

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Characterization of Chromate Sorption on α -alumina.

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ABSTRACT

The objective of the present study is the evaluation of the effects of various parameters on chromate adsorption on α -Al₂O₃ through macroscopic experiments. Batch experiments were performed to investigate the effects of alumina dose, pH and contact time. The obtained results show that the chromate uptake by the used alumina is maximal around pH 7. Its evolution in function of time indicates two steps. The kinetics experimental data are well described by the Elovich model.

Keywords: α -alumina, chromate, adsorption, kinetic study.

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INTRODUCTION

Chromium found in the environment exists mainly in two oxidation states, Cr (III) and Cr (VI). Trivalent form is generally essential in glucose metabolism in mammals [1] while hexavalent form which is found in form of oxyanions in aqueous solution is highly toxic. It is generally introduced into the environment by industrial activities. In aquatic system, hexavalent chromium species are characterized by height mobility.

Sorption reactions onto common soil minerals regulate the bioavailability and the mobility of anions and can retard significantly their dissemination in waters. In natural environments, aluminum oxides and oxyhydroxydes are abundant and can exist in many forms, such as corundum ($\alpha\text{-Al}_2\text{O}_3$), gibbsite ($\alpha\text{-Al(OH)}_3$), boehmite ($\gamma\text{-AlOOH}$) and bayerite ($\beta\text{-Al(OH)}_3$) [2, 3]. The main objective of the present study is to characterize the removal of chromate from aqueous solutions by adsorption on $\alpha\text{-Al}_2\text{O}_3$.

MATERIAL AND METHODS

All chemicals reagents used in this study were of analytical grade; all solutions were prepared with distilled water. Commercial alumina (BIOCHEM CHEMOPHARMA) was used without any treatment. The stock solution of chromate was prepared by dissolving $\text{Na}_2\text{Cr}_2\text{O}_7$. The pH was adjusted by adding NaOH or HCl solution prior to each experiment.

Characterization of alumina

The point of zero charge (PZC) was determined by titration method. The infrared spectrum was recorded in the 4000 to 400 cm^{-1} range using Hyper IR Shimatzu E spectrophotometer. X-ray powder diffraction pattern was recorded using PERTE PANAYTICAL diffractometer employing Cu-K α radiation.

Chromate adsorption experiments

The adsorption experiments were performed in batch system. The effects of alumina dose, pH and contact time were evaluated. The chromate analyses were performed by diphenylcarbazine method using UV-Visible SCHIMADZU 1650 PC spectrophotometer.

RESULTS AND DISCUSSION

Characterization of alumina

In the Infrared spectrum (Figure 1), the bands observed at about 444 cm^{-1} and 559 cm^{-1} are attributed to Al-O bonding [4-7]. The bands observed in the range $3400\text{-}3700\text{ cm}^{-1}$ and at about 1643 cm^{-1} are in a relation to the adsorbed water. The DRX spectrum (Figure 2) confirms that the used alumina is identified as ($\alpha\text{-Al}_2\text{O}_3$). The observed peaks are in agreement with the spectra obtained by many authors [8-10]. The used alumina is characterized by PZC equal to 7.61. This value is lower than that measured by Mikkola and coauthors [11], but it is included in the range given in the literature [12].

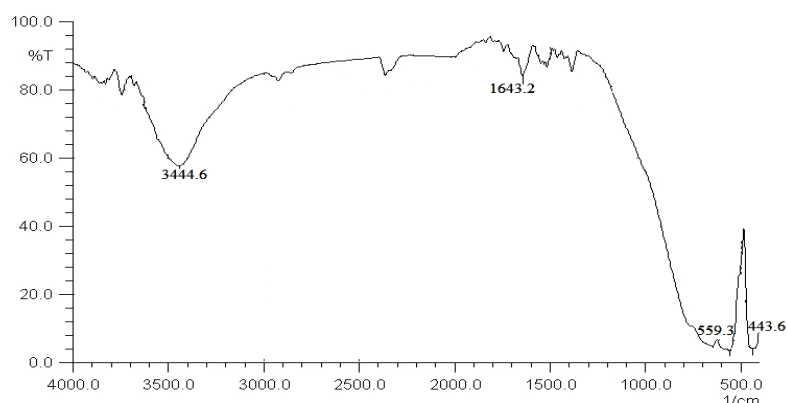


Figure 1: FTIR spectrum of the used alumina

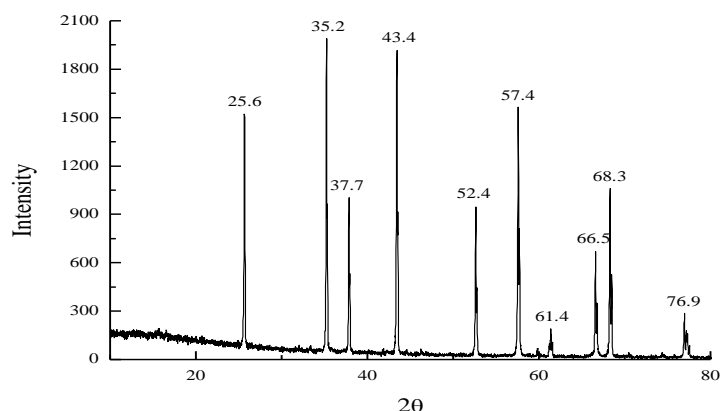


Figure 2: X-ray diffraction pattern of the used alumina

Effect of alumina dose

The adsorbent dose is an important parameter; it determines the capacity of adsorption for a given initial concentration. The results shown in Figure 3 imply that the increase in α -alumina dose induces a rapid increase in chromate uptake. For the initial concentration tested (10mg/L) and a contact time equal to 60min, the adsorption reaches a maximum for a dose of 3 g/L.

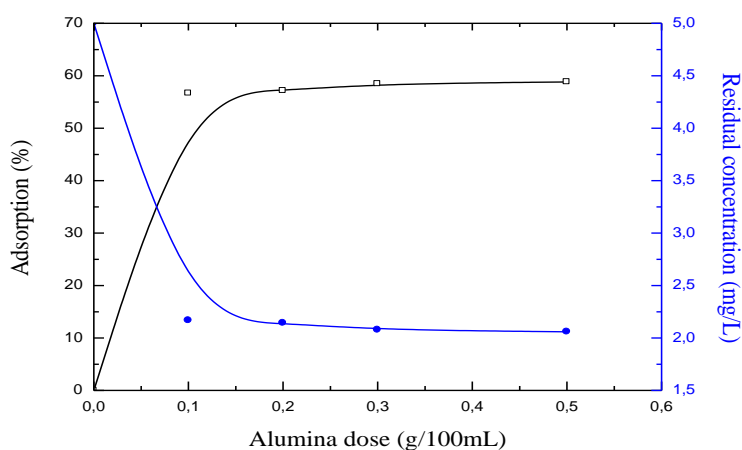


Figure 3: Effect of α -alumina dose (C_0 :10 mg/L; t:60min)

Effect of pH

In general, the pH is considered as an important parameter in controlling adsorption. At acidic pH, the chromate removal increases gradually to attain a maximum in the pH range [7-7.5] (Figure 4). This finding is not in agreement with what has been observed by Ajouyed and coauthors, where a very low chromium concentration was used [13]. According to the PZC value, the surface of the α -alumina is positively charged at pH less than 7.6 favoring the adsorption of anions. At higher pH, the observed decrease in chromate uptake can be explained by the increase of negative surface sites inducing a repulsion of negatively charged ions. However, the adsorption rate values observed in this pH range can reflect that the interaction with the α -alumina surface is not only physical and can be attributed to a chemical interaction. Consequently, the effect of pH on the absorption capacity of α -alumina towards chromate can be attributed to the combined effects of alumina surface charge and chromate speciation. The evolution of chromate adsorption in function of pH reveals that α -alumina has affinity for both $HCrO_4^-$ and CrO_4^{2-} .

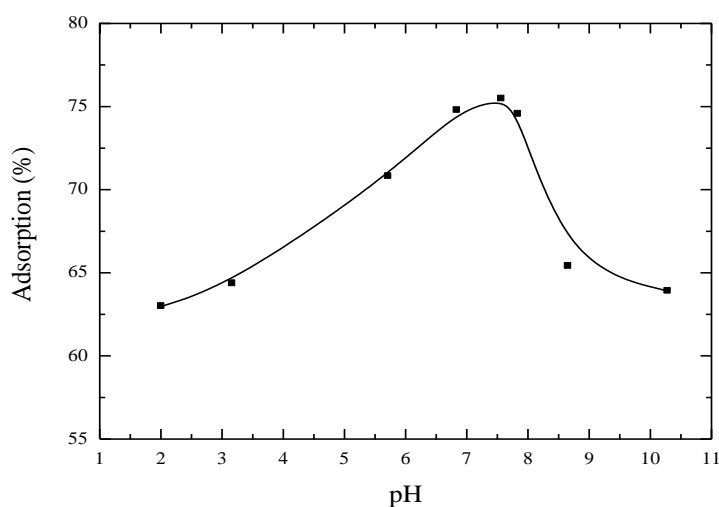


Figure 4: Effect of solution pH (C_0 :10 mg/L, t: 60 min; α -alumina dose: 3g/L)

Effect of time

The time evolution of chromate adsorption on α -alumina is characterized by two steps (Figure 5). For the initial concentration used (10 mg/L), 90% of the total removed chromate is adsorbed in the first step.

The chromate adsorption kinetic data are fitted with several kinetics equations (6, 7, 8, 9). The obtained parameters are summarized in Table 1. According to the calculated correlation coefficients, the kinetic can be described by the four models in the order: pseudo-first order < Elovich \approx diffusion < pseudo-second order. However, the calculated kinetic curves given in Figure 5 show that the chromate adsorption on α -alumina can be well described by Elovich model, implying chemical interaction of chromate ions with the α -alumina surface at the used pH. The diffusion model is more suitable to explain the experimental data in the first step. This result has been also found for chromate adsorption on iron oxide [14].

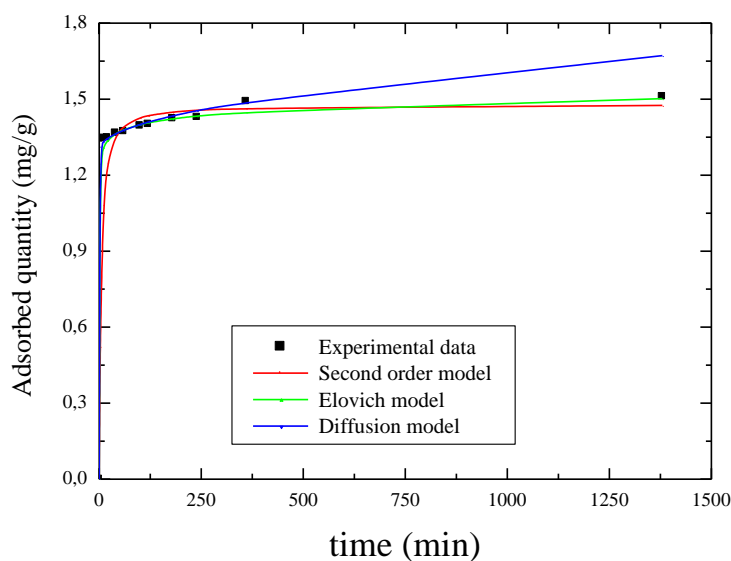


Figure 5: Effect of time (C_0 :10 mg/L, α -alumina dose 3g/L, pH: 7)

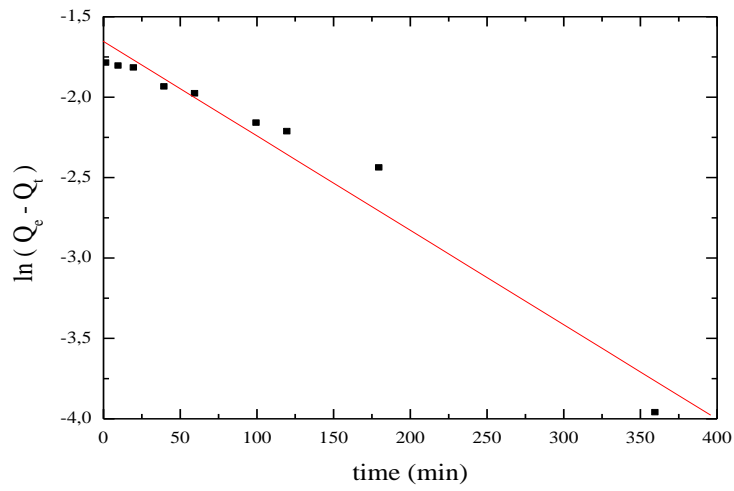


Figure 6: Pseudo first order plot

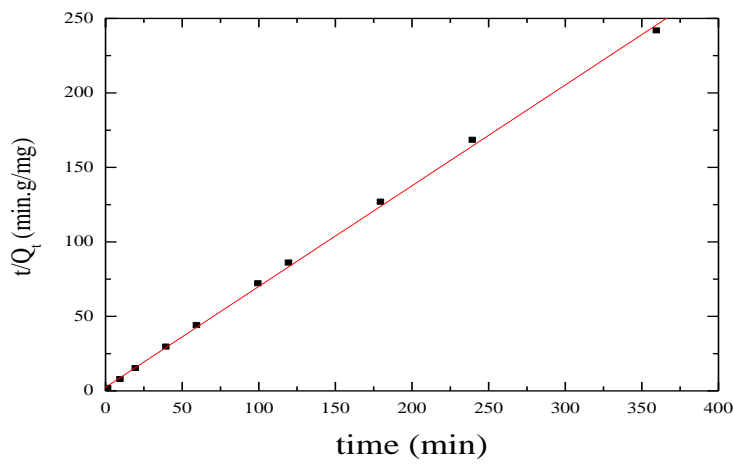


Figure 7: Pseudo second order plot

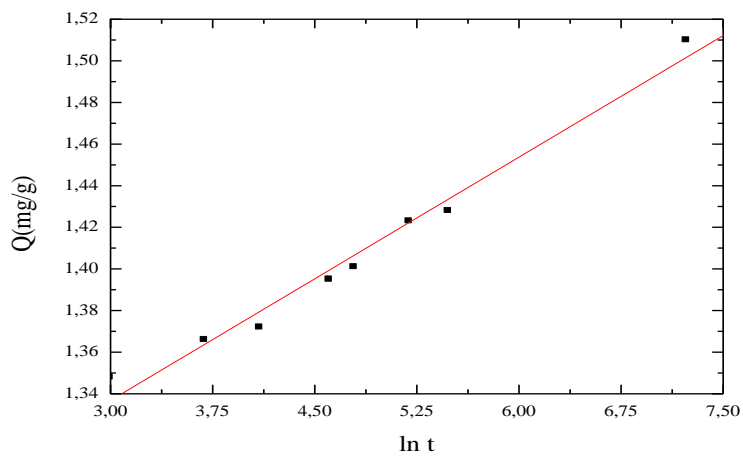


Figure 8: Elovich plot

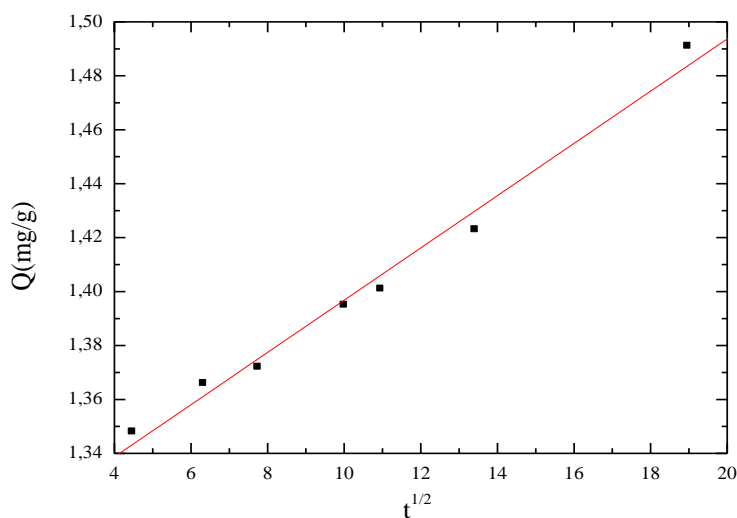


Figure 9: Intraparticles diffusion plot

Table 1: Kinetics models parameters

| Model | R | K |
|--------------|-------|--------|
| First order | 0.977 | 0.0059 |
| Second order | 0.999 | 0.1855 |
| Elovich | 0.990 | - |
| Diffusion | 0.993 | 0.010 |

CONCLUSION

The results of the present study show that the chromate adsorption by α -alumina is mainly chemical. The kinetics is successfully described by Elovich model. The optimum pH range to achieve maximum uptake is around 7.

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