH

The pH of the aqueous solution is an important parameter in many adsorption processes, especially when the involved ions are sensitive to pH, as it is the case of chromate. The removal of chromate oxyanions by CST/clay bionanocomposites was also found to be pH dependent. The effect of pH on the adsorption process was studied at 25 ± 1 °C, an initial CrO_4^{2-} ion concentration of 0.383 mmol/L, a contact time of 120 min, and with an adsorbent dosage of 0.5 g. The adsorbed amounts of Cr(VI) species onto CST/clay bionanocomposites at a pH range of 3–11 are shown in Fig. 6.

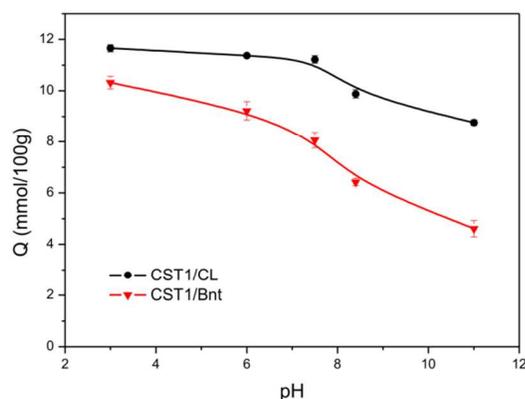


Fig. 6 Effect of pH on the adsorption of chromate by CST1/clay bionanocomposites.

It can be observed that the extent of adsorption on both CST/CL bionanocomposites shows the maximum values at pH below 7. Generally, the Cr(VI) species may be represented in various forms as chromic acid (H_2CrO_4), hydrogen chromate ion (HCrO_4^-) and chromate ion (CrO_4^{2-}), depending on the pH. H_2CrO_4 predominates at pH below 1, HCrO_4^- at pH between 1 and 6, and CrO_4^{2-} at pH values above 6. The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$), a dimer of HCrO_4^- minus a water molecule, is only formed when the concentration of Cr(VI) exceeds approximately 1 g/L.²⁰ Thus, in the current study the predominant species are HCrO_4^- at pH below 6, and CrO_4^{2-} above such value (Fig. S4). Given that the positive charge of the CST/CL bionanocomposites is assured in all the pH range due to the presence of the quaternary ammonium groups, electrostatic interaction can be established with both HCrO_4^- and CrO_4^{2-} species in the whole pH range. Thus, the decrease in the adsorbed amount of Cr(VI) as pH increases could be attributed to the predominance of CrO_4^{2-} anions, which require two ion-exchange sites for binding to the adsorbent, as well as to a possible competing effect with the increasing number of OH^- ions at the highest pH values. In fact, as above indicated it was observed a similar behavior of zeta potential, which was also slightly reduced at pH values higher than 6.

3.4. Effect of competing anions

In many cases, industrial wastewater, surface and underground waters contain various kinds of ions such as Cl^- , SO_4^{2-} , NO_3^-

and ClO_4^- which can interfere in the adsorption of hexavalent chromium. Therefore, it is necessary for a sorbent to afford a high selectivity toward the here considered hazardous ion. Fig. 7 shows the chromate adsorption in the presence of different competing anions from solutions at pH 7.5. This figure illustrates that chloride ions do not affect strongly the Cr(VI) adsorption, but NO_3^- , ClO_4^- and H_2PO_4^- ions can slightly reduce the uptake of chromate oxyanions by the occupation of the cationic sites of the bionanocomposite. The main competing anion was sulfate, leading to a reduction of the chromate adsorption amount around 35.5%. This effect can be due to the similar charge and hydration radius of sulfate and CrO_4^{2-} , which is the predominant species at pH 7.5. Table 3 collects the hydrated radius of CrO_4^{2-} and the studied competing anions. The degree of interference follows the sequence $\text{SO}_4^{2-} \gg \text{H}_2\text{PO}_4^- > \text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^-$, that is in agreement with the hydrated radii and charges of the different anions except for the phosphate species. In that case, the coexistence of the two species H_2PO_4^- and HPO_4^{2-} at pH 7.5 (Fig. S5) can be responsible for the considerable effect of this anion on the adsorption of chromate.

Table 3 Hydrated radius of CrO_4^{2-} and coexisting anions

Anions	Hydrated radius (Å)
Cl^- , NO_3^-	3
ClO_4^-	3.5
SO_4^{2-} , CrO_4^{2-}	4
H_2PO_4^-	4 - 4.5

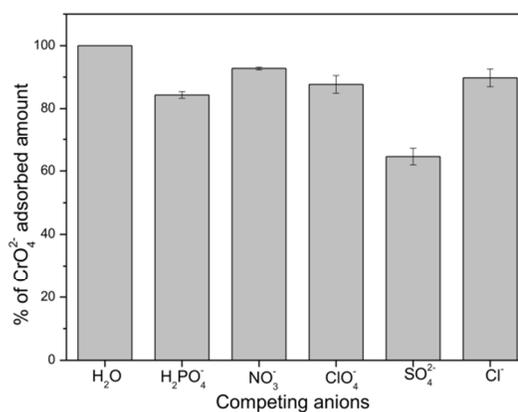


Fig. 7 Effect of competing anions on the chromate adsorption.

3.5. Regeneration tests and reuse experiments

In order to regenerate the adsorbent for its repeated use and for recovery of the adsorbed contaminants, two different extractants were studied: 0.1 M NaCl at pH 10 and 0.28 M Na_2CO_3 at pH 12. In both cases the regeneration mechanism is based on the anion exchange of adsorbed Cr(VI) species by chloride or carbonate anions. Fig. 8a shows that the most successful extraction was achieved in the first regeneration cycle, with both extractants giving similar extraction efficiency values around 95 and 92% for NaCl and Na_2CO_3 solutions,

respectively. In all cases, the extraction efficiency decreased after consecutive adsorption/regeneration cycles. In a second regeneration test, around 90% of the adsorbed chromate was extracted, and after a third use the extracted amounts were reduced to only 72 and 78% for NaCl and Na₂CO₃ solutions, respectively.

Fig. 8b shows the amount of adsorbed Cr(VI) after each regeneration test in consecutive adsorption/regeneration cycles. From this result, it was found that the regeneration with carbonate anions allows to adsorb the highest amount of Cr(VI) in the second and the third adsorption runs than the regeneration with chloride anions. These results can be explained by the increased affinity of the adsorbent towards CO₃²⁻ anions, due to its higher anionic charge, which can be more efficient for replacing the adsorbed CrO₄²⁻ anions by anion exchange. It is also noteworthy to mention that we can reuse this adsorbent several times by simple and low cost regeneration.

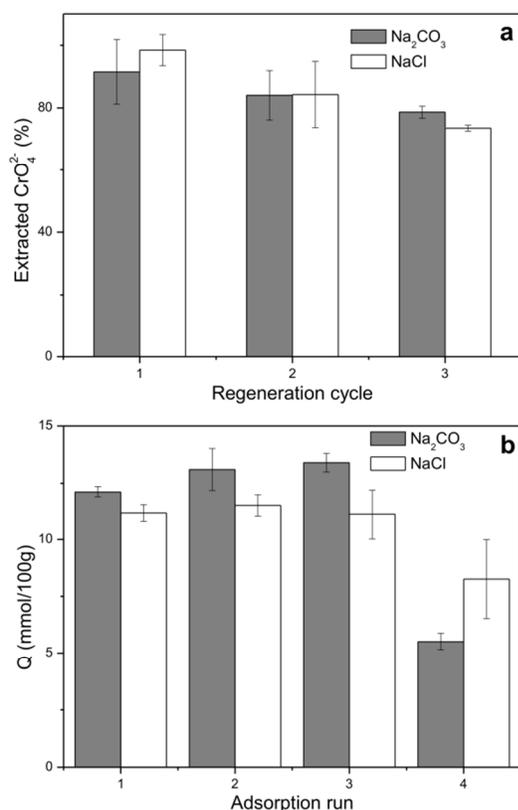


Fig. 8 Percentage of chromate extracted by different extractants from CST1/CL bionanocomposite (a) and the re-use of the regenerated adsorbent in consecutive adsorption runs (b).

Conclusions

Cationic starch (CST)/clay bionanocomposites were prepared by assembling the modified biopolymer to two layered silicates: a commercial Cloisite[®] and a purified bentonite. Starch was previously functionalized with quaternary ammonium groups in order to introduce anion-exchange properties and to facilitate its

assembly to the silicate layers. The bionanocomposites based on CST with small degree of substitution (DS = 0.55) show a large amount of assembled biopolymer, as well as high interlayer spacing values, compared with those based on CST with a higher DS (0.85). However, the latter materials show the highest zeta potential values, pointing out to an increased anion-exchange capacity of these CST/clay bionanocomposites. In fact, the material involving Cloisite[®] and CST with DS 0.85 exhibits the best efficiency in the removal of hexavalent chromium ions, reaching adsorption values around 20.6 mg Cr(VI)/g adsorbent. The adsorption process was well described by the Langmuir isotherm model, and the kinetic data were fitted by the pseudo-second-order model. The efficiency of the adsorption process was also successfully proved in the presence of competing anions, such as NO₃⁻, ClO₄⁻, SO₄²⁻ and Cl⁻, as well as the possibility of regenerating the adsorbents for reusing them in several adsorption cycles. The presence of the silicate layers within the bionanocomposite material was crucial to increase the stability in water of the cationic starch and to allow its easy recovery from aqueous solution after the adsorption process. These results show the potential interest of this type of low-cost biosorbents based on layered silicates of different origin in the removal of pollutants with potential interest in countries with tannery industry.

Acknowledgements

This work was supported by the CICYT, Spain (project MAT2012-31759) and the EU COST Action MP1202. The authors also thank Mr. A. Valera and Mr. C. Sebastián for technical assistance in the EDX measurements.

Notes and references

- 1 M. Darder, P. Aranda and E. Ruiz-Hitzky, *Adv. Mater.*, 2007, **19**, 1309.
- 2 E. Ruiz-Hitzky, M. Darder and P. Aranda, in *Bio-Inorganic Hybrid Materials: Strategies, Synthesis, Characterization and Application*, ed. E. Ruiz-Hitzky, K. Ariga and Y. Lvov, Wiley-VCH, Weinheim, 2008, Ch. 1, p. 1.
- 3 E. Ruiz-Hitzky, P. Aranda and M. Darder, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Hoboken, NJ., 2008, p. 1.
- 4 E. Ruiz-Hitzky, M. Darder and P. Aranda, in *Annual Review of Nanoresearch*, ed. G. Cao, Q. Zhang and C. J. Brinker, World Scientific Publishing, Singapore, 2010, p. 149.
- 5 E. Ruiz-Hitzky, P. Aranda, M. Darder and M. Ogawa, *Chem. Soc. Rev.*, 2011, **40**, 801.
- 6 E. Ruiz-Hitzky, P. Aranda and M. Darder, in *Tailored Organic-Inorganic Materials*, ed. E. Brunet, J. L. Colón and A. Clearfield, Wiley, (in press).
- 7 F. Bergaya, M. Jaber and J.-F. Lambert, in *Environmental silicate nano-bio-composites*, ed. L. Avérous and E. Pollet, Springer-Verlag, London, 2012, p. 41.

- 8 E. Ruiz-Hitzky, P. Aranda, M. Darder and G. Rytwo, *J. Mater. Chem.*, 2010, **20**, 9306.
- 9 R. Celis, M.A. Adelino, M.C. Hermosín and J. Cornejo, *J. Hazard. Mater.*, 2012, **209**, 67.
- 10 L. Wang and A. Q. Wang, *J. Hazard. Mater.*, 2007, **147**, 979.
- 11 J.H. An and S. Dultz, *Clays Clay Miner.*, 2008, **56**, 549.
- 12 Y. Koriche, M. Darder, P. Aranda, S. Semsari, and E. Ruiz-Hitzky, *Sci. Adv. Mater.*, 2013, **5**, 994.
- 13 G.-X. Xing, S.-F. Zhang, B.-Z. Ju and J.-Z. Yang, *Carbohydr. Polym.*, 2006, **66**, 246.
- 14 G. Xie, X. Shang, R. Liu, J. Hu and S. Liao, *Carbohydr. Polym.*, 2011, **84**, 430.
- 15 F. Chivrac, E. Pollet, M. Schmutz and L. Avérous, *Biomacromolecules*, 2008, **9**, 896.
- 16 S. Loyaux-Lawniczak, P. Lecompte and J.J. Ehrhardt, *Environ. Sci. Technol.*, 2001, **35**, 1350.
- 17 N. Sankararamkrishan, A. Dixit, L. Iyengar, S. Rashmi, *Bioresource Technol.*, 2006, **47**, 2377.
- 18 A.K. Meena, K. Kadirvelu, G.K. Mishra, C. Rajagopal, P.N. Nagar, *J. Hazard. Mater.*, 2008, **150**, 604.
- 19 K. Mukherjee, R. Saha, A. Ghosh and B.Saha, *Res. Chem. Intermediat.*, 2013, **39**, 2267.
- 20 D. Mohan and C. U. Pittman Jr, *J. Hazard. Mater.*, 2006, **B137**, 762.
- 21 E. Álvarez-Ayuso, A. García-Sánchez and X. Querol, *J. Hazard. Mater.*, 2007, **142**, 191.
- 22 V. Gosshu, Y.V. Tsarev and V.V. Kastrov, *Russ. J. Appl. Chem.*, 2009, **82**, 801.
- 23 J. J. Zachara, C. E. Cowan and R. L. Schmidt, *Clay. Miner.*, 1988, **36**, 317.
- 24 K. H. Goh, T. T. Lim and Z. Dong, *Water Res.*, 2008, **42**, 1343–1368.
- 25 D. C. Sharma and C. F. Forster, *Bioresource Technol.*, 1994, **49**, 31–40.
- 26 R. Chand, K.Narimura, H. Kawakita, K. Ohto, T. Watari and K. Inoue, *J. Hazard. Mater.*, 2009, **163**, 245.
- 27 H. Li, Z. Li, T. Liu, X. Xiao, Z. Peng and L. Deng, *Bioresource Technol.*, 2008, **99**, 6271–6279.
- 28 J. Pradhan, S.N. Das and R. Thakur, *J. Colloid Interface Sci.*, 1999, **217**, 137.
- 29 J.P. Chen and X. Wang, *Sep. Purif. Technol.*, 2000, **19**, 157.
- 30 B. Sandhya and A. K. Tonni, *Chemosphere*, 2004, **54**, 951.
- 31 K. Selvi, S. Pattabhi, and K. Kadirvelu, *Bioresource Technol.*, 2001, **80**, 87–89.
- 32 M. Bhaumik, A. Maity, V.V. Srinivasu and M. S. Onyango, *J. Hazard. Mater.*, 2011, **190**, 381.
- 33 C. Yao, Y. Xu, Y. Kong, W. Liu, W. Wang, Z. Wang, Y. Wang and J. Ji, *Appl. Clay Sci.*, 2012, **67–68**, 32.
- 34 H. Khalaf, O. Bouras and V. Perrichon, *Microporous Mater.*, 1997, **8**, 141.
- 35 O. Bouras, J. C. Bollinger, M. Baudu and H. Khalaf, *Appl. Clay Sci.*, 2007, **37**, 240.
- 36 J. Bendoraitiene, R. Kavaliauskaite, R. Klimaviciute and A. Zemaitaitis, *Starch/Stärke*, 2006, **58**, 623.
- 37 M. Zhang, B. Z. Ju, S. F. Zhang, W. Ma and J. Z. Yang, *Carbohydr. Polym.*, 2007, **69**, 123.
- 38 P. Wang, X. Wu, X. Dong-Hua, X. Kun, T. Ying, D. Xi-Bing and L. Wen-Bo, *Carbohydr. Res.*, 2009, **344**, 851.
- 39 M. Kosmulski and P. Dahlsten, *Colloid. Surface. A*, 2006, **291**, 212.
- 40 R. Goh, Y-K. Leong and B. Lehane, *Rheol. Acta*, 2011, **50**, 29.
- 41 M. M. Hoffmann, J. G. Darab and J. L. Fulton, *J. Phys. Chem. A*, 2001, **105**, 1772.
- 42 R. Aravindhnan, B. Madhan, J. Raghava Rao, B. U. Nair and T. Ramasami, *Environ. Sci. Technol.*, 2004, **38**, 300.
- 43 N. Rajesh, A.S. Krishna Kumar, S. Kalidhasan and V. Rajesh, *J. Chem. Eng. Data*, 2011, **56**, 2295.
- 44 I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1361.
- 45 H. Freundlich, *Z. Phys. Chem.* 1906, **57**, 385.
- 46 T.R. Santana Cadaval Jr., A.S. Camara, G.L. Dotto and L.A. de Almeida Pinto, *Desalin. Water Treat.*, 2013, **51**, 7690.
- 47 S. Qian, G. Huang, J. Jiang, F. He and Y. Wang, *J. Appl. Polym. Sci.*, 2000, **77**, 3216.
- 48 M. Y. Arica and G. Bayramoglu, *Colloid. Surface. A*, 2005, **253**, 203.
- 49 J. Bajpai, R. Shrivastava and A.K. Bajpai, *Colloid. Surface. A*, 2004, **236**, 81.
- 50 Y. S. Ho and G. McKay, *Process Saf. Environ.*, 1998, **76**, 183.

Bionanocomposites based on layered silicates and cationic starch as eco-friendly adsorbents for hexavalent chromium removal

Yamina Koriche,^{a,b,c} Margarita Darder,^a Pilar Aranda,^a Saida Semsari,^b and Eduardo Ruiz-Hitzky^{*a}

Graphical Abstract:

Functional bionanocomposites with ability to adsorb Cr(VI) anions were prepared by intercalation of cationic starch bearing quaternary ammonium groups in two layered silicates, a commercial Cloisite[®] and an Algerian bentonite.

