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# Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide

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#### **Abstract**

The adsorption behaviour of amorphous aluminium oxide was studied with respect to Cr(VI) in order to consider its application to purify electroplating wastewaters. A batch method was employed using Cr(VI) concentrations ranged from 10 to 200 mg/l. The Langmuir model was found to describe the adsorption process well, offering a maximum adsorption capacity of 78.1 mg/g. The effect of ionic strength  $(0-0.1 \text{ M KNO}_3)$ , pH (3-9) and competitive solutes (molar ratio  $[Cr(VI)]/[SO_4^{2-}]=1$  and 100) on the retention process was evaluated. Cr(VI) adsorption on amorphous aluminium oxide appeared to be dependent on ionic strength with a more pronounced effect in acid conditions. Conversely, adsorption was not affected by pH in acid medium, but decreased when pH sifted to alkaline values. The presence of  $SO_4^{2-}$  greatly reduced Cr(VI) removal across the entire pH range when both solutes were present in similar concentrations. Amorphous aluminium oxide also showed a high adsorption capacity when used in the purification of Cr(VI) electroplating wastewaters. The adsorbent doses required to attain more than 90% of Cr(VI) removal varied between 1 and 5 g/l depending on Cr(VI) concentration in wastewaters.

Keywords: Chromium; Adsorption; Aluminium oxide; Wastewaters; Electroplating

# 1. Introduction

Chromium is usually encountered in the environment as Cr(III) or Cr(VI). These two oxidation states have different chemical, biological and environmental properties. Cr(III) is relatively insoluble and an essential micronutrient for animals and humans, having an important role in the glucose, lipid and protein metabolism [1–3]. On the contrary, Cr(VI) is highly mobile and is considered acutely toxic and mutagenic for most organisms; in humans its main effects are on skin, liver, kidney and respiratory organs, resulting in a variety of diseases such as dermatitis, hepatic and renal tubular necrosis, bronchitis, perforation of the nasal septum and bronchogenic carcinoma [4,5].

The chromium electroplating treatment is one of the largest sources of Cr(VI) emissions to the environment. In this process a layer of chromium is electrodeposited on a base material to provide a surface with decorative or functional properties

such as wear and corrosion resistance, low friction and hardness. Such a surface treatment is performed in baths composed of chromic acid (180-350 g/l), sulphuric acid (1.8-3.5 g/l) and water. Chromium electroplating generates Cr(VI) containing wastewaters from the rinsing steps following the baths of treatment. Such effluents can contain chromium at concentrations ranging from tenths to hundreds of mg/l, whereas the permissible limit of Cr(VI) for industrial waste streams to be discharged to surface water ranges between 0.1 and 0.5 mg/l [6]. Different techniques have been employed for the purification of these wastewaters, including physico-chemical treatment, reverse osmosis, evaporation and ion-exchange [7]. Among these techniques the physico-chemical treatment is the most applicable and considered to be the most economical. Such a method involves two steps; firstly Cr(VI) is chemically reduced to Cr(III) using generally sodium metabisulphite as reducing agent, and secondly Cr(III) is precipitated as chromium hydroxide using sodium hydroxide or lime as precipitating agents. The main concern of this technique is the generation of a great amount of sludge that requires further treatment. The other available treatments, although usually effective, are not free of

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drawbacks, high capital investment, running costs and capability to treat only small wastewater volumes and low metal concentrations are the most common. Therefore, the need exists for a treatment strategy that is simple, effective and low-cost. In this way, adsorption appears as a highly promising alternative to purify such wastewaters. Several studies have been reported using different low-cost adsorbents for the Cr(VI) removal, including activated carbon [8,9], wool [10], agricultural byproducts such as coconut husks and palm pressed fibres [11], sugar cane bagasse, sugar beet pulp, maize cob, saw dust, olive cake, pine needles, almond shell and cactus leaves [12,10], waste materials such as fly ashes [13], red mud [14,15] and biogas residual slurry [16] and minerals such as feldspar [17], hydrotalcite-like compounds [18-22], crystalline iron oxyhydroxides [23–29] and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [30,31]. From the light of these studies adsorption emerges as a robust and versatile method that could solve the problems of sludge handling and render the purification system more economically viable, especially if lowcost adsorbents are involved. The advantages of the adsorption process prompt to extend such an approach to other materials with structural, compositional or chemical characteristics suitable to make them systems with high Cr(VI) retention values and so potential means of Cr(VI) wastewater purification.

Within the normal pH range in waters Cr(VI) is present as chromate  $(CrO_4^{2-})$ , hydrogenchromate  $(HCrO_4^{-})$  or/and dichromate  $(Cr_2O_7^{2-})$ , depending on its concentration and the pH of the medium. Among materials having better features to be used as adsorbents of anionic species there are low-crystalline and amorphous (Fe, Al) oxides and oxyhydroxides [32]. These variable-charge materials posses numerous valence-unsatisfied surface hydroxyl ions that are responsible for ligand exchange reactions and for electrostatic attraction interactions as well. Numerous researches have been performed in order to characterise their adsorption behaviour with respect to different oxyanions, including the adsorption of arsenite and arsenate [33–36], phosphate [37], molybdate and tungstate [38] on ferrihydrite, selenite on poorly ordered aluminium hydroxide [39], arsenate and arsenite on amorphous aluminium and iron oxides and hydroxides [40,41] and chromate on amorphous iron oxyhydroxide [42]. Although both amorphous iron and aluminium oxides and oxyhydroxides have been subject of study, it is undeniable that when chromate was the anion involved iron compounds focused the attention, as happened when characterising the adsorption of Cr(VI) on crystalline oxides and oxyhydroxides.

The main objectives of the present study were to characterise the adsorption behaviour of amorphous aluminium oxide with respect to Cr(VI) and to explore the applicability of this material to purify actual chromium industrial wastewaters.

#### 2. Materials and methods

# 2.1. Chemicals

Cr(VI) synthetic solutions were prepared with deionised water from  $K_2Cr_2O_7$  (AR grade, Merck). Their pH was adjusted using 0.01 and 0.1 M HNO\_3 and NaOH solutions.

Table 1
Textural properties and particle size distribution of synthesised amorphous aluminium oxide.

| Property  | Value |  |
|---|-------|--|
| Textural properties                             |       |  |
| Specific surface area (m <sup>2</sup> /g)       | 15.5  |  |
| Specific total pore volume (mm <sup>3</sup> /g) | 63.5  |  |
| Mean pore diameter (Å)                          | 171   |  |
| Particle size distribution                      |       |  |
| 90th percentile (µm)                            | 77.9  |  |
| 50th percentile (μm)                            | 15.1  |  |
| 10th percentile (μm)                            | 2.4   |  |

The actual chromium industrial wastewaters used in this study correspond to dilutions of a typical chromium electroplating solution from the bath of treatment ([Cr(VI)]: 74.67 g/l; [SO<sub>4</sub> $^2$ -]: 1.66 g/l). The concentrations of this solution as well as those of solutions prepared from it were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a thermo Jarrell-Ash iris advantage radial ER/S unit.

#### 2.2. Adsorbent material

The aluminium oxide used as an adsorbent in this study was synthesised using the method described by Sims and Bingham [43]. A 2 M NaOH solution was slowly added to a 1.5 M AlCl<sub>3</sub> solution in a volume ratio of 2:1 under continuous stirring. The resulting precipitate was washed thoroughly with deionised water, filtered and dried at  $70\,^{\circ}\text{C}$  for 24 h.

The precipitated solid was characterised as amorphous aluminium oxide by X-ray diffraction (XRD). X-ray diffraction analysis was performed on a Siemens D 501 diffractometer using CuK $\alpha$  radiation. The precipitated solid was scanned as an unoriented powder sample from 4 to 60 °C 2 $\theta$  with a 0.04 °C 2 $\theta$  step interval and a 1s per step counting time. The textural analyses were carried out from the nitrogen adsorption isotherms at -196 °C obtained from a static volumetric apparatus (Micromeritics Tristar 3000 adsorption analyser). The determination of particle size distribution was performed by laser diffraction using a MALVERN unit. The properties of synthesised aluminium oxide are given in Table 1.

# 2.3. Adsorption studies

All adsorption studies were carried out in polypropylene flasks of 50 ml by subjecting a given dose of aluminium oxide to a period of shaking with 25 ml of metal solution on a vertical rotary shaker in a chamber set at 22 °C. The adsorbent was separated using a centrifugation step (6000 rpm) over 5 min. Chromium concentrations in the supernatant were determined by ICP-OES. All assays were carried out in triplicate and only mean values are presented.

# 2.3.1. Chromium synthetic solutions

The adsorption studies with chromium synthetic solutions were performed using the following conditions:

*Kinetic study*. Aluminium oxide dose 2 g/l; initial chromium concentrations 50 and 150 mg/l; pH 6; shaking time 0.5, 1, 2, 4, 8, 24 and 48 h.

Adsorption isotherms. Aluminium oxide dose 2 g/l; initial chromium concentrations 10–200 mg/l; pH 6; shaking time 24 h. The background electrolyte (KNO<sub>3</sub>) concentrations were adjusted to 0, 0.01, 0.05 and 0.1 M.

Effect of pH. Aluminium oxide dose 2 g/l; initial chromium concentration 150 mg/l; pH 3–9; shaking time 24 h. The background electrolyte (KNO<sub>3</sub>) concentrations were adjusted to 0, 0.01, 0.05 and 0.1 M.

Competitive adsorption study. Binary-solute systems  $(Cr(VI) + SO_4^{2-})$  were designated for understanding the relative binding strength between these anions and so the possible inhibition of Cr(VI) adsorption in the presence of  $SO_4^{2-}$ .

Aluminium oxide dose 2 g/l; initial concentrations  $[Cr(VI)] = 150 \text{ mg/l} + [SO_4^{2-}] = 277 \text{ mg/l} \text{ (molar ratio } [Cr(VI)]/[SO_4^{2-}] = 1)$  and  $[Cr(VI)] = 150 \text{ mg/l} + [SO_4^{2-}] = 2.77 \text{ mg/l} \text{ (molar ratio } [Cr(VI)]/[SO_4^{2-}] = 100, \text{ concentration ratio similar to that found in chromium electroplating wastewaters); pH 3–9; shaking time 24 h.$ 

#### 2.3.2. Actual chromium industrial wastewaters

The adsorption studies with actual chromium industrial wastewaters were performed using the following conditions:

*Kinetic study*. Aluminium oxide dose 2 g/l; initial chromium concentrations 57 and 158 mg/l; shaking time 0.5, 1, 2, 4, 8, 24 and 48 h.

*Adsorption isotherm.* Aluminium oxide dose 2 g/l; initial chromium concentrations 11–223 mg/l; shaking time 24 h.

Effect of adsorbent dose. Aluminium oxide dose 0.2, 0.5, 1, 2, 5, 7.5 and 10 g/l; initial chromium concentrations 57, 119 and 223 mg/l; shaking time 24 h.

## 3. Results and discussion

# 3.1. Chromium synthetic solutions

#### 3.1.1. Kinetic study

The kinetic curves obtained for the adsorption of Cr(VI) from aqueous solutions by amorphous aluminium oxide are shown in Fig. 1. These curves clearly show that the time required to reach equilibrium depends on the initial chromium concentration. For the highest value (150 mg/l) adsorption increased sharply at short contact times and slowed gradually as equilibrium was approached; 24 h of interaction were needed to attain values above 99% of the chromium amount adsorbed at equilibrium. For the lowest concentration (50 mg/l), the adsorption process took place very quickly, being almost completed (>99%) after 30 min of interaction.

The kinetic data were evaluated using the pseudo-secondorder model [44]. This model was developed for the adsorption system of divalent metal ions on sphagnum moss peat, and afterwards it has been successfully applied to different systems such as metal cations on activated carbons, clays and zeolites [45–50] and anions (halures as well as oxyanions, including Cr(VI) species) on ion-exchange fibers, minerals and biosor-

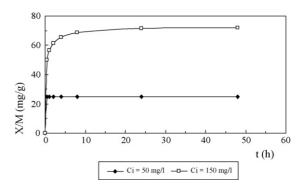


Fig. 1. Kinetic curves of Cr(VI) adsorption from synthetic solutions on amorphous aluminium oxide (conditions: aluminium oxide dose 2 g/l; initial chromium concentrations 50 and 150 mg/l; pH 6; shaking time 0.5, 1, 2, 4, 8, 24 and 48 h).

bents [51–55]. The model assumes that the adsorption process is of pseudo-second order and that the rate-limiting step is of chemisorption nature. The mechanism may involve valence forces by sharing or through the exchange of electrons between adsorbent and adsorbate. The model equation is given by:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k(q_{\mathrm{e}} - q_{\mathrm{t}})^{2} \tag{1}$$

where  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time t, respectively, and k is the adsorption rate constant. The integrated expression of Eq. (1) rearranged in linear form is:

$$\frac{t}{q_{\rm t}} = \frac{1}{kq_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{2}$$

where  $h = kq_e^2$  can be regarded as the initial adsorption rate as  $q_t/t$  approaches 0.

The pseudo-second order model parameters and the statistical fits of the kinetic data to this equation are given in Table 2. Based on  $\mathbb{R}^2$  values, the kinetic of  $\mathrm{Cr}(\mathrm{VI})$  adsorption from aqueous solutions on amorphous aluminium oxide can be satisfactorily described by the pseudo-second order model. Furthermore, the values of  $q_{\mathrm{e}}$  predicted by the model agree closely with those determined experimentally. The adsorption rate constant decreased with chromium initial concentration as well as the initial adsorption rate.

#### 3.1.2. Adsorption isotherms

The adsorption isotherms obtained for the removal of Cr(VI) from aqueous solutions at different ionic strengths are shown in Fig. 2. According to the classification of Giles et al. [56], all isotherms are L-type, reflecting an increasing difficulty for chromium to find adsorption sites on amorphous aluminium oxide as they become occupied.

Table 2
Characteristic parameters and determination coefficient of kinetic data of Cr(VI) adsorption from synthetic solutions on amorphous aluminium oxide according to the pseudo-second-order model

| $C_i$ (mg/l) | k (g/mg min)          | $q_{\rm e}~({\rm mg/g})$ | $R^2 (p < 0.001)$ |
|--------------|-----------------------|--------------------------|-------------------|
| 50           | 0.816                 | 24.8                     | 1                 |
| 150          | $6.90 \times 10^{-4}$ | 72.5                     | 1                 |

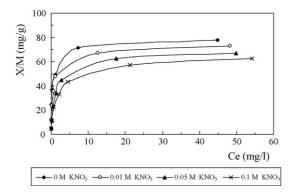


Fig. 2. Equilibrium isotherms of Cr(VI) adsorption from synthetic solutions on amorphous aluminium oxide at different ionic strengths (conditions: aluminium oxide dose 2 g/l; initial chromium concentrations 10–200 mg/l; pH 6; shaking time 24 h).

The adsorption data were fitted to the Langmuir equation:

$$\frac{X}{M} = \frac{KbC_{\rm e}}{1 + KC_{\rm e}} \tag{3}$$

where X/M is the amount of solute retained per unit weight of the adsorbent,  $C_e$  the equilibrium concentration of solute remaining in solution, K the equilibrium constant (affinity term) and b represents the maximum amount that can be adsorbed. The rearranged expression of Eq. (3) used to obtain its most suitable linear form is:

$$\frac{C_{\rm e}}{X/M} = \left(\frac{1}{Kb}\right) + \left(\frac{C_{\rm e}}{b}\right) \tag{4}$$

The Langmuir model parameters and the statistical fits of equilibrium data to this equation are given in Table 3. This model effectively describes adsorption of Cr(VI) on amorphous aluminium oxide with  $R^2$  values >0.99. The b parameter reflects high adsorption capacity values, but decreasing with the ionic strength increase, this decease is close to 20% at the highest ionic strength. The K parameter values also reflect a decrease in the affinity of chromium for the amorphous aluminium oxide surface with the ionic strength increase, as was derived from the decreasing slope of the first part of the isotherms as the ionic strength was raised. Evaluation of the effect of ionic strength on anion adsorption represents a macroscopic method of inferring adsorption mechanisms. Anions forming outer-sphere complexes show decreasing adsorption with increasing solution ionic strength, while anions that form inner-sphere complexes show little ionic strength dependence or show increasing adsorption with increasing solution ionic strength. In the light of these results, the

Table 3
Characteristic parameters and determination coefficient of equilibrium data of Cr(VI) adsorption from synthetic solutions on amorphous aluminium oxide according to the Langmuir equation

| Ionic strength     | b (mg/g) | K (l/mg) | $R^2 (p < 0.001)$ |
|--------------------|----------|----------|-------------------|
| $[KNO_3] = 0 M$    | 78.1     | 2.84     | 0.9998            |
| $[KNO_3] = 0.01 M$ | 73.5     | 1.81     | 0.9997            |
| $[KNO_3] = 0.05 M$ | 68.5     | 0.918    | 0.9997            |
| $[KNO_3] = 0.1 M$  | 63.7     | 0.668    | 0.9990            |

Table 4
Summary of adsorption capacity values of Cr(VI) on different adsorbent materials reported in literature

| Adsorbent                                    | b (mg/g) | Reference |
|--|----------|-----------|
| Calcined hydrotalcite                        | 122.2    | [18]      |
| Wool   | 41.15    | [10]      |
| Saw dust                                     | 39.70    | [12]      |
| Olive cake                                   | 33.44    | [10]      |
| Coconut husk fibres                          | 29.0     | [11]      |
| Activated carbon (from terminalia nuts)      | 28.43    | [9]       |
| Pine needles                                 | 21.50    | [10]      |
| Sugar beet pulp                              | 17.2     | [12]      |
| Saw dust                                     | 15.823   | [10]      |
| Palm pressed fibres                          | 15.0     | [11]      |
| Maize cob                                    | 13.8     | [12]      |
| Sugarcane bagasse                            | 13.4     | [12]      |
| Almond shell                                 | 10.616   | [10]      |
| Cactus leaves                                | 7.082    | [10]      |
| Biogas residual slurry                       | 5.87     | [16]      |
| Activated carbon (from coconut tree sawdust) | 3.46     | [8]       |

participation of outer-sphere complexes in the adsorption of Cr(VI) on amorphous aluminium oxide could be suggested. The formation of outher-sphere complexes has also been proposed for the adsorption of chromate on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by Wu et al. [31] from a study of competitive adsorption of anions and by Mikami et al. [30] using the pressure-jump technique; conversely, for the adsorption of chromate on goethite, using the same latter technique, Grossl et al. [28] suggested the formation of inner-sphere surface complexes as well as was determined by Fendorf et al. [27] by extended X-ray absorption fine structure (EXAFS).

Table 4 shows the maximum capacity values reported in literature for the adsorption of Cr(VI) on different materials; such adsorption data were also derived from the Langmuir equation. Except for calcined hydrotalcite, the chromium retention capacities displayed by these materials are in general much lower than that achieved on amorphous aluminium oxide. The value of removal attained by this product appears high enough to consider its use in the purification of chromium industrial wastewaters.

#### 3.1.3. Effect of pH

The effect of pH in Cr(VI) removal from aqueous solutions on amorphous aluminium oxide is illustrated in Fig. 3. No significant differences were found between the adsorption capacities attained across the acid pH range, nevertheless a progressive adsorption decrease was produced when pH sifted from acidic to alkaline conditions. Cr(VI) adsorption on amorphous aluminium oxide appeared to be dependent on ionic strength along the entire pH range, although this dependence was more pronounced in acidic conditions where this decrease attained values close to 25% at the highest ionic strength employed, changing to about 10% at the most alkaline conditions. Chemisorption of anions on variable-charge minerals can be affected by pH in two different ways, the speciation of solute species and the surface charge of mineral. In almost all the acid pH range Cr(VI) is present as  $HCrO_4^{2-}$  (p $K_{a_1} = 0.75$ , p $K_{a_2} = 6.5$  [57]), therefore adsorption cannot be influenced by chromium speciation in such conditions. In the other hand, low pH values favour the

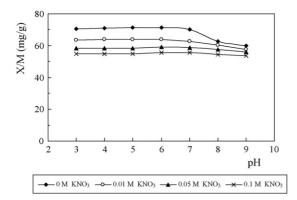


Fig. 3. Effect of pH in the adsorption of Cr(VI) from synthetic solutions on amorphous aluminium oxide at different ionic strengths (aluminium oxide dose 2 g/l; initial chromium concentration 150 mg/l; pH 3–9; shaking time 24 h).

protonization of hydroxyl groups and so their replacement by oxyanions by means of the ligand exchange mechanism, since water molecules are easier to displace from metal binding sites than hydroxyl groups [32]. No adsorption increase was observed in the acidic conditions as pH was lowered, therefore this second factor appears to have a minor contribution to the adsorption of Cr(VI) on amorphous aluminium oxide. This behaviour suggests that chromium adsorption on amorphous aluminium oxide may occur by electrostatic interactions, forming outer-sphere complexes with the charged surface of adsorbent rather than coordinative bonds.

## 3.1.4. Competitive adsorption study

Fig. 4 shows the results obtained for the co-adsorption of Cr(VI) and  $SO_4{}^{2-}$ at different concentration ratios. Competitive adsorption effects became apparent when both solutes were present in similar (molar) concentrations. In this case, Cr(VI) adsorption was greatly reduced by the presence of  $SO_4{}^{2-}$  across the entire pH range. Nevertheless this reduction did not show a constant trend; at low pH co-adsorption of  $SO_4{}^{2-}$  reduced Cr(VI) adsorption by as much as 75%, while at high pH this reduction was established at about 45%. This behaviour

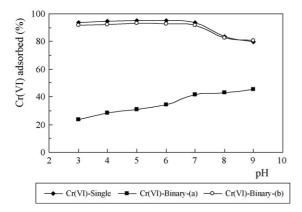


Fig. 4. Competitive adsorption of Cr(VI) and  $SO_4{}^{2-}$  from synthetic solutions on amorphous aluminium oxide as a function of pH (conditions  $[Cr(VI)] = 150 \, \text{mg/l}$ ; binary:(a) molar ratio  $[Cr(VI)]/[SO_4{}^{2-}] = 1$  and (b) molar ratio  $[Cr(VI)]/[SO_4{}^{2-}] = 100$ ; aluminium oxide dose 2 g/l; pH 3–9; shaking time 24 h).

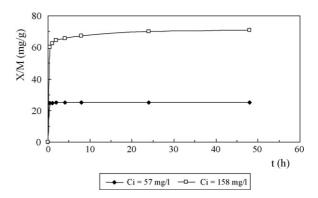


Fig. 5. Kinetic curves of Cr(VI) adsorption from electroplating wastewaters on amorphous aluminium oxide (conditions: aluminium oxide dose 2 g/l; initial chromium concentrations 57 and 158 mg/l; shaking time 0.5, 1, 2, 4, 8, 24 and 48 h).

seems to be related to the lower  $pK_{a_2}$  of sulphate (1.9 [57]) with respect to that of chromate. Previously, it has also been found that oxyanions with low  $pK_{a_2}$  most successfully compete with chromate for hydroxylated surfaces at low pH [42,58,31]. When Cr(VI) is present in large excess with respect to  $SO_4^{2-}$  ([Cr(VI)]/[ $SO_4^{2-}$ ] = 100), as happens in chromium electroplating wastewaters, competitive adsorption effects can be considered negligible.

#### 3.2. Actual chromium industrial wastewaters

#### 3.2.1. Kinetic study

The adsorption of Cr(VI) from actual electroplating wastewaters on amorphous aluminium oxide (Fig. 5) also appeared dependent on initial chromium concentration. The time required to reach equilibrium increased with concentration, showing the same values as those found for the adsorption of chromium from aqueous solutions. The pseudo-second order model effectively describes these kinetic data (Table 5) with all  $R^2$  values >0.99 and with calculated  $q_e$  values agreeing well with those determined from adsorption experiments. The adsorption rate and initial adsorption rate values were also decreased with chromium initial concentration.

#### 3.2.2. Adsorption isotherm

The adsorption isotherm obtained for the removal of Cr(VI) from actual electroplating wastewaters is shown in Fig. 6. The Langmuir model describes well adsorption of Cr(VI) from electroplating wastewaters on amorphous aluminium oxide with a  $R^2$  of 0.9556 (p<0.001), offering a maximum adsorption capacity (b) of 91.7 mg/g and a K value of 0.065. The b parameter reflects a high adsorption capacity value that could make

Table 5
Characteristic parameters and determination coefficient of kinetic data of Cr(VI) adsorption from electroplating wastewaters on amorphous aluminium oxide according to the pseudo-second-order model

| $C_i \text{ (mg/l)}$ | k (g/mg min)          | q <sub>e</sub> (mg/g) | $R^2 (p < 0.001)$ |
|----------------------|-----------------------|-----------------------|-------------------|
| 57                   | 0.121                 | 25.1                  | 1                 |
| 158                  | $9.21 \times 10^{-4}$ | 71.4                  | 0.9999            |

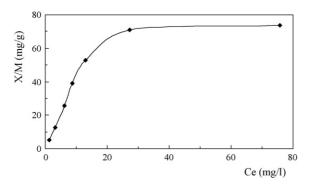


Fig. 6. Equilibrium isotherm of Cr(VI) adsorption from electroplating wastewaters on amorphous aluminium oxide (conditions: aluminium oxide dose 2 g/l; initial chromium concentrations 11–223 mg/l; shaking time 24 h).

amorphous aluminium oxide an interesting adsorbent material to be used in Cr(VI) wastewater purification systems. Literature recovers a quite limited number of works dealing with the Cr(VI) adsorption from electroplating wastewaters. Materials studied include phosphate treated sawdust [59], activated carbons [60], montmorillonite and silica gel [61] and calcined and uncalcined Mg–Al–CO<sub>3</sub>–hydrotalcite [62]. Among them, only calcined hydrotalcite displayed a higher adsorption capacity (128 mg Cr(VI)/g).

# 3.2.3. Effect of adsorbent dose

The influence of the amorphous aluminium oxide dose in the removal of Cr(VI) from actual electroplating wastewaters is shown in Fig. 7. A sharp increase in the percentage of Cr(VI) uptake was produced with the amorphous aluminium oxide dose increase until reaching a maximum value. This value is established above 90% for all the chromium concentrations subject of study. The amorphous aluminium oxide dose required to attain this removal was dependent on the initial chromium concentration, increasing as the chromium concentration was increased. Doses of 1, 2 and 5 g/l were needed for the aforementioned removal for initial chromium concentrations of 57, 119 and 223 mg/l, respectively.

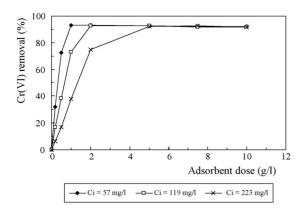


Fig. 7. Effect of adsorbent dose in the adsorption of Cr(VI) from electroplating wastewaters on amorphous aluminium oxide (conditions: aluminium oxide dose 0.2, 0.5, 1, 2, 5, 7.5 and 10 g/l; initial chromium concentrations 57, 119 and 223 mg/l; shaking time 24 h).

#### 4. Conclusions

The kinetic of Cr(VI) adsorption on amorphous aluminium oxide can be satisfactorily described by the pseudo-second order model, showing that the adsorption rate constant decreased with Cr(VI) initial concentration. The Langmuir model was found to describe the adsorption equilibrium process well, offering a maximum adsorption capacity of 78.1 mg/g. Ionic strength, pH and competitive solutes (SO<sub>4</sub><sup>2-</sup>) influenced the adsorption of Cr(VI) on amorphous aluminium oxide. Adsorption decreased with increasing ionic strength, this effect being more pronounced in acidic conditions. Nevertheless, adsorption was not affected by pH in acid medium but decreased when pH sifted to alkaline conditions. Cr(VI) adsorption was greatly reduced by the presence of SO<sub>4</sub><sup>2-</sup> across the entire pH range when both solutes (Cr(VI) and SO<sub>4</sub><sup>2-</sup>) were present in similar concentrations, this decrease being sharper at low pH. Amorphous aluminium oxide also showed a high adsorption capacity when used in the purification of Cr(VI) electroplating wastewaters. The adsorbent doses required to attain more than 90% of Cr(VI) removal from wastewaters varied between 1 and 5 g/l depending on Cr(VI) initial concentration. This behaviour suggests that amorphous aluminium oxide could represent an interesting adsorbent material to be used in Cr(VI) wastewater purification systems.

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