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Characterization of Chromium (III) Sorption on γ-alumina

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ABSTRACT

In the present work, experiments studies of Cr(III) adsorption on γalumina were carried out involving process parameters such as contact time, chromium concentration, pH and the presence of sulfate ions. The adsorption was fitted by different kinetics and isotherms models. The evolution of chromium adsorption with pH is typical cationic. The presence of sulfate ions implies an enhancement in chromium adsorption in acidic pH range. The kinetics experimental data are well described by the second order model. The calculated rate adsorption constants are 0.01672 $mg^{-1}.g.min^{-1}$ at pH:5.2 and 0.04016 $mg^{-1}.g.min^{-1}$ at pH:6.7. The adsorption isotherm is well described by both Lamgmuir and Freundlich models.

Key words: γ-alumina, chromium(III), adsorption, kinetic, isotherm.

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INTRODUCTION

Heavy metals contamination of the aquatic system has become an important issue with respect to environment preservation and human health. Chromium is one of the most common pollutants. It is widely used in many industrial fields such as plating, alloying, dyeing, tanning, finishing, wood preserving and refractory technologies [1, 2]. Trivalent chromium is characterized by limited mobility in the aquatic environment, due on one hand to its low hydroxide solubility in neutral and alkaline pH and on the other hand to its tendency to form strong complexes with common soil minerals [3]. Among these minerals, metals oxyhydroxides are ubiquitous in soils and sediments. Alumina is found naturally in clays [4]. The work presented in this paper is a study of the uptake efficiency of chromium (III) from aqueous solutions using γalumina under batch conditions.

MATERIAL AND METHODS

All chemicals reagents used in this study were of analytical grade. Commercial alumina was purchased from Merck. It was used without any chemical treatment. The stock chromium solution was prepared by using $Cr(NO_3)_3,9H_2O$. Sulfate ions were used as the corresponding sodium salt. The pH was adjusted by adding NaOH or HCl solutions.

Characterization of Alumina

X-ray powder diffraction pattern was recorded with a scanning speed of 0.05°2θ step size by using PERTE PANAYTICAL diffractometer employing Cu-Kα radiation. The point of zero charge (PZC) was determined by titration method.

Chromium adsorption experiments

The chromium adsorption was performed by batch experiments. The effects of pH, time, chromium concentration and the presence of sulfate ions were evaluated. In all experiments, chromium analyses were performed in solutions obtained after centrifugation. The progress of adsorption was measured by determining the concentration of Cr(III) after conversion to Cr(VI) by oxidation using H_2O_2 in alkaline medium at elevated temperature. The formed Cr(VI) was determined by the colorimetric method using UV-Visible SCHIMADZU 1650 PC spectrophotometer. The efficiency of chromium removal was calculated from the difference between the initial and the final concentration in each case.

RESULTS AND DISCUSSION

Characterization of alumina

The DRX spectrum (Figure 1) reveals that the used alumina is identified as γalumina. The peaks observed at 37.29, 45.94 and 66.8° 2θ are in agreement with the spectra obtained in other studies [5, 6]. The measured PZC is neutral and equal to 7.62; this value is slightly lower than those measured by other authors [7, 8].

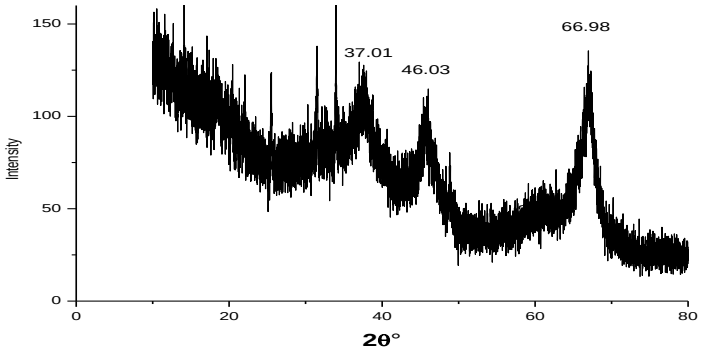

Figure 1: DRX spectrum of the used alumina

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Chromium adsorption

Effects of pH and the presence of sulfate ions

The pH effect on the adsorption of chromium on γalumina in the absence and in the presence of sulfate ions is showed in Figure 2. The low adsorption observed at pH<3 is due to the competition of protons. As pH increases, the adsorption increases. This evolution has been reported in several studies [2, 9] and is generally in a relation to the adsorbent surface charge and the metal speciation. In the present study, chromium uptake occurs below the measured pH_{PZC}. In the pH range 2-4 the dominant chromium species are Cr(III) and $Cr(OH)^{2+}$. However, in the pH range 4-6, the main species is $CrOH^{2+}$. Consequently, γalumina has more affinity for $CrOH^{2+}$. At pH greater than 6, the chromium uptake is also attributed to the chromium hydroxide precipitation.

In the presence of sulfate ions, an enhancement in chromium removal is observed. The same effect has been found for chromium (III) adsorption on ferrihydrite [10]. The formation of a ternary complex in the presence of sulfate ions has been proposed for the sorption of copper [11], lead [12] and cadmium ions [13] on goethite. It has been also suggested that both electrostatic effects and ternary complex formation may cause SO_4^{2-} ions to enhance trace metal adsorption [14].

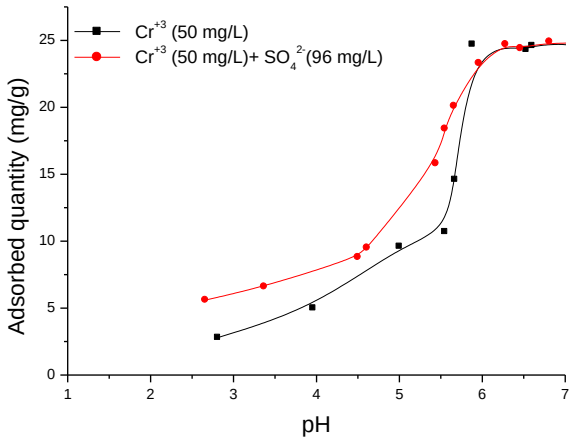

Figure 2: Effect of pH and sulfate ions on Cr(III) adsorption onto γalumina (γalumina dose 2g/L; t:1h)

Effect of time

The obtained results are illustrated in Figure 3. A maximum adsorption capacity (14mg/g) representing 57% of chromium removal is attained within 4 h at pH 5.2. In several studies, it has been observed that the adsorption of metals on γ-alumina is slow [5, 15]. At pH 6.7, the chromium uptake is rapid; it reaches 98% in the first ten minutes.

In order to investigate the controlling mechanism of the adsorption processes, the experimental data are analyzed by various kinetic models (Figures 4, 5, 6). The calculated parameters of the pseudo first order, second order and Elovish equations are listed in Table 1.

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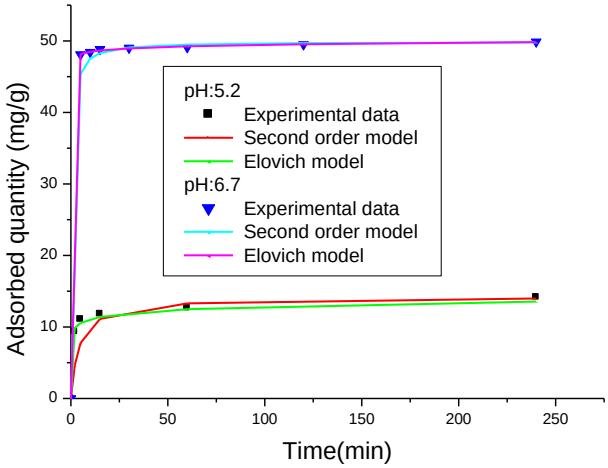

Figure 3: Effect of contact time on Cr(III) adsorption onto γalumina-Experimental data and kinetics models (C_0: 50 mg/L, γalumina dose:2 g/L)

According to the correlation coefficients, the three models may describe the kinetics experimental data. However, the calculated curve of the first order model does not give acceptable values compared to experimental data. The two other models describe well the chromium adsorption on γalumina (Figure 3). The Elovich model is used to describe activated chemisorption; the related calculated constant (β) which is in a relation to the activation energy is about 1.13 g/mg at pH:5.2 and 2.34 at pH 6.7. By using the second order model, the calculated values of the equilibrium adsorption capacity agree with the experimental data (Table 1). This result is in agreement with that obtained in several studies on chromium sorption on various sorbents [16, 17]. The second order model admits a chemisorption mechanism where the adsorption takes place on localized sites with no interaction between the adsorbed molecules [18]. The calculated adsorption rate constants are 0.01672 $mg^{-1}.g.min^{-1}$ at pH 5.2 and 0.04016 $mg^{-1}.g.min^{-1}$ at pH 6.7.

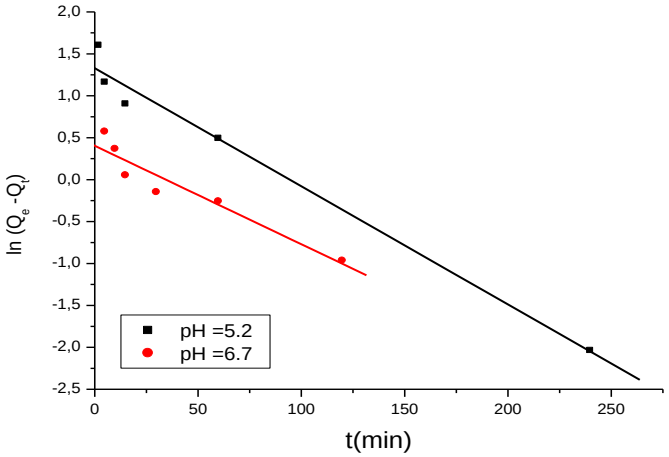

Figure 4: Pseudo-first order plots for Cr(III) adsorption onto γalumina

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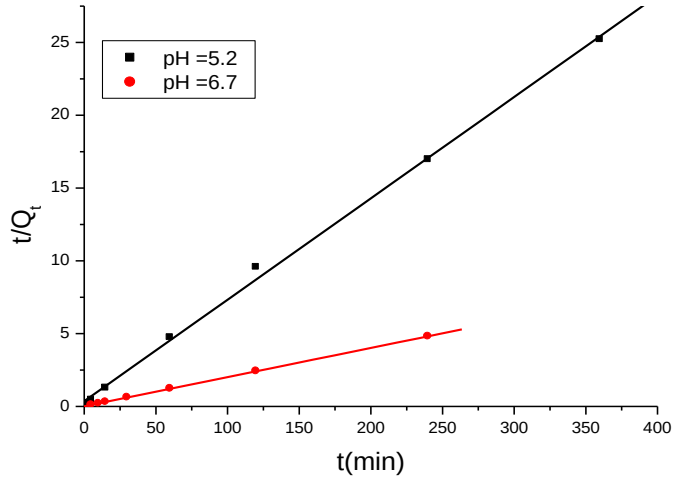

Figure 5: Pseudo-second order plots for Cr(III) adsorption onto γalumina

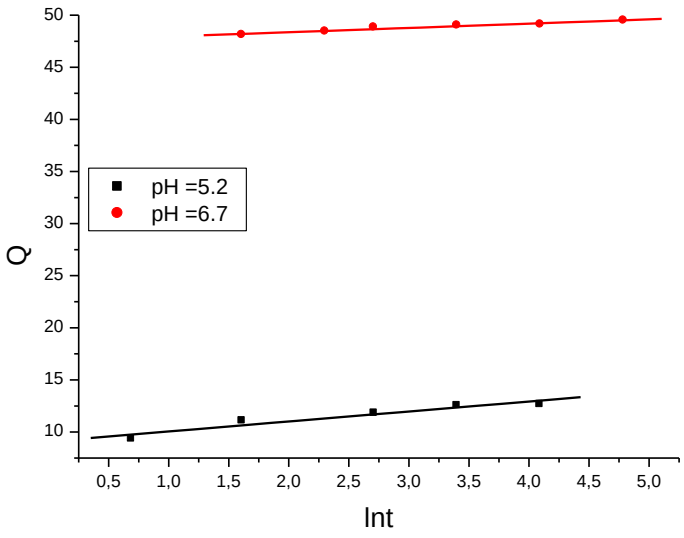

Figure 6: Elovich plots for Cr(III) adsorption onto γalumina

Table 1: Kinetic parameters for Cr (III) adsorption on γalumina

pH	Model	R^2	K
5.2	First order	0.991	0.01409
	Second order	0.999	0.01672
	Elovich	0.982	-
6.7	First order	0.953	0 .01174
	Second order	0.999	0.04016
	Elovich	0.985	-

Effect of chromium concentration

The adsorbed chromium quantity increases with the increase of its initial concentration. The saturation is obtained for a concentration greater than 150mg/L. The application of Langmuir, Freundlich and Temkin equations to the experimental data gives correlation coefficients values superior to 0.99 for Langmuir and Freundlich models indicating that the two models can be used for describing the experimental isotherm.

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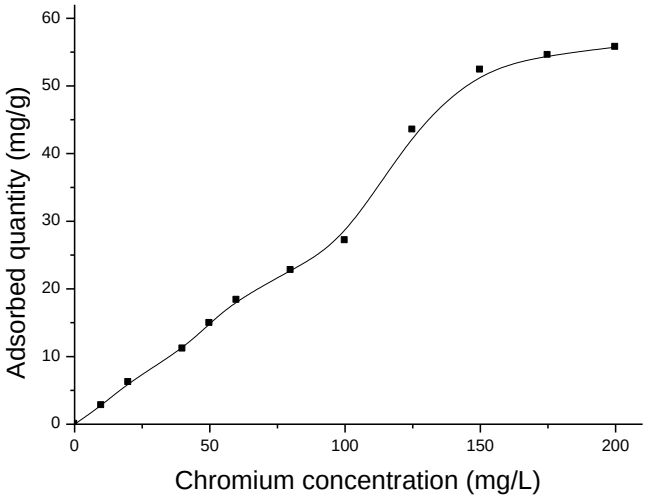

Figure 7: Effect of initial concentration on chromium adsorption onto γalumina (γalumina dose:1g/L; t:4h)

CONCLUSION

The results of the present study show that the chromium (III) adsorption efficiency by γalumina is pH dependent; it enhances in the presence of sulfates ions. The kinetics follows the pseudo second order and Elovich models. The experimental equilibrium data are well described by Langmuir and Freundlich isotherms.

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