



Sorption of Cr(VI) onto natural iron and aluminum (oxy)hydroxides: Effects of pH, ionic strength and initial concentration

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ABSTRACT

The aim of this work is to study the performances of removal of hexavalent chromium from aqueous solution by three different oxy-hydroxides: hematite, goethite and α -alumina. Batch experiments were conducted to measure the effects on adsorption of Cr(VI) of different parameters such as pH of the medium, ionic strength, and initial concentration. Results showed that the adsorption of Cr(VI) depends strongly on the pH, but is independent of ionic strength for hematite and goethite. For α -alumina, adsorption is strongly dependent on pH values and ionic strength. Equilibrium studies showed that Cr(VI) had a high affinity in an acidic medium, but decreased as solution pH increased. Equilibrium isotherms were measured experimentally. Results were analyzed by the Langmuir and Freundlich equations using linearized correlation coefficient at room temperature. The characteristic parameters for each isotherm have been determined. Langmuir equation was found to fit the equilibrium data for Cr(VI) adsorption.

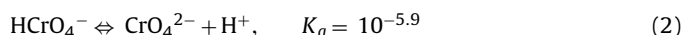
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1. Introduction

Activities of dredging are necessary for the development of the ports and to maintain sufficient sailing depth. Dredging is also a crucial operation for some engineering works. In Morocco, approximately 4 Mm³ of the sediments are dredged each year. Dredged sediments are frequently accumulating chemicals and present an effective contamination risk for coastal waters, affecting the ecosystems durably. Chromium is found in various oxidation stages ranging from –II to +VI. Cr(III) and Cr(VI) are of major environmental significance depending on pH and redox conditions [1,2]. In sediments, chromium can be present in two oxidation states [Cr(III) and Cr(VI)], trivalent chromium being an essential element in animal and human nutrition, and hexavalent chromium being toxic to organisms. Due to the severe toxicity of Cr(VI), the Agency for Toxic Substances and Diseases Registry (ATSDR) classifies it as the top 16th hazardous substance [3]. The World Health Organization [4] requires 50 μ g/L of Cr(VI) in drinking water. The sediments dredged are indeed often polluted with heavy metals and organic matter

and may present a risk for the environment and human health. It is therefore necessary to propose appropriate treatment techniques that satisfy environmental as well as economic criteria.

The mobility and the toxicity of chromium depend on its speciation. The speciation of chromium (VI) and (III) depends on the solution pH, their concentration and the availability of ligand. The Cr(VI) has high solubility in water and is more dangerous to living bodies even at low concentrations, with a potential carcinogenic effect. It exists in several stable forms in aqueous solution including CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ depending on the Cr(VI) concentration and pH of the medium [5,6]. The different species of Cr(VI) in aqueous solutions are given by the following equilibrium equations (1) and (2):



In contrast, trivalent chromium is relatively less toxic and less mobile. The Cr(III) species in aqueous solutions, however, may take the form of Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, or $\text{Cr}(\text{OH})_4^-$ depending on the solution pH.

Organic matter (both soluble and insoluble), ferrous iron, oxidants (e.g., MnO_2), and sulfides are capable of reducing Cr(VI) to Cr(III) and vice versa. Aqueous Cr(VI) can be reduced to Cr(III) when it interacts with solids that contain Fe(II) in the near-surface region [7,8]. The Cr(VI) is also reduced to Cr(III) when sorbed on the surface

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of magnetite, $\text{Fe(II)Fe(III)}_2\text{O}_4$ [7,8]. However, no such reduction is expected when aqueous Cr(VI) sorbs on maghemite [$\gamma\text{-Fe(III)}_2\text{O}_3$], hematite [$\alpha\text{-Fe(III)}_2\text{O}_3$], goethite [$\alpha\text{-Fe(III)OOH}$], or hydrous ferric oxides unless some Fe(II) is present in the near-surface region of these solids [9,10].

The commonly used treatment methods for removing metal ions from wastewaters include adsorption, biosorption, complexation, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, filtration and membrane processes. Among them, adsorption is one of the most popular methods for the removal of chromium from the wastewaters [2,11,12]. Metal ions are adsorbed onto the solid adsorbent surface from the wastewater with the quantity of the removed pollutant depending on the adsorption capacity of the adsorbent.

Mineral oxides, especially Fe- and Al-oxides, are very common in the environment and have active sorption capability for metal ions in the pH range of most natural waters. The properties of the surface of (oxy)hydroxides strongly depend on pH. In an acidic medium, below pH_{PZC} (PZC, point of zero charge, the pH value at which the net surface charge is zero), the surface is positively charged. At a basic medium ($\text{pH} > \text{pH}_{\text{PZC}}$) the surface is negatively charged. In an acidic medium, crystalline and amorphous Fe- and Al-oxides present a potential affinity to sorb Cr(VI) [2,13].

Adsorption of metal ions on adsorbent from aquatic environments is governed by electrostatic (coulombic) and non-electrostatic interactions, coming mainly from the surface charges generated on adsorbent after its immersion into water. Non-electrostatic interactions can be of different nature, predominantly of van der Waals type [14]. Factors that control both electrostatic and non-electrostatic interactions that lead to the adsorption process are the surface oxygen complexes content, the pH at the point of zero charge (pH_{PZC}), the solution pH and its ionic strength, the adsorption temperature, the nature of the metal ion (given by its speciation diagram), its solubility, and its size in adsorption conditions.

The aim of this work is to examine the Cr(VI) ions adsorption behavior from aqueous solution on commercial adsorbent: hematite [$\alpha\text{-Fe}_2\text{O}_3$], goethite [$\alpha\text{-FeOOH}$] and alumina [$\alpha\text{-Al}_2\text{O}_3$] by batch method as a function of initial pH solution, ionic strength and initial metal ion concentration. Langmuir and Freundlich adsorption isotherms are employed to understand the nature of sorption. This study falls under the context of the treatment of dredged sediments, by addition of commercial adsorbent as an additive for the immobilisation of metals in a polluted sediment.

2. Experimental work

2.1. Materials

The hematite (Johnson Matthey, purity equal to 99.999%), the α -alumina (Sigma-Aldrich, purity equal to 99%) and the goethite (Sigma-Aldrich, purity equal to 35% Fe) used for this study are commercial powders purchased. The mean particle size, determined by laser granulometer (Mastersizer 2000, Malvern Instruments), is equal to 53, 99.8 and 10 μm , respectively. The surface area, determined by the BET nitrogen adsorption method, is equal to 1.7, 12.7 and 11.6 m^2/g , respectively.

A stock solution of Cr(VI) was prepared in ultrapure water with potassium dichromate (Sigma-Aldrich, purity equal to 99.5%). NaNO_3 (0.01 M) was used as the supporting electrolyte to maintain the ionic strength constant during the adsorption experiments. Solutions of (0.01 and 0.1 M) NaOH and HNO_3 were used for pH adjustment. We have adjusted the pH manually. Small amounts of acid or base (HNO_3 or NaOH) was added to the suspension using Micro-pipette. The pH of the solutions was measured using a WTW pH meter, with a combined pH electrode, calibrated using buffer

solutions at pH 4.00 and 7.01 at room temperature. Chromium concentrations in the supernatant were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP MS-Elan DRC II-Perkin Elmer).

All glassware and plastic materials used were previously treated for 24 h in 10% (v:v) nitric acid (HNO_3 , 69%) and rinsed with ultrapure water.

2.2. Batch adsorption experiment

The adsorption of Cr(VI) on hematite, goethite and α -alumina was investigated in batch mode. The effect of solution pH (range 2–10), ionic strength (0.01, 0.05 and 0.1 M) and initial concentration (0.1 and 0.5 mg/L) on the adsorption were studied at room temperature.

2.2.1. Effect of pH

The pH of the aqueous solution is a significant controlling factor in adsorption mechanism, in order to optimize the pH for maximum removal efficiency, batch experiments at room temperature were carried out by taking in contact 0.1 mg/L of chromium solution with 0.2 g of hematite, α -alumina and goethite in 50 mL of solution for 3, 24 and 1 h of shaking time, respectively (period needed to reach the complete adsorption equilibrium between the two phases), at several pH values (2–10). Afterwards, the final pH was measured and the suspensions were centrifuged, filtered, acidified, and the percentage of chromium adsorbed by solid was determined from the difference between initial C_i and final C_f concentrations of chromium ion in aqueous solution, before and after contact. The following equation was used for calculations:

$$S\% = \frac{C_i - C_f}{C_i} 100$$

2.2.2. Effect of ionic strength

In batch experiments, anion (0.1 mg/L) was equilibrated with solid suspension (0.2 g) in the presence of 0.01, 0.05 and 0.1 M NaNO_3 . A small amount of HNO_3 or NaOH was added to cover the pH range (2–10). All experiments were performed in a tightly capped 50 mL polypropylene centrifuge tube at room temperature. At the end of the equilibrium period, the pH of each suspension was determined. The suspensions were centrifuged, filtered and acidified for later analysis of anion concentration.

2.2.3. Effect of initial concentration

Batch experiments were conducted in a 50 mL polypropylene centrifuge tube containing 0.2 g of adsorbents and 0.1 or 0.5 mg/L of Cr(VI) solution prepared from potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The tubes were shaken at 70 rpm in the solution pH (range 2–10) and contact time of 3 h for hematite, 24 h for α -alumina and 1 h for goethite. The reaction mixtures were centrifuged, filtered and acidified for later analyses of anion concentration.

2.2.4. Adsorption isotherms

The adsorption isotherms were determined by a batch technique in a background electrolyte of 0.01 M NaNO_3 . In the experiments, 0.2 g of adsorbents were mixed with 50 mL solutions of various Cr(VI) concentrations between 0.1 and 16 mg/L . The pH of the system was maintained at 8 characteristic of pH of sediment equilibrated with water. After the samples were shaken, the suspensions were centrifuged, filtered through a 0.45 μm pore size acetate filters, acidified, and analyzed for metal ion concentrations.

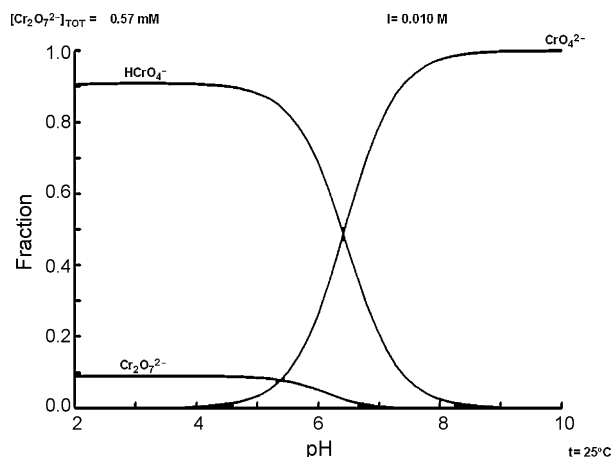


Fig. 1. Species distribution of Cr(VI) in an aqueous system.

3. Results and discussion

Cr(VI) exists in solution as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- or CrO_4^{2-} depending on the pH and the Cr(VI) concentration. The pH and concentration ranges used in this study meant that the HCrO_4^- in an acidic medium and the CrO_4^{2-} in an neutral and basic medium would be the predominant form of Cr(VI) which participate in adsorption (Fig. 1).

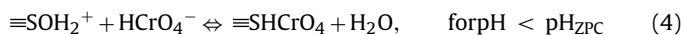
3.1. Effect of pH

The pH of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent, and the ionic forms of chromium in solution. The amount of Cr(VI) adsorbed as a function of solution pH is shown in Fig. 2. Maximum Cr(VI) adsorption occurred when pH was ≤ 5 for hematite, ≤ 3 for goethite and ≤ 5.5 for α -alumina. Cr(VI) adsorption decreased as solution pH increased. According to the speciation diagram, the dominant form of Cr(VI) at these pH is HCrO_4^- [15,16]. Increasing the pH will shift the concentration of HCrO_4^- to other form, CrO_4^{2-} as shown in Fig. 1. Similar observations have also been reported by other investigators [17,18]. It can be concluded that the active form of Cr(VI) that can be adsorbed by all adsorbents chosen in this study is HCrO_4^- . Thus, there were two possible reactions, as shown in

Eqs. (3) and (4):



or



with $\equiv\text{SOH}_2^+$ symbolising protonated surface sites.

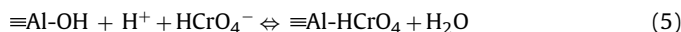
These mechanisms are in agreement with the findings of previous studies on other adsorbents [15,17].

The behavior for better adsorption at low pH by these solids may be attributed to the large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbents surface. That results in strong electrostatic attraction between positively charged adsorbent surface and HCrO_4^- leading to higher adsorption. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on these adsorbents does not favor the adsorption of Cr(VI) due to the electrostatic repulsion. Furthermore, lower adsorption of Cr(VI) in alkaline medium is also due the competition from excess OH^- ions with the anions CrO_4^{2-} for the adsorption sites.

3.2. Effect of ionic strength

Ionic strength, besides pH, is also one of the important factors that influence adsorption. Fig. 3 shows the influence of ionic strength (0.01, 0.05 and 0.1 M) as a function of pH (2–10) on the adsorption of Cr(VI) onto hematite, goethite and α -alumina. The results indicate that Cr(VI) adsorption is independent of ionic strength and dependent on pH values for hematite and goethite, but strongly dependent on pH values and ionic strength for α -alumina. These results are in agreement with the findings of previous studies by other authors [19–21]. The ionic strength can influence the double layer thickness and interface potential, thereby can affect the binding of the adsorbed species. Outer-sphere complexes are expected to be more susceptible to ionic strength variations than inner-sphere complexes, since the background electrolyte ions are placed in the same plane for outer-sphere complexes. In general, the sorption mechanism of surface complexation is significantly affected by pH, whereas the sorption mechanism of ion exchange is influenced by ionic strength. The strong pH dependent and ionic strength independent adsorption of Cr(VI) to hematite and goethite, suggest that the adsorption of Cr(VI) is mainly dominated by surface complexation rather than ion exchange with the formation of an inner-sphere complex, contrary to the case of α -alumina.

If one considers sorption as an ion exchange reaction between the surface site $\equiv\text{Al-OH}$ and the ions HCrO_4^- the ion exchange reaction can be, therefore expressed with the following Eq. (5):



Nevertheless, this surface stoichiometry has to be confirmed by further experiments (e.g. by using surface spectroscopies techniques), before extraction of the associated equilibrium constants using modelling (e.g. surface complexation models).

3.3. Effect of initial concentration

The initial adsorbate concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases [22]. Fig. 4 shows the percent (%) metal removal efficiency as a function of pH (2–10) of hematite, goethite and α -alumina for various concentrations (0.1 and 0.5 mg/L) of Cr(VI). It was found that the adsorption of Cr(VI) onto hematite was strongly dependent on initial metal ion concentration and pH values. As seen in Fig. 4(a), the percentage of

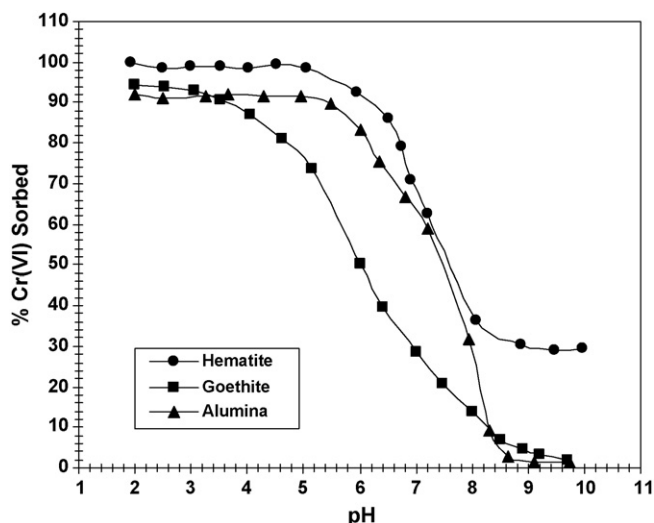


Fig. 2. Effect of pH on the sorption of Cr(VI) onto adsorbents.

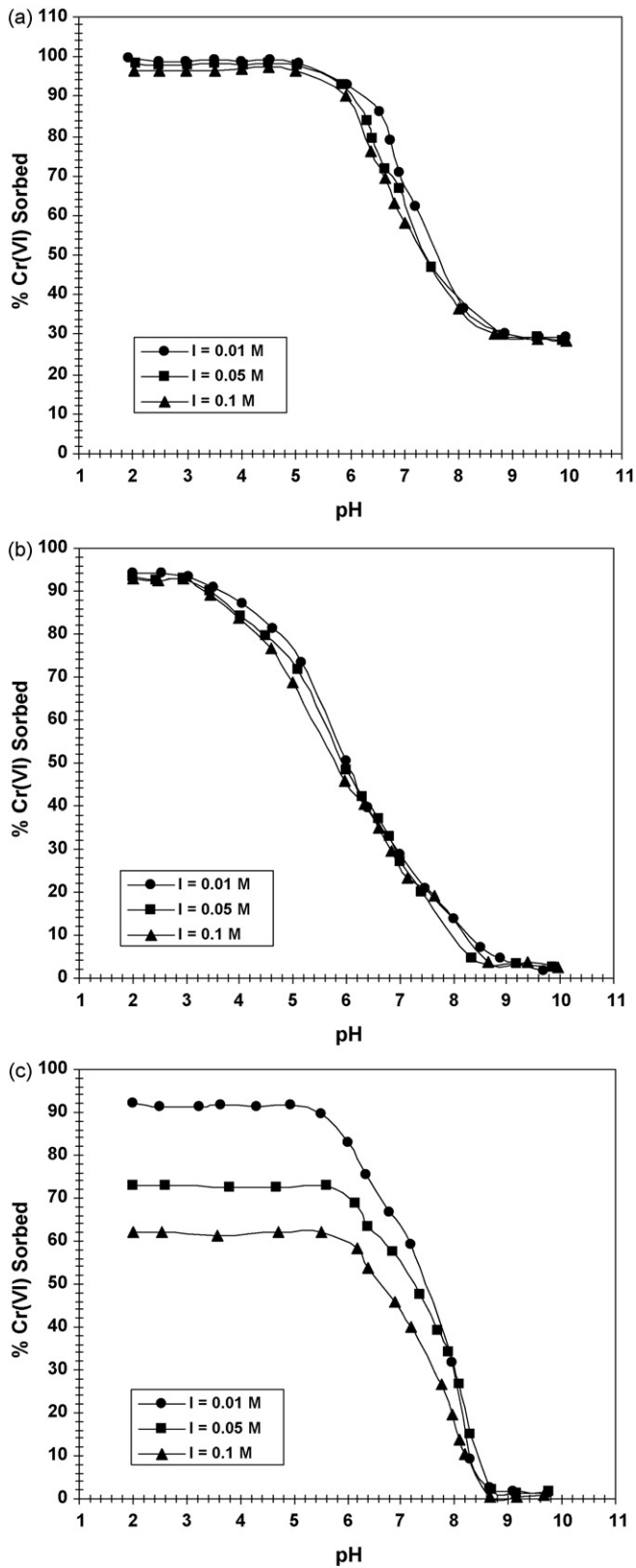


Fig. 3. Adsorption of Cr(VI) onto (a) hematite, (b) goethite and (c) α -alumina as a function of pH at different ionic strengths.

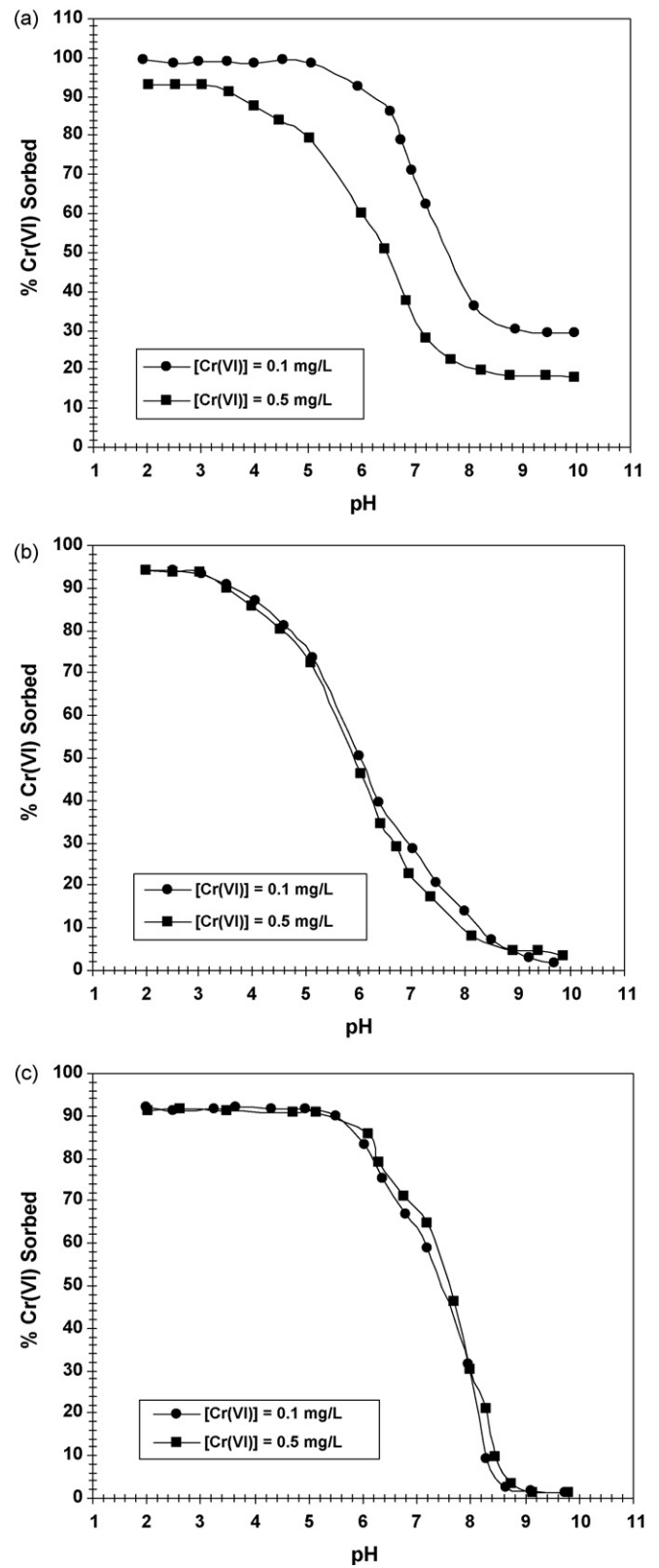


Fig. 4. Adsorption of Cr(VI) onto (a) hematite, (b) goethite and (c) α -alumina as a function of pH at different initial concentration.

adsorption decreased when initial concentration of chromium ions increased, because of the saturation of the surface sites of hematite. This can be explained by the hematite limited number of active sites. For goethite and α -alumina, the results indicate that Cr(VI) adsorption is independent of initial metal ion concentration. This discrepancy is explained by the partial saturation of the surface sites of these adsorbents by Cr(VI).

Though surface area can help to compare surfaces reactivities, we have measured specific surface for each adsorbent. The specific surface area value for the goethite ($11.6 \text{ m}^2/\text{g}$) and the α -alumina ($12.7 \text{ m}^2/\text{g}$) is higher than for the hematite ($1.7 \text{ m}^2/\text{g}$). This indicates that the concentration of surface sites is higher for goethite and α -alumina than for hematite when the same amount of solid is used. This observation is confirmed by the results obtained in Fig. 4.

3.4. Adsorption isotherms

The fixation capacity of an adsorbent towards a specific adsorbate can be described by different equilibrium sorption isotherm models, which are characterized by constants that express the surface properties and the affinity between the adsorbent and the adsorbate. The Langmuir and Freundlich isotherms are used frequently to describe the adsorption data.

The Langmuir model is valid for monolayer sorption a surface with a finite number of similar active sites [16,23]. The well-known expression of the Langmuir model is given by the following Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (6)$$

C_e (mg/L) is the concentration of adsorbate left in solution at equilibrium, b is the Langmuir bonding energy coefficient, Q (mg/g) is the adsorption maximum, and q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent.

The empirical Freundlich equation based on sorption onto a heterogeneous surface [16,23] is given below by the following Eq. (7):

$$q_e = K_f(C_e)^{1/n} \quad (7)$$

where K_f (mg/g) and n are the Freundlich constants characteristic of the system. K_f and n are indicators of adsorption capacity and adsorption intensity, respectively.

Fig. 5 shows the equilibrium isotherms for adsorption of chromium onto hematite, goethite and α -alumina at room temperature and pH 8 (a value close to the pH of sediment equilibrated

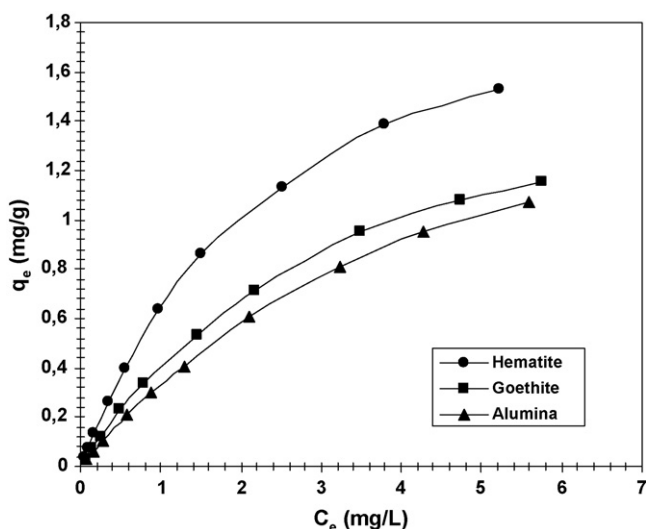


Fig. 5. Adsorption isotherms at room temperature and pH 8 for Cr(VI) on the hematite, goethite and α -alumina.

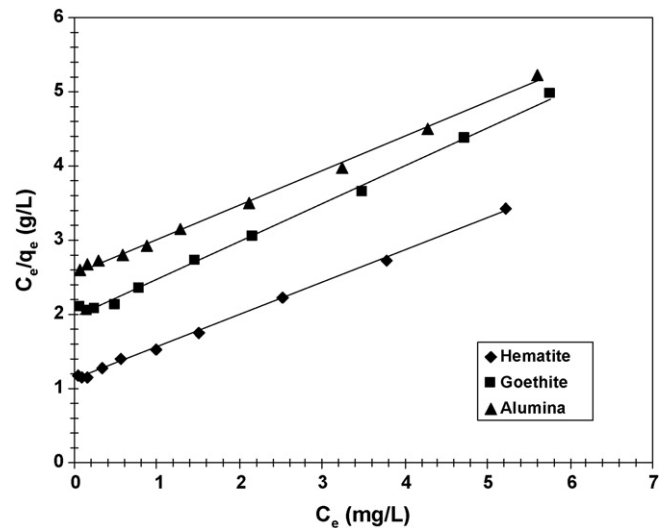


Fig. 6. Langmuir isotherm plots for adsorption of Cr(VI) onto hematite, goethite and α -alumina.

with water). The isotherm rises in the initial stages with higher slope at low C_e and q_e values. This indicates that, initially, there are numerous readily accessible sites. At higher C_e values, a plateau occurs. This confirms the monolayer coverage of Cr(VI) onto these adsorbents particles.

Two linearized models are tested at room temperature and pH 8 to describe the adsorption experimental results, namely the Langmuir and the Freundlich. A plot of (C_e/q_e) versus C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of Q and b . Langmuir plots of adsorption of Cr(VI) on hematite, goethite and α -alumina at room temperature were given in Fig. 6. The adsorption coefficients and the correlation coefficients were given in Table 1. The Freundlich constants were determined from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$ (Fig. 7) and were reported in Table 1.

The magnitude of the n shows an indication of the favorability of adsorption. Values of n larger than 1 show the favorable nature of adsorption. The values of n (Table 1) suggest that Cr(VI) are favorably adsorbed by these adsorbents. Examination of the adsorption maxima (Q (mg/g), Table 1) suggests that goethite and α -alumina have lower capacities to sorb Cr(VI) than hematite. The value of R^2 showed that the Langmuir model fits better than the Freundlich model to the experimental data. This suggests the presence of homogeneous surface sites and that monolayer adsorption is occurring in for chromium adsorption.

The adsorption capacities of the adsorbents for the removal of Cr(VI) have been compared with those of other adsorbents reported in literature and the values of adsorption capacities have been presented in Table 2. The values are reported in the form of the Langmuir and Freundlich equation. The direct comparison of adsorbent capacity of these solids with other sorbents reported in the literature is difficult due to the varying experimental condi-

Table 1

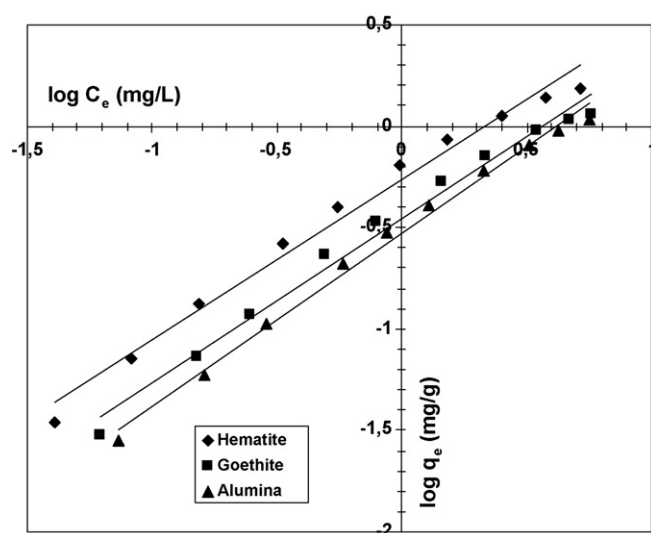
Constant parameters and correlation coefficients calculated for Langmuir and Freundlich adsorption models.

Adsorbent	Langmuir			Freundlich		
	Q (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2
Hematite	2.299	0.388	0.999	0.544	1.272	0.985
Goethite	1.955	0.261	0.997	0.348	1.238	0.987
α -Alumina	2.158	0.182	0.997	0.297	1.175	0.993

Table 2

Comparison of results obtained in this study for the removal of Cr(VI) with those of other adsorbents.

Adsorbents	pH	Langmuir		Freundlich		References
		Q (mg/g)	b (L/mg)	K _f (mg/g)	n (L/mg)	
Activated alumina	4	7.44	0.945	3.126	3.438	[24]
Hydrous Ti(IV) oxide	2	5	0.047	–	–	[25]
γ-Alumina	4	3.468	0.175	–	–	[26]
γ-Alumina	2	2.985	0.288	–	–	[26]
Hematite	8	2.299	0.388	0.544	1.272	This study
α-Alumina	8	2.158	0.182	0.297	1.175	This study
Calcined bauxite	7.4	2.021	0.274	–0.288	0.429	[27]
Goethite	8	1.955	0.261	0.348	1.238	This study
MWCNTs	4.28	1.177	0.526	0.057	0.514	[28]
γ-Alumina	7	0.645	0.004	–	–	[26]
Kaolinite	4	0.447	0.016	–	–	[26]
Montmorillonite	2	0.167	0.023	–	–	[26]

**Fig. 7.** Freundlich isotherm plots for adsorption of Cr(VI) onto hematite, goethite and α-alumina.

tions employed in those studies. However, the solids in this study possess reasonable adsorption capacity in comparison with other sorbents. Then, if adsorption isotherms are semi-empirical models which are not able to provide surface reaction mechanisms, they could give the opportunity (i) to evaluate maximum adsorption capacity of solids in given experimental conditions, and (ii) to compare adsorption capacities of different solids in given experimental conditions.

4. Conclusions

From the results of Cr(VI) adsorption on the three tested adsorbents under our experimental conditions, the following conclusions can be drawn:

- The optimum pH ranges for the maximum adsorption of Cr(VI) onto α-alumina, hematite and goethite were found to be 2–5.5, 2–5 and 2–3, respectively.
- The chromium (VI) adsorption to hematite and goethite is ascribed to an inner-sphere surface complexation rather than ion exchange, in the contrary to the case of α-alumina.
- Comparison of experimental values and Langmuir and Freundlich isotherms showed that Langmuir isotherm confirms very well with the experimental data. The best correlation coefficient values also support this observation. This observation suggests that the adsorption of chromium ion on these adsorbents is a monolayer adsorption. The maximum adsorption capacity at pH equal

to 8 was obtained for hematite, α-alumina and goethite is 2.299, 2.158 and 1.955 mg/g, respectively.

Based on these results, hematite, α-alumina and goethite can be used for the stabilization of chromium into dredged sediments. Nevertheless, depending on the contamination rate, the goethite and the α-alumina should be selected for the high contamination rate and the hematite, for the low contamination rate.

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