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Characterization of Chromium (III) Sorption on Ferrihydride.

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ABSTRACT

In the present work, experiments studies of Cr(III) adsorption on characterized Ferrihydrite are carried out involving process parameters such as contact time, chromium concentration, pH and the presence of sulfate ions. Three kinetics models are tried to describe the experimental data; the obtained results show that the second order model is the best. The calculated rate adsorption constant is about 0.00123 $mg^{-1}.g.min^{-1}$ at pH 5 and 0.1100 $mg^{-1}.g.min^{-1}$ at pH 6. The adsorption isotherm is well described by both Langmuir and Freundlich equations. The evolution of chromium adsorption with pH is typical cationic. The presence of sulfate ions implies an enhancement in chromium adsorption.

Keywords: chromium; adsorption; ferrihydrite; kinetics; isotherm

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INTRODUCTION

Heavy metal contamination of the aquatic environment has become an important issue with respect to environmental and human health. Chromium is one of the most common pollutants in soils and aquifers [1]. It is used in many industrial fields such as plating, alloying, dyeing, tanning, finishing, wood preserving and refractory technologies [2, 3]. Trivalent chromium is characterized by limited mobility in the environmental media, due to its low hydroxide solubility in neutral and alkaline pH and its tendency to form strong complexes with common soil minerals [1]. Among these minerals, iron oxyhydroxides are ubiquitous in soils and sediments. Ferrihydrite is a low-crystallinity environmentally relevant iron oxyhydroxide [4]. The aim of the present study is to investigate the effects of various parameters on chromium adsorption on ferrihydrite prepared and characterized in laboratory.

MATERIAL AND METHODS

Ferrihydrite was prepared in laboratory using the method described by Shwertmannite and Cornell (2000) [4]. It was characterized by infrared analysis using Hyper IR Shimatzu E spectrophotometer. Its point of zero charge (PZC) was determined by titration method.

The chromium adsorption was performed by batch experiments. The effects of ferrihydrite dose, time, chromium concentration, pH 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 concentrations 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. In each case, the efficiency of chromium removal was calculated from the difference between the initial and the final concentrations in solution.

RESULTS AND DISCUSSION

Characterization of Ferrihydrite

The prepared ferrihydrite is characterized by neutral PZC equal to 7.50. In the obtained IR spectrum (Figure 1), the absence of bands at wavenumber below 1000cm^{-1} confirms the formation of ferrihydrite. The observed bands at 1380, 1508 and 1631 cm^{-1} are attributed to nitrate, carbonate and adsorbed water respectively.

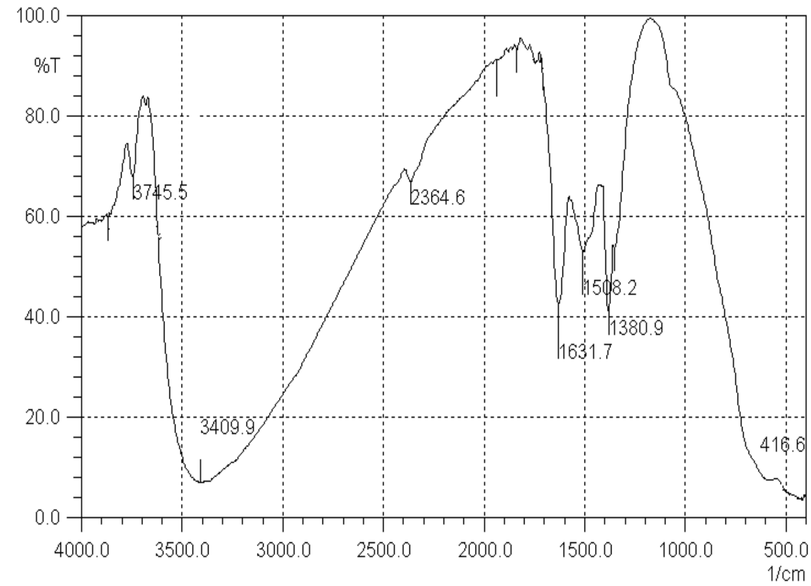

Figure 1: FTIR spectrum of the prepared ferrihydrite

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Chromium adsorption

Effect of ferrihydrite dose

For a concentration of 50mg/L and a contact time equal to 60min, the increase in ferrihydrite dose induces a rapid increase in chromium uptake due to the increase of adsorption sites number (Figure 2). After this, a gradual low increase in chromium uptake is observed.

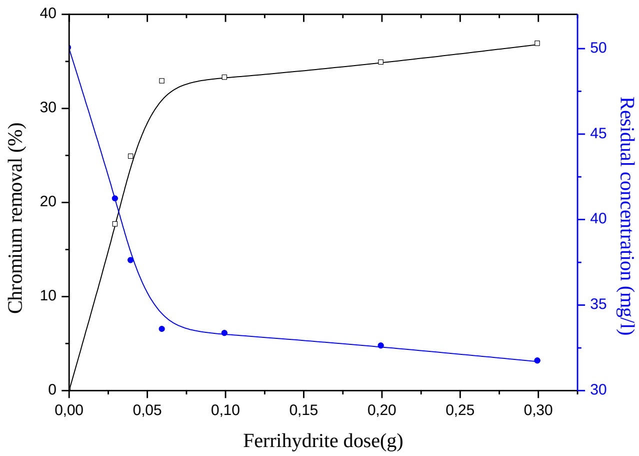

Figure 2: Cr(III) adsorption - Effect of ferrihydrite dose

(C_0:50mg/L, t= 60 min)

Effect of time - Kinetic study

The kinetics study was evaluated at pH 5 and 6. The obtained results (Figure 3) show that at pH 5, the uptake of Cr(III) by ferrihydrite is slow and the equilibrium is reached within 24h. However at pH 6, the removal is rapid, it attains a maximum in the first 30 minutes. This can be also attributed to the precipitation of chromium hydroxide.

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

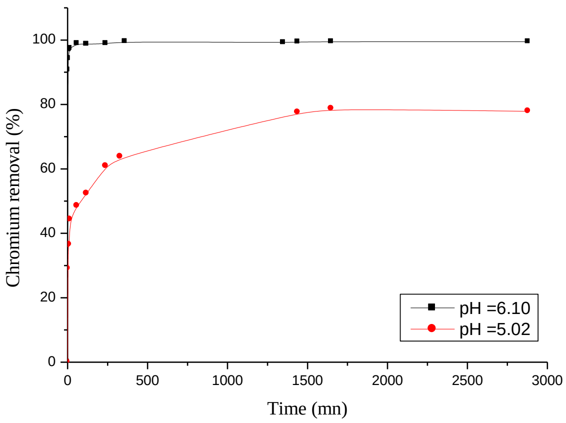

Figure 3: Cr(III) adsorption onto ferrihydrite - Effect of contact time

(C_0: 50 mg/l, ferrihydrite dose: 2g/L)

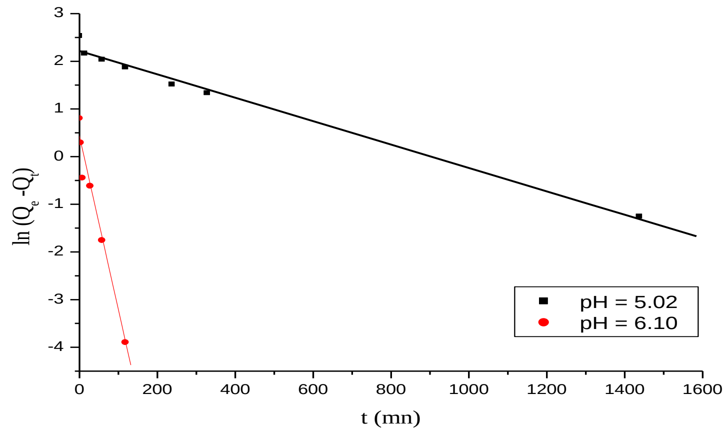

Figure 4: Pseudo-first order plots for Cr(III) adsorption onto ferrihydrite

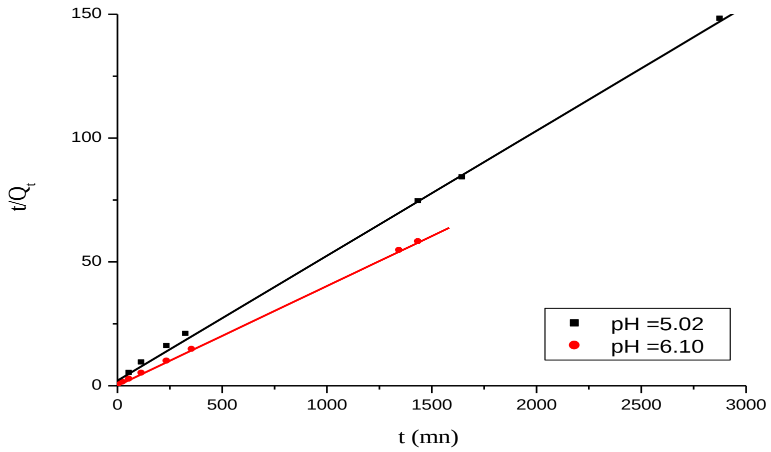

Figure 5: Pseudo-second order plots for Cr(III) adsorption onto ferrihydrite

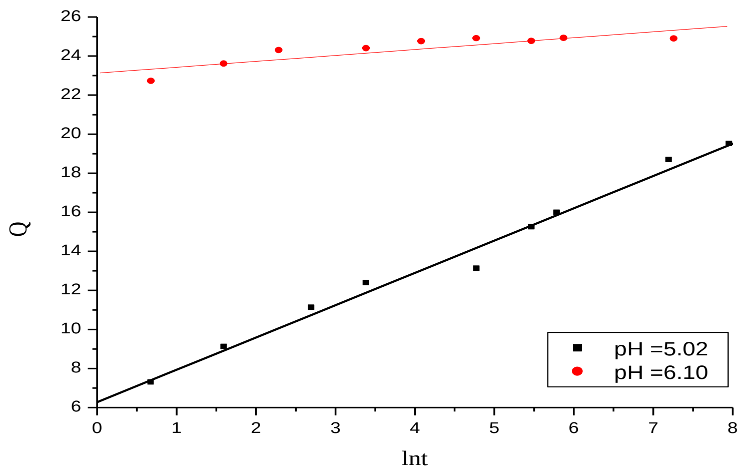

Figure 6: Elovich plots for Cr(III) adsorption onto ferrihydrite

According to the correlation coefficients, the three models may describe the kinetics experimental data at pH 5. However, at pH 6, the obtained coefficient of the Elovich model is lower than those of the two other models.

Table 1: Kinetic parameters for the removal of Cr (III) by Ferrihydrite

pH	Model	R^2	K	Q_e
5	First order	0.993	0.00245	9.18
	Second order	0.999	0.00123	19.83
	Elovich	0.993	-	-
6	First order	0.983	0 .03642	1.53
	Second order	0.999	0.1100	24.86
	Elovich	0.911	-	-

In the two cases, the calculated curves of the first order model do not give acceptable values compared to experimental data. As shown in Figure 7, the equilibrium adsorption capacities calculated by the second order model equation, agree with the experimental data. The calculated adsorption rate constants are about 0.00123 $mg^{-1}.g.min^{-1}$ at pH 5 and 0.1100 at pH 6. At pH 5, the Elovich model is more suitable for describing the experimental data in the first step of adsorption. The calculated Elovich constant (β) which is in a relation to the activation energy is about 0.60g/mg.

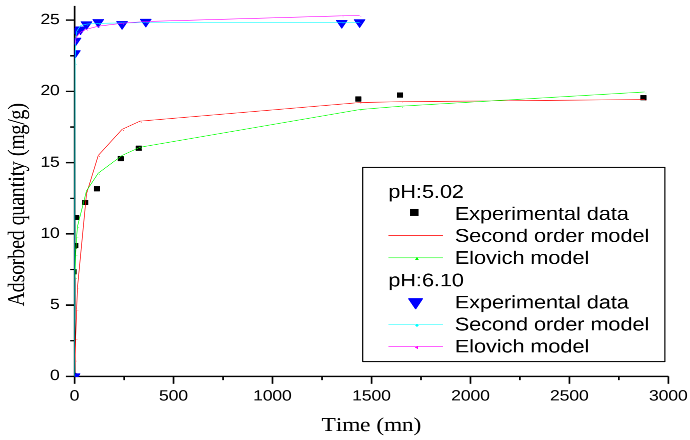

Figure 7: Adsorption kinetics of Cr(III) adsorption on ferrihydrite - Experimental data and Kinetics models

Effect of chromium concentration - Adsorption isotherm

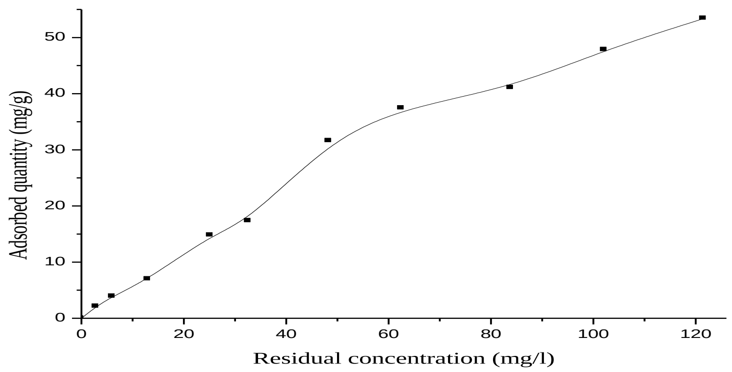

Figure 8: Cr(III) adsorption onto ferrihydrite - Effect of chromium concentration

(C_0: 50 mg/l, Ferrihydrite dose: 1g/L ; t: 24h)

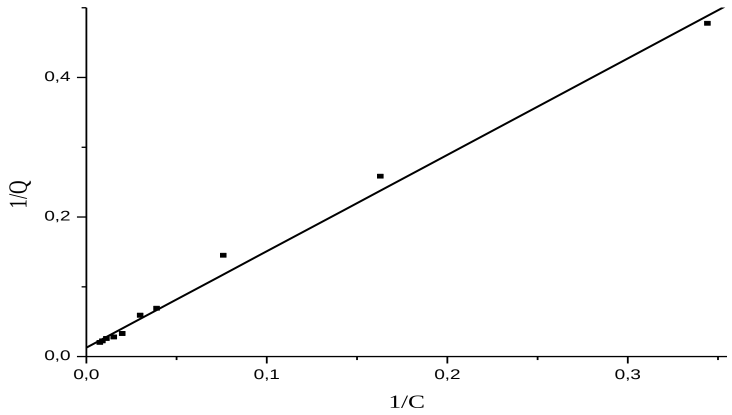

Figure 9: Langmuir plot for Cr (III) adsorption on ferrihydrite

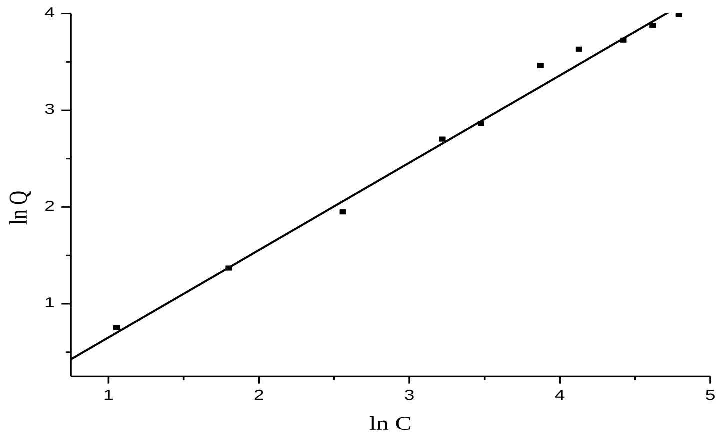

Figure 10: Freundlich plot for Cr(III) adsorption on ferrihydrite

The obtained experimental isotherm (Figure 8) shows an increase in the adsorption capacity with the increase of the equilibrium concentration. In the concentrations range studied no saturation is observed. The application of the Langmuir and Freundlich equations (Figures 9, 10) gives the parameters presented in Table 2. The correlation coefficients values are superior to 0.99 indicating that the two models can be used for describing the experimental data. However the form of the obtained experimental curve shows that the Freundlich model is more suitable. The calculated Freundlich coefficient is greater than 1 showing strong affinity of Cr(III) for Ferrihydrite**.**

Table 2: Isotherm parameters for the removal of Cr (III) by ferrihydrite

Model	R^2	K	Q_{max}(mg/g)	n
Langmuir	0.996	0.00918	78.80	-
Freundlich	0.995	0.7775	-	1.107

Effects of pH and the presence of sulphate ions

The pH effect on chromium adsorption on ferrihydrite in the absence and in the presence of sulfate ions is depicted in Figure 11. The chromium uptake increases with the increase in pH. This evolution has been reported in several studies [5] and is generally in a relation to the adsorbent surface charge and the metal speciation. If the electrostatic forces are involved, the increase in metal adsorption with pH can be in a relation to the increase in negative functions at the surface of the adsorbent. In the present study, the chromium uptake occurs well below the measured pH_{PZC}. Consequently, the chromium interaction with ferrihydrite is mainly chemical. This is in agreement with the results obtained in kinetics and isotherm experiments. At pH greater than 6, the increase in chromium uptake is also attributed to chromium hydroxide precipitation.

In the presence of sulfate ions, an enhancement in chromium removal is observed at acidic pH. This effect has been observed in other studies concerning the adsorption of other metals on ferrihydrite [6, 7]. The increase of sulfate concentration implies the displacement of the adsorption edge to acidic pH.

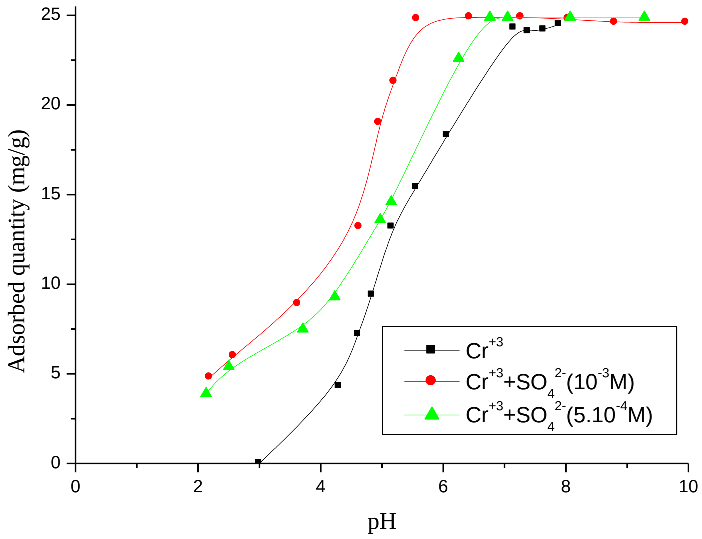

Figure 11: Evolution of chromium adsorption on ferrihydrite – Effects of pH and sulphate ions

(C_0: 50 mg/l, Ferrihydrite dose: 1g/L ; t: 1h)

CONCLUSION

The results of the present study show that chromium has a height affinity for ferrihydrite. Its uptake at acidic pH occurs mainly by chemical sorption and increases in the presence of sulfates ions. The calculated sorption capacity by Langmuir equation is about 78.8mg/g.

REFERENCES

[1] K Papassiopi, C Vaxevanidou, EC Karagianni, GSE Antipas. J Hazard Mater 2014; 264: 490-497.
[2] R Fonseca-Correa, L Giraldo, CJ Moreno-Piraján. J Anal App Pyrol 2013; 101:132-141.
[3] M Gurua, D Venedikb, A Murathana. J Hazard Mater 2008;160:318-323.
[4] U Schwertmann, RM Cornell. Iron Oxides in the Laboratory: Preparation and Characterization, Wiley-VCH. 2000.
[5] A Chakir, J Bessiere, K ELKacemi, M Bouchaıb. J Hazard Mater 2002;B95: 29-46.
[6] C Boukhalfa, A Mennour, L Reinert, M Dray, L Duclaux. Asian J Chem 2007;19(6):4267-4276.
[7] J Peter, G Swedlund,' Jenny, W Gordon, M Miskelly. App Geochem 2003;18:1671-1689.