



Effects of sulfate ions and slightly acidic pH conditions on Cr(VI) adsorption onto silica gelatin composite

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ARTICLE INFO

Article history:

Received 23 July 2009

Received in revised form 24 August 2009

Accepted 25 August 2009

Available online 31 August 2009

Keywords:

Organogel

Silica

Microemulsion

Chromate

Isotherm

CTAB

ABSTRACT

The feasibility of utilizing CTAB–silica gelatin composite (C-SGC) to remove hexavalent chromium from aqueous solutions under different conditions was investigated. Removal of chromate was assessed through evaluation of the adsorption kinetics of chromate ions on the composite under equilibrium conditions in the presence of sulfate ions and at a slightly acidic pH condition (pH 5.8). Adsorption competition tests in the presence of sulfate ions showed that Cr(VI) was still effectively adsorbed from aqueous solution regardless of the presence of the competing anions. In fact, the adsorption kinetics performed at different initial chromate concentrations were unaffected by the presence of 100 mg L⁻¹ sulfate ions (pH 7.5). The equilibrium adsorption data were fitted by Freundlich adsorption isotherms which confirmed that the adsorption efficiency of chromium on the CTAB–silica gelatin composite was unchanged in the presence of sulfate ions. Further, the adsorption process was shown to be pH dependent and more efficient at slightly acidic pH (5.8). These findings demonstrated a high specificity of the CTAB–silica gelatin composite for chromium, and highlight the possibility of using this matrix for efficient removal of chromium from industrial wastewater without the need to eliminate contaminant sulfate ions.

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1. Introduction

Owing to the high toxicity of heavy metals to many life forms, a number of experimental efforts have been put on the creation of novel strategies to reduce heavy metals concentration to environmentally acceptable levels, and on the construction of novel devices to constantly monitor their presence in the environment. Chromium is a naturally occurring element found in soil and groundwater in several different forms. The most common oxidation states of chromium are Cr(VI) and Cr(III) which represent the prickliest issues in terms of environmental safety [1]. While Cr(III) is generally non-toxic and is believed to be essential in glucose metabolism in mammals [2], Cr(VI) is toxic to animal and plant cells [3]. Furthermore, because of its mutagenic and carcinogenic properties, the hexavalent form has been included in the group “A” of human carcinogens [4].

Several methods, such as: adsorption and co-precipitation, transformation, ion exchange and reverse osmosis have been used to treat Cr(VI) contaminated water. In many cases, the environmentally most compatible and cost effective solution comprises a combination of two or more of these processes. In the past decades,

adsorption techniques have widely been studied and seem to be a reasonable choice for this matter. Several materials have been developed and tested, ranging from low cost waste material, such as: moss peat [5], sawdust [6], zeolites, clay, hazelnut shell [7], to more sophisticated adsorbents, such as: activated carbon, modified zeolite, modified clay [8], modified steel slag [9], nanoscale magnetic material [10], chitosan based composite [11]. This has pointed to the need for highly economic and extremely efficient materials [12,13].

Among the cited materials, in a recent study we proposed the new device C-SGC and showed that this composite is able to adsorb chromate from contaminated water at neutral pH [14]. The ability of gelatin to jellyfy organic solvents, when dissolved in reverse micelles, was previously reported [15,16] and used in microemulsions based gels (MBGs) prepared by mixing an aqueous gelatin solution with a w/o microemulsion. Also the use of microemulsion systems as advantageous methods in heavy metals extraction was demonstrated by different groups [17,18]. The new adsorbent silica gelatin composite, consisting of a biological component (gelatin), a mineral component (silicate) and a positively charged surfactant hexadecyltrimethylammonium bromide (CTAB), offers several advantages over normal extraction systems, e.g. a high manipulability, a good ionic mobility, a fine chemical and physical stability, a high binding capacity and good mechanical stability. Our previous contribution also showed that after the adsorption procedure

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the C-SGC was able to transform Cr(VI) in Cr(III) without further treatments although the process was demonstrated to be very slow [14].

Adsorption of target metal ions by effluent or wastewater solutions and gaseous emissions from many industries might be hindered by the presence of sulfur-containing pollutants and different inorganic anions that could lead to a reduction of the adsorption efficiency of the materials employed.

Previous experimental observations by Bartlett and James [19] demonstrated that there might be similarities on the adsorption of chromate and sulfate on colloids with positively charged surfaces.

Hence, the aim of the present investigation was to study in further details the process of Cr(VI) removal by C-SGC and determine whether chromate ions adsorption, defined here as a mechanism based on electrostatic and hydration interactions, could be affected by the presence of sulfate ions and a slightly acidic pH (5.8).

Collectively, our data demonstrate a high specificity of the C-SGC composite in chromium adsorption and exclude a reduction of the adsorption efficiency in the presence of sulfate ions.

2. Materials and methods

2.1. Chemicals

Hexadecyltrimethylammonium bromide (CTAB), 1-pentanol, hexane, tetraethyl orthosilicate (TEOS), gelatin type A from porcine skin (bloom 300), were purchased from Sigma. CTAB was three times re-crystallized from anhydrous ethanol, and stored over dried silica gel under vacuum. Sodium hydroxide, potassium chromate, sodium sulfate, ammonia solution 30 wt.% and 1,5-diphenylcarbazide (DFC) were from Carlo Erba. Water was twice distilled in quartz devices.

2.2. C-SGC preparation

The C-SGC preparation method [14] was slightly modified for large-scale production. Mole ratios water/CTAB (W_0), pentanol/CTAB and the overall surfactant concentration were used to define the microemulsion composition. The microemulsion was prepared by weighing in a volumetric flask the amounts of surfactant, alcohol, and 10 wt.% ammonium solution in water to obtain the mole ratios $W_0 = 5$ and pentanol/CTAB = 4.9. Hexane was then added to obtain a concentration of 100 mM CTAB. The CTAB organogel was prepared by adding 1 g of 10 wt.% ammonium solution and 0.65 g of gelatin to 7.5 mL of the microemulsion [16,20]. The mixture was kept at 72 °C for 20 min and then cooled at 25 °C. The organogel was obtained under stirring condition. The hardening process was performed at 42 °C by adding 2.25 mL of TEOS to the above prepared organogel. The resulting mixture was subsequently vigorously stirred and cooled at 0 °C for 20 min. The C-SGC was stored in 200 mL hexane for 12 h at 25 °C to eliminate ethanol from the composite [21]. Finally, the wet composite was divided into suitable parts and dried resulting in a dry white composite. Such a composite was hydrated for 12 h before use.

2.3. Batch adsorption experiments

Equilibrium adsorption studies were conducted with aqueous solutions of Cr(VI) prepared by dissolving appropriate amounts of potassium chromate in water. The experiments were conducted at pH 7.5, at pH 5.8, at pH 7.5 in presence of 100 mg L⁻¹ sulfate ions and at pH 10.5. Adsorption experiments were performed by adding in 50 mL Erlenmeyer flasks amounts of composite (100 mg) in a fixed volume (50 mL) containing variable amount of chromium.

The initial Cr(VI) concentrations ranged from 3.5 to 260 mg L⁻¹. The samples were placed in an orbital shaker bath and shaken at 25 °C at 100 rpm for various time intervals. At pre-determined time intervals, samples were withdrawn and the Cr(VI) content was determined spectrophotometrically at 540 nm by measurement of the intense red-violet complex formed by reaction of chromium(VI) with DFC in acidic medium [22]. Chromate adsorption was determined from differences between initial and final solution concentrations with appropriate corrections based on blanks. The initial and final sulfate content was determined by means of a Dionex ICS 3000 dual pump ion chromatography system [23].

3. Results

3.1. Effect of Cr(VI) concentration

In a previous study we showed that the C-SGC is able to adsorb Cr(VI) from water solutions and that the first step of this mechanism is mainly related to the presence of the cationic surfactant CTAB [14]. SEM and NMR analysis showed that this material is composed by an interconnected network of gelatin, silicate and surfactant in which water molecules maintain a high mobility [14]. Analyses of the elemental content in the CTAB-silica gelatin composite indicated that the adsorption of chromium also takes place in internal areas of the composite [14]. As a significant index of homogeneity, a linear correlation between dried weight and the wet weight after hydration was also demonstrated.

To analyze in further details the efficiency of CTAB-silica gelatin composite in Cr(VI) removal, here we measured the time-dependent adsorption of Cr(VI) in batch systems containing different initial concentrations of Cr(VI) (3.6, 14 and 100 mg L⁻¹, pH 7.5) (Fig. 1). The rationale of the experiment was to vary the initial Cr(VI) concentrations while keeping the amount of the composite constant (100 mg). The experimental data, expressed with the ratio $Cr(VI)_t/Cr(VI)_0$ as a function of time at 25 °C, indicate that while the adsorption of Cr(VI) ions is quite rapid initially, it becomes slower with time, reaching a constant value after different time intervals depending on the initial concentration of the heavy metal (equilibrium time). The initial rate, which remains linear for longer times at low chromate concentrations, is due to the large availability of the positively charged quaternary ammonium of CTAB molecules on the uncovered surface area of the adsorbent. As

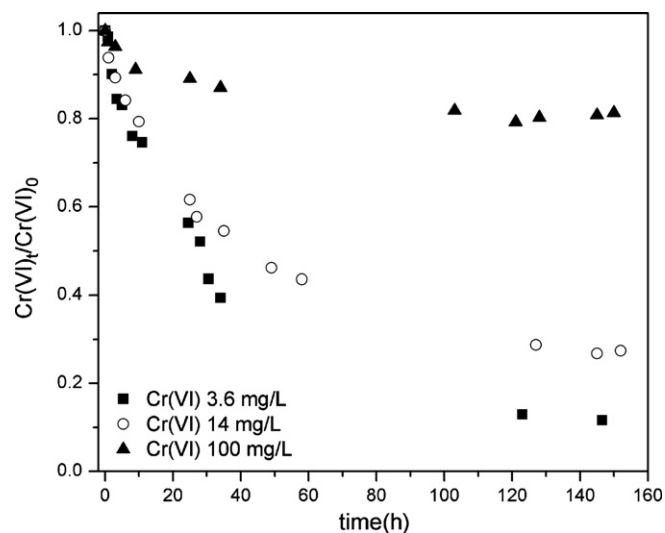


Fig. 1. Time courses of hexavalent chromium adsorption by the C-SGC at 25 °C at three different initial Cr(VI) concentrations (3.6, 14, and 100 mg L⁻¹).

Table 1

The initial concentrations and the adsorption percentage of Cr(VI) at three different conditions: pH 7.5, pH 7.5 in presence of sulfate ions (100 mg L^{-1}) and pH 5.8.

pH 7.5		pH 7.5 + sulfate		pH 5.8	
Initial Cr(VI) (mg/L)	Adsorbed Cr(VI) (%)	Initial Cr(VI) (mg/L)	Adsorbed Cr(VI) (%)	Initial Cr(VI) (mg/L)	Adsorbed Cr(VI) (%)
3.6	88.1	3.6	83	3.6	89.2
14	73.5	14	72.3	14	83.5
27.4	59.6	27.4	60.4	27.4	79.1
100	19.7	100	21.2	100	32
264	9.1	264	8.2	263	15

clearly shown in Fig. 1, the percentage of adsorption at equilibrium decreases with the increase of Cr(VI) ion concentration (see also Table 1).

3.2. Effect of slightly acidic pH conditions

The pH of the aqueous solution has been shown to be a crucial factor influencing the efficiency of chromium adsorption: different reports have clearly shown a rise in chromate adsorption at low pH [24].

It is also well known that the predominant species in total chromium depends on both the total chromium concentration and the pH. In particular, the concentrations of the various chromium species present in the solution can be calculated by using an equilibrium constant reported by Saha et al. [25].

In order to get further insights into the mechanism determining the efficiency of chromium removal and the specific chromium species adsorbed by the CTAB–silica gelatin composite we next compared the Cr(VI) adsorption efficiency on the composite at pH 5.8 and 7.5. These two pH values were chosen because of the specific mole fractions of the two species CrO_4^{2-} and HCrO_4^- calculated with the equilibrium constant described above [25].

In fact, at the selected pH 7.5 and pH 5.8 there are two predominant species in solutions, namely bichromate (HCrO_4^-) and chromate (CrO_4^{2-}). In particular, the average mole fractions of chromium species at pH 7.5 within the range of our experimental conditions ($3.6\text{--}264 \text{ mg L}^{-1}$) are $\text{CrO}_4^{2-} = 0.85$ and $\text{HCrO}_4^- = 0.15$. At pH 5.8 the mole fractions of mostly all the initial concentrations considered are $\text{CrO}_4^{2-} = 0.15$ and $\text{HCrO}_4^- = 0.85$. Note that the contribution of the dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is appreciable only at the highest initial Cr(VI) concentrations tested. In this work the

approximate mole fractions used above refer to low initial Cr(VI) concentrations according to Ref. [25] that reports for a 0.001 M Cr(VI) solution a negligible amount of dichromate.

Fig. 2 shows the time-dependent adsorption kinetics of Cr(VI) at two different initial Cr(VI) concentrations (14 and 100 mg L^{-1}) carried out at pH 7.5 and 5.8. In both cases the amount of Cr(VI) removed at the equilibrium was higher for the acidic solution. At pH 7.5 and 14 mg of initial Cr(VI) concentration, the percentage of chromium removal was 73.5% against a value of 83.5% obtained at pH 5.8. The same trend was found in experiments performed with different initial chromate concentrations (see Table 1).

It should be noticed that after chromate adsorption the composite becomes yellow for all the initial concentrations tested at pH 7.5. At the lower pH (5.8), the composite develops a yellow-orange color, due to the increase in the mole fraction of dichromate, appreciable only at the higher Cr(VI) concentrations tested (above 100 mg L^{-1}).

3.3. Effect of sulfate ions

Among the factors known to influence the adsorption rate of chromate to the different adsorbents, there is the concentration of competing ions. Due to the similar configuration of chromate and sulfate anions, the effect of sulfate anions on the adsorption kinetics of Cr(VI) was evaluated. The kinetics of chromate removal by the CTAB–silica gelatin composite obtained at two chromate concentrations (3.6 and 100 mg L^{-1}) in the absence and in presence of sulfate ions (100 mg L^{-1}) are reported in Fig. 3. The removal efficiency of the composite toward Cr(VI) was demonstrated to be completely unaffected by the presence of the competing sulfate anions. At both concentrations tested, the composite was able to

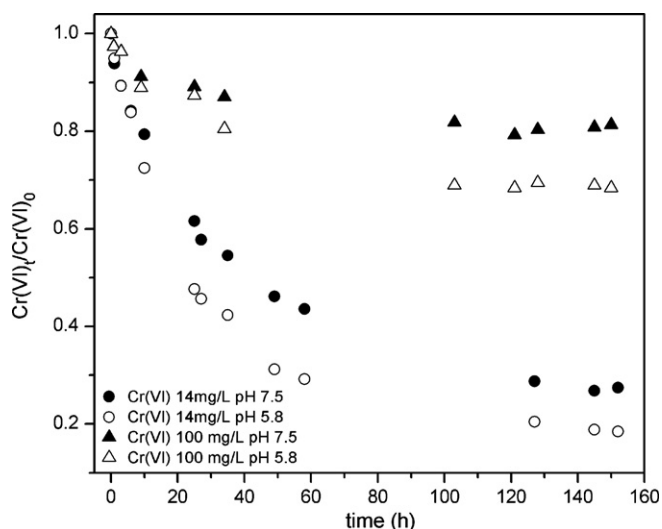


Fig. 2. Time courses of hexavalent chromium adsorption by the C-SGC at 25°C at two different Cr(VI) concentrations (14 and 100 mg L^{-1}) performed at pH 7.5 and 5.8.

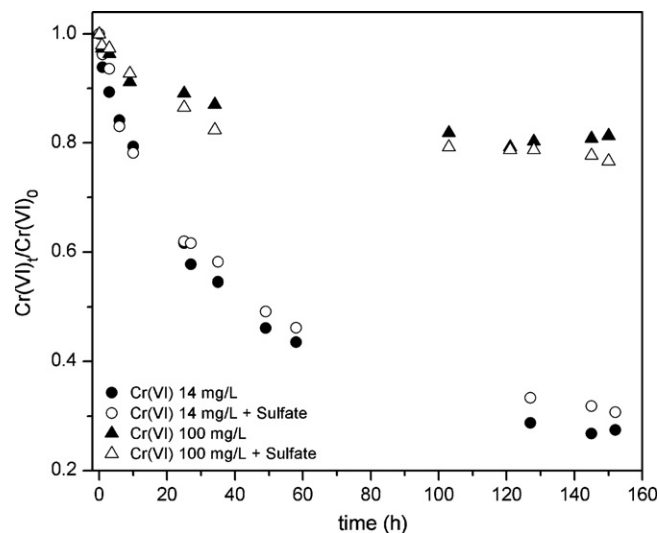


Fig. 3. Time courses of hexavalent chromium adsorption by the C-SGC at 25°C at two different Cr(VI) concentrations (14 and 100 mg L^{-1}) performed in the absence and presence (100 mg L^{-1} of sulfate ions).

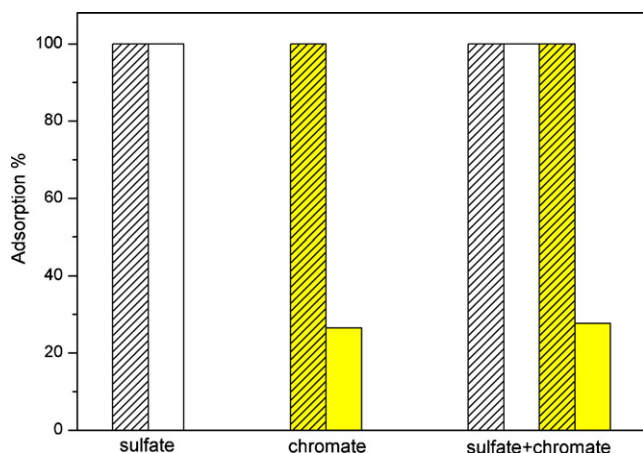


Fig. 4. Removal adsorption efficiency of chromate and sulfate by C-SGC at 25 °C. The first couple of columns represents the initial sulfate concentration (100 mg L^{-1}) (white sparse column) and the amount of sulfate left in solution (white column) after the contact with the C-SGC. The second couple of columns refers to the initial Cr(VI) concentration (14 mg L^{-1}) (yellow sparse column) and the amount of Cr(VI) left in solution (yellow column) after the contact with the C-SGC. The third group of columns refers to the experiments performed in the presence of both ions: 100 mg L^{-1} initial sulfate concentration (white columns) and 14 mg L^{-1} initial chromate concentration (yellow columns). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

remove the hexavalent chromium to the same extent regardless of the presence of SO_4^{2-} (see also Table 1).

This evidence was further confirmed by analyzing the efficiency of the CTAB–silica gelatin composite in removing sulfate ions in comparison to chromate ions. In Fig. 4 some of the previously shown results are plotted together with new data regarding the ability of the composite to adsorb sulfate ions. An aqueous solution containing 100 mg L^{-1} of sulfate was incubated with the C-SGC for 160 h, at which time the adsorption kinetic of chromate ions reached the equilibrium (see also Fig. 3). The amount of sulfate into the aqueous solution was thereafter measured by means of Dionex ion chromatography and compared to the initial sulfate concentration (the first two columns in Fig. 4).

For comparison the percentage of chromate measured after 160 h of incubation with the C-SGC (at 14 mg L^{-1} initial chromium solution) is reported. The third group of columns represents the experiment performed in the presence of both anions (100 mg L^{-1} sulfate and 14 mg L^{-1} chromium). These data further demonstrate that the sulfate ions are not adsorbed to the C-SGC matrix both in the presence and in the absence of chromate. Remarkably, this experimental evidence suggests that despite the similarity of the two anions SO_4^{2-} and CrO_4^{2-} no adsorption competition effects occur on the surface of the positively charged composite.

3.4. Adsorption isotherm of Cr(VI)

Adsorption kinetics of Cr(VI) at different initial chromate concentration were fitted to the Freundlich adsorption isotherm. The adsorption capacity depends on the chemical and physical properties of the adsorbent. The adsorption isotherms of Cr(VI) on the CTAB–silica gelatin composite obtained at pH 7.5, at pH 7.5 in the presence of sulfate and at pH 5.8 are shown in Fig. 5. The data points on the binding isotherms of Cr(VI) fitted well with the Freundlich model represented by the Eq. (1):

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

where Q_e is the amount of chromium taken up per gram of composite (mg/g) and C_e is the chromium concentration left in solution at the equilibrium (mg L^{-1}). K and n are the constant isotherm param-

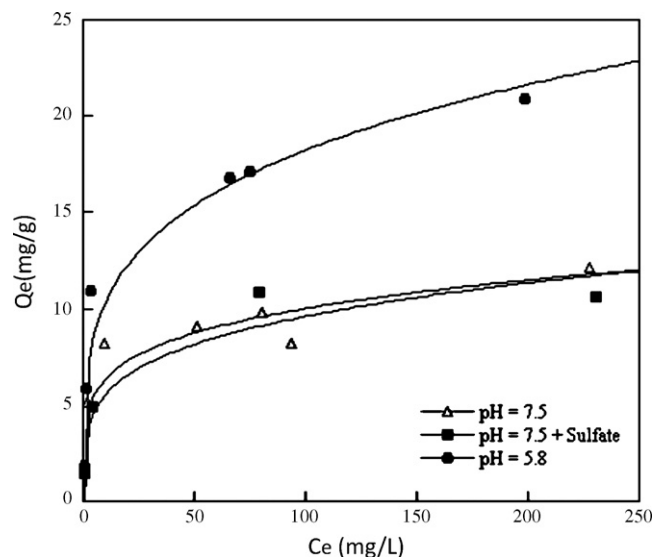


Fig. 5. Adsorption isotherms of Cr(VI) removal by C-SGC at 25 °C at three sets of experiment: pH 7.5 ($K=4 \pm 0.8$; $n=5 \pm 0.9$), pH 7.5 in presence of sulfate ions (100 mg L^{-1}) ($K=3.1 \pm 1$; $n=4.2 \pm 0.9$), and pH 5.8 ($K=5.8 \pm 1$; $n=4 \pm 0.9$).

eters, indicating the adsorption capacity and adsorption intensity, respectively.

As shown in Fig. 5, the chromate absorption efficiency of the composite achieved at pH 7.5 does not change in the presence of sulfate ions. On the contrary, the adsorption capacity of the CTAB–silica gelatin composite, indicated by the K value, is significantly increased at slightly acidic conditions. The K value goes from 4 at pH 7.5 to 5.8 at pH 5.8. Furthermore, the values of adsorption intensity for chromate n are in all cases higher than 1, indicating a low competition between the solvent water and the composite for chromate binding.

4. Discussion

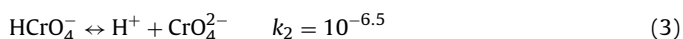
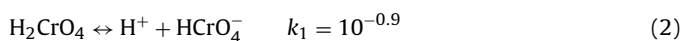
Although we previously reported [14] that the C-SGC is able to adsorb chromate ions from neutral water solution, a role for the species HCrO_4^- was only indirectly argued. Moreover, if a prominent role for the positively charged head group of the CTAB molecules in the adsorption mechanism was suggested, further details to explain the mechanism of chromium removal were needed.

In order to gain further insights into the molecular mechanisms involved in the high capacity of chromium removal of the C-SGC composite, we here decided to investigate the effects of similar ions on the adsorption kinetics of Cr(VI). The data collected in the presence of sulfate ions, clearly showed that despite the similarity of the two metal anions SO_4^{2-} and CrO_4^{2-} no adsorption competition effects were measurable. We reasoned that the adsorption selectivity of the composite for CrO_4^{2-} ions would have resulted from the different affinities between the composite and the two anion species. In fact, the diffusivity D and the Stokes radii R for both ions CrO_4^{2-} and SO_4^{2-} are very close to each other. The reported diffusivities D are 1.14 for CrO_4^{2-} and $1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for SO_4^{2-} , the Stokes radii R for CrO_4^{2-} and SO_4^{2-} are 0.22 nm and 0.23 nm , respectively [26]. Hence, these parameters should not be the reason causing the strong selective adsorption of CrO_4^{2-} over SO_4^{2-} ions on C-SGC.

In general, the adsorption of a solute from water on a solid material is due to electrostatic interactions between the solute and both the material and water. This means that the free energy change derives from a balance between the electrostatic and the hydration contributions. Thus given the obvious similarity of the above cited

parameter for both the divalent anions to explain the ineffective adsorption of sulfate ions onto the composite the hydration energy (ΔG_{hydr}) for the species was considered. The term ΔG_{hydr} is strictly dependent on the species in the solution and their equilibrium constants.

As for the chromate ion, it is well known that at concentration below than 10 mM or at neutral pH, chromium exists as H_2CrO_4 , HCrO_4^- and CrO_4^{2-} [25]. These species are involved in the acid dissociation reactions, as follows:



The pK values for Eq. (2) and Eq. (3) are 0.9 and 6.5, respectively. Thus, the CrO_4^{2-} species is predominant above pH = 6.5, while H_2CrO_4 prevails only at pH < 0.9 and HCrO_4^- prevails in the pH range from 0.9 to 6.5.

As reported in Section 3.2, at pH 7.5 the mole fractions of the species CrO_4^{2-} and HCrO_4^- are 0.85 and 0.15, respectively. On the contrary, at pH 5.8 the mole fractions of the species CrO_4^{2-} and HCrO_4^- are reversed (0.15 and 0.85, respectively). As we will show our hypothesis is based essentially on the very different values of ΔG_{hydr} for the two species CrO_4^{2-} and HCrO_4^- being, -950 kJ mol^{-1} and -184 kJ mol^{-1} , respectively [27,28]. At pH 5.8, the exchange surface would be surrounded by a consistent amount of HCrO_4^- ions, which then would enhance the Cr(VI) interaction with binding sites of the CTAB molecules. On the contrary, at pH 7.5 the mole fractions of the species CrO_4^{2-} and HCrO_4^- are reversed (0.85 and 0.15, respectively) and thus the amount of the adsorbed Cr(VI) resulted reduced. This hypothesis fully emphasizes the high contribution of HCrO_4^- species in the Cr(VI) adsorption process.

To experimentally validate our hypothesis we next performed the chromium adsorption process onto the C-SGC at higher pH. Fig. 6 shows the time-dependent adsorption of Cr(VI) (initial concentration 100 mg L^{-1}) onto the composite at different pH (pH 5.8, 7.5 and 10.5). This figure points out that at high pH the amount of chromium adsorbed is almost negligible due to the absence of HCrO_4^- . As stated before, at this pH (10.5) the only species in solution should be represented by CrO_4^{2-} which has a high value of ΔG_{hydr} (-950 kJ mol^{-1}). Thus, the reduction of the adsorption efficiency could be, again, mainly ascribed to the absence of HCrO_4^- .

On the other hand, to take into account the amount of Cr(VI) adsorbed at high pH (10.5) minor significant interaction should

also be considered. The quantity of Cr(VI) is strictly related to the properties of the adsorbent, C-SGC a positively charged surfactant compound, and its colloidal particles that possess not only permanent positive charges but also variable charges due to H^+ and OH^- . At lower pH values, the surface of exchanger would also be surrounded by the H^+ , which enhanced the Cr(VI) interaction with binding sites of the sorbent by greater attractive forces. As the pH is increased, however, the overall surface charge on the composite became less positive and ion exchange decreased [29].

Also the reason causing the strong selective adsorption of CrO_4^{2-} over SO_4^{2-} ions on C-SGC is easily explainable by our previous hypothesis. In fact, for sulfate the species H_2SO_4 and HSO_4^- cannot exist in solution because the reactions:



are completely shifted to the right. As a consequence, the only species present in solution is SO_4^{2-} . Hence, the ΔG_{hydr} is given only by the SO_4^{2-} species contribution (hydration energy $-1080 \text{ kJ mol}^{-1}$). As a result, we can state that sulfate ions are more bonded to water molecules than chromate ions because of their favorable hydration energy.

Additionally, experiments performed at lower pH (lower than 5.8) indicated, as expected, a higher adsorption efficiency of the composite toward chromate (data not shown). Nonetheless, since we observed that at pH lower than 5.0, in the presence of chromate ions, the C-SGC resulted mechanically unstable (a significant increment of the surface area of the composite was appreciable), we elected not to put these data together with the sets of experiments shown in this paper. In fact, the aim of this study is the evaluation of the suitability of the CTAB silica gelatin composite for a fast and easy chromate removal from water solution at neutral pH without further treatments.

5. Conclusion

In summary, our results suggest that the presence of sulfate ions does not affect the chromate adsorption efficiency of the CTAB silica gelatin composite. This study also points out that the chromium adsorption efficiency on the C-SGC is increased by slightly acidic pH conditions (pH 5.8).

The data collected in the three different sets of experiments performed in this paper (Cr(VI) removal at pH 7.5, pH 7.5 in the presence of sulfate ions and pH 5.8) are best fitted by the Freundlich isotherm (at 25°C). The whole data set is successfully accounted for assuming that a difference in terms of hydration energy between the chromate species exists. While supporting the widely accepted idea of a prominent role of CTAB in the adsorption mechanism, our study highlights the role played by the species HCrO_4^- in chromate adsorption from water solution.

As a whole, these findings while adding new insights into the mechanisms of chromate adsorption on the CTAB silica gel composite, further demonstrate the specificity and the suitability of this mechanically stable matrix for the removal of chromate from industrial wastewater, without the need to eliminate contaminant sulfate ions.

Acknowledgements

This work was supported by the MIUR of Italy (PRIN 2003 NANOSCIENZE PER LO SVILUPPO DI NUOVE TECNOLOGIE) and by Consorzio Interuniversitario per lo sviluppo dei Sistemi a Grande Interfase (CSGI-Firenze).

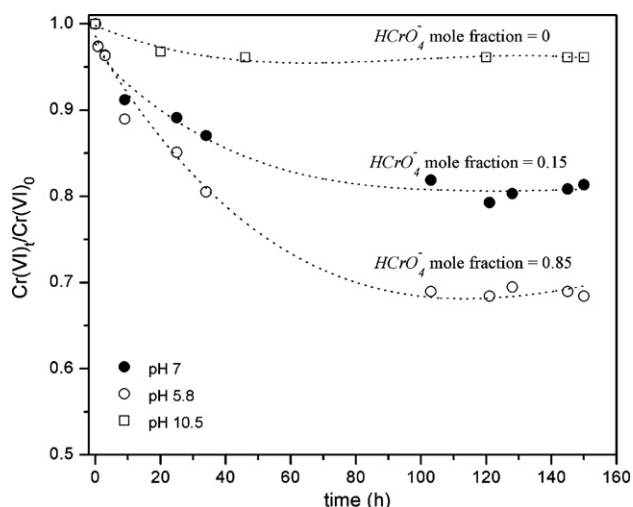


Fig. 6. Time courses of hexavalent chromium adsorption by the C-SGC at 25°C for three different pHs (5.8, 7.5, 10.5); lines are guides for the eyes.

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