



Characterization of Chromium (III) Removal from Water by River bed Sediments - Kinetic and Equilibrium studies

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Abstract

In the present study, chromium sorption capacity was investigated in surface sediments derived from two rivers located in the northeast of Algeria. Adsorption experiments were undertaken in batch; kinetic and equilibrium studies of Cr(III) removal from aqueous solutions were carried out and the pH effect was evaluated. DRX and FTIR analysis of the studied sediments reveal the predominance of quartz, calcite, illite and kaolinite. The sediment characterized by the highest quartz quantity has the less adsorption capacity for chromium. In order to understand the kinetics of Cr(III) removal by the sediments, three models are tried. Finally, the second order model is found suitable for describing the experimental data. The rate constants of adsorption for the two sediments are found to be $9.8 \times 10^{-3} \text{ mg}^{-1} \cdot \text{g} \cdot \text{min}$ and $4.5 \times 10^{-3} \text{ mg}^{-1} \cdot \text{g} \cdot \text{min}$ respectively. The adsorption data isotherms are successfully modeled by Temkin equation. The calculated constants ($\text{L} \cdot \text{mg}^{-1}$) are 4.36 and 5.59 for the two sediments respectively. The chromium uptake increases with pH increasing.

Key words: Chromium; Adsorption; Sediments; Sorption kinetics, Sorption isotherms

1. Introduction

Because of the toxicity, persistence and non-degradability, excess concentrations of heavy metals in water and soils have caused disruption of natural ecosystems [1, 2]. Among these metals, chromium is a ubiquitous contaminant widely used in industrial applications such as stainless steel production, leather tanning, metallurgy and electroplating. The predominant forms of chromium in nature are Cr(III) and Cr(VI) which have different physicochemical characteristics including mobility, toxicity, and bioavailability [3, 4]. Generally, in the natural environment, only manganese oxides and molecular oxygen can oxidize Cr (III) to Cr (VI) [5]. Organic matter with oxygen-containing functional groups has a strong reductive ability for Cr(VI) under acidic conditions [6, 2]. Once Cr(VI) has been reduced, Cr(III) is stable in aquatic environments and oxidation to Cr(VI) is improbable, even when dissolved oxygen or manganese oxide are present [7, 8, 9]; because Cr(VI) reducers are more abundant than Cr(III) oxidants in natural sediments [8, 9, 10]. Once formed, Cr(III) rapidly precipitates and accumulates eventually in sediments, which may become a source of water pollution.

The present work deals with the kinetic and equilibrium studies of the process of Cr(III) removal by riverbed sediments.

2. Experimental

2.1. Samples collection and preparation

Sediments were collected from Rhumel and Hemimim rivers in Constantine city (Algeria) (Figure1) in November 2013. Samples were taken from upper 5cm of the sediments where flow rates were low and sedimentation was assumed to occur. Samples were transported to laboratory in cold in polyethylene bags, dried at 105°C, sieved then conserved until use in polyethylene bottles.

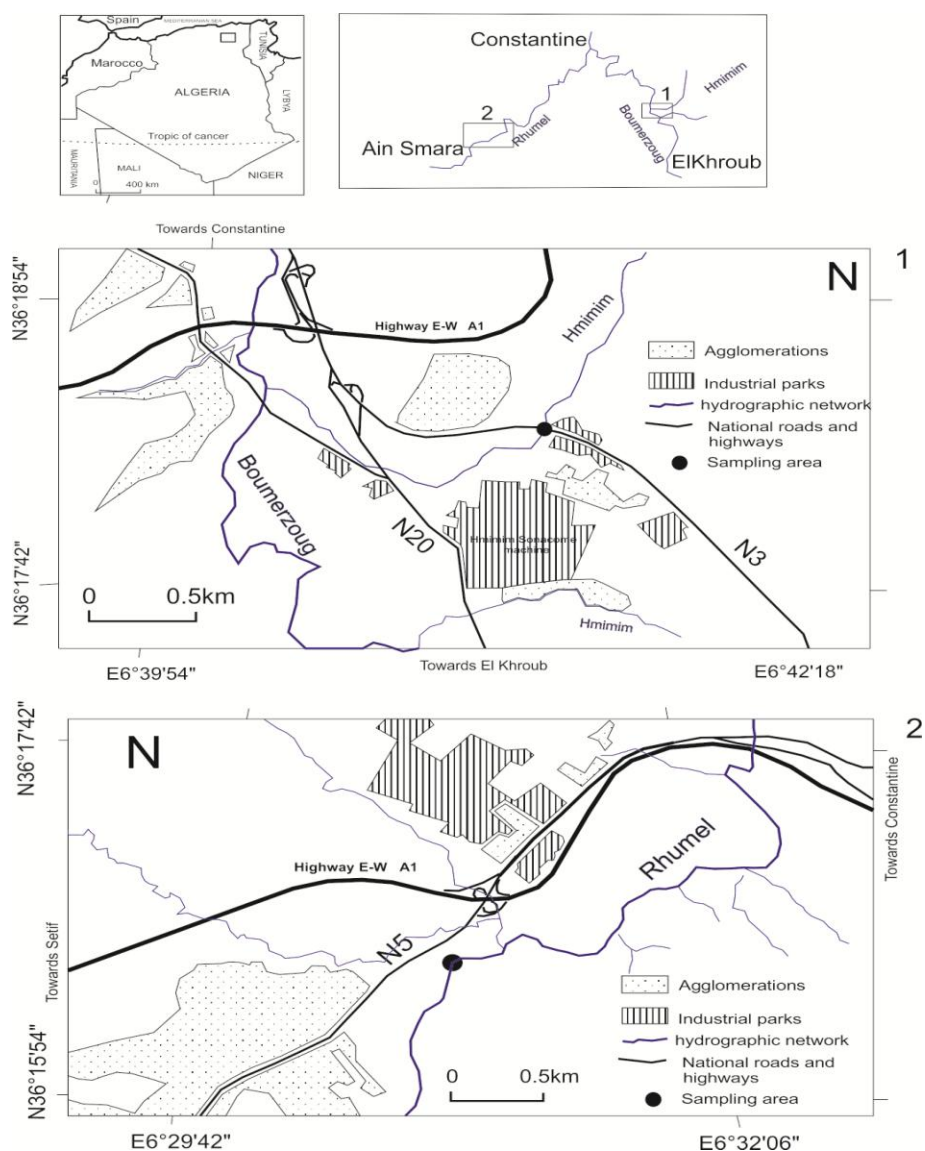


Figure 1: Localization of Rhumel and Hemimim Rivers

2.2. Sediments characterization

The pH was measured in suspensions formed with distilled water. X-ray powder diffraction patterns were recorded from 5 to 60° 2 θ with a scanning speed of 0.05° 2 θ step size using PERTE PANAYTICAL diffractometer employing Cu-K α radiation. IR analyses were performed in the range 4000 to 400 cm⁻¹ using HyperIR Shimadzu E spectrophotometer.

2.3. Chromium adsorption experiments

Cr(NO₃)₃·9H₂O was used as a source of Cr (III); a synthetic stock solution containing 100 mg Cr(III) was prepared. Chromium (III) solutions of desired concentrations were prepared by diluting the stock solution with distilled water. The chromium adsorption was performed by batch experiments. The effects of sediment dose, time, chromium concentration and pH 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 H₂O₂ 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 concentrations in solution.

3. Results and discussion

3.1. Characterization of sediments

The dominant crystalline phases in sediments samples (Figure 2) are quartz, calcite, illite and kaolinite (Figure 2, 3). In the DRX spectra, the relatively low intensity peaks correspond to iron oxyhydroxides. In the IR spectra, the bands at 1033 cm^{-1} , 528 cm^{-1} and 419 cm^{-1} are assigned to alumina-silicates, those at 694 cm^{-1} and 1431 cm^{-1} are assigned to quartz and carbonate respectively. According to the DRX peaks intensity, the Hemimim sediment is characterized by the higher content of quartz.

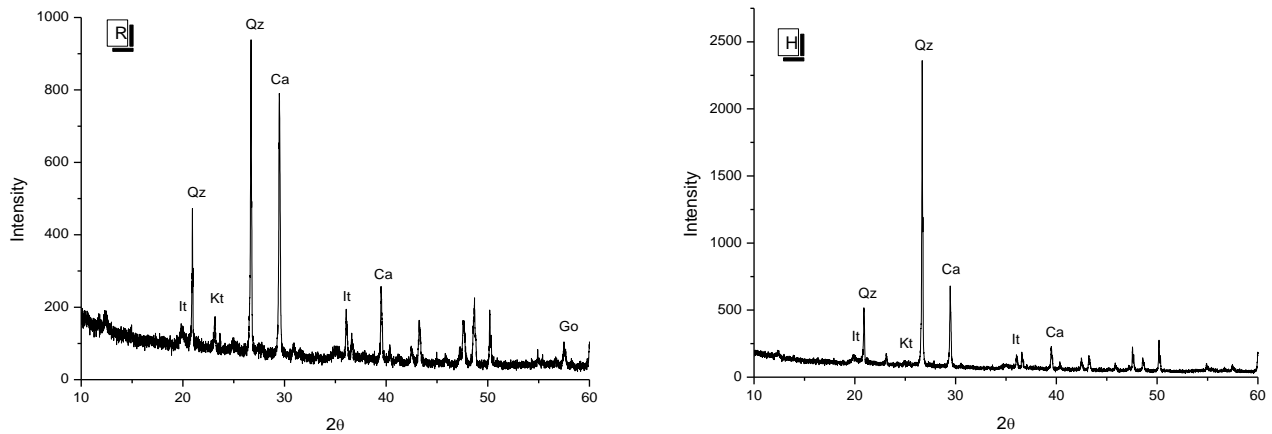


Figure 2: X-ray diffraction spectra of sediments (Qz: quartz; Ca: calcite; It: illite; Kt: kaolinite; Go: goethite)

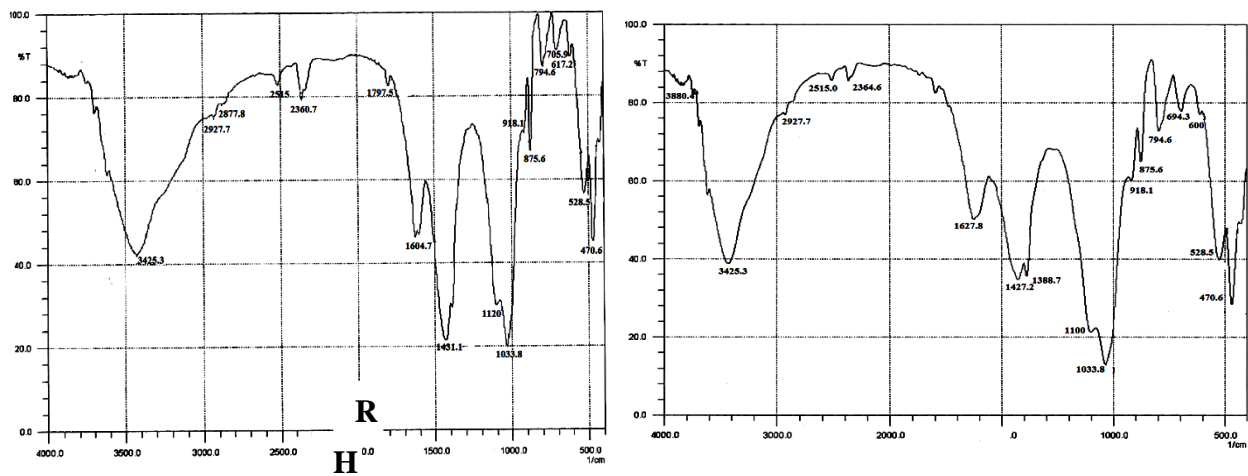


Figure 3: FTIR spectra of sediments

3.2. Chromium adsorption

3.2.1. Effect of sediment dose

The relationship between chromium removal and sediment dose is presented in Figure 4. It shows the existence of two intervals, where the adsorption capacity changes for the two samples. The first one indicates an increase of chromium retention from low doses to 1 g/L . In the second interval, the increase in the sediment dose does not affect the adsorption rate.

3.2.2. Effect of contact time - Adsorption kinetics

The evolution of chromium adsorption with time is shown in Figure 5. It can be seen that the removal rate is rapid at the beginning of the adsorption. The equilibrium is reached within 1 hour for the two samples. Thereafter, a gradual increase in chromium uptake occurred. The same evolution has been observed in a study on cadmium adsorption on river sediments [11]. To understand the involved mechanisms, three kinetics models are used: the pseudo-first order, pseudo-second order and Elovich.

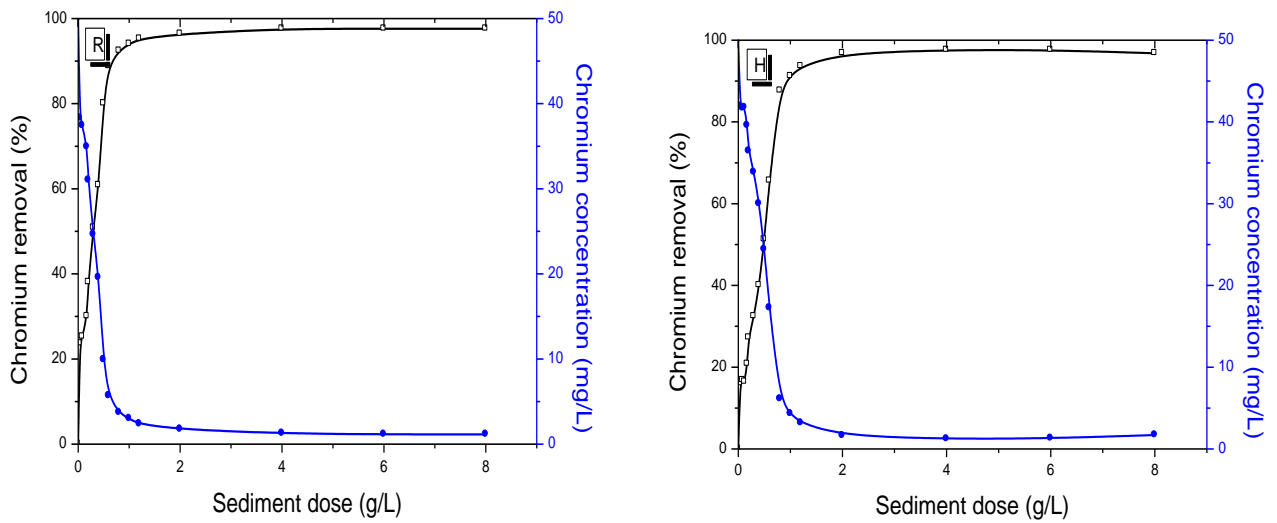


Figure 4: Effect of sediment dose on chromium adsorption (C_0 :50mg/L, t: 60 min)

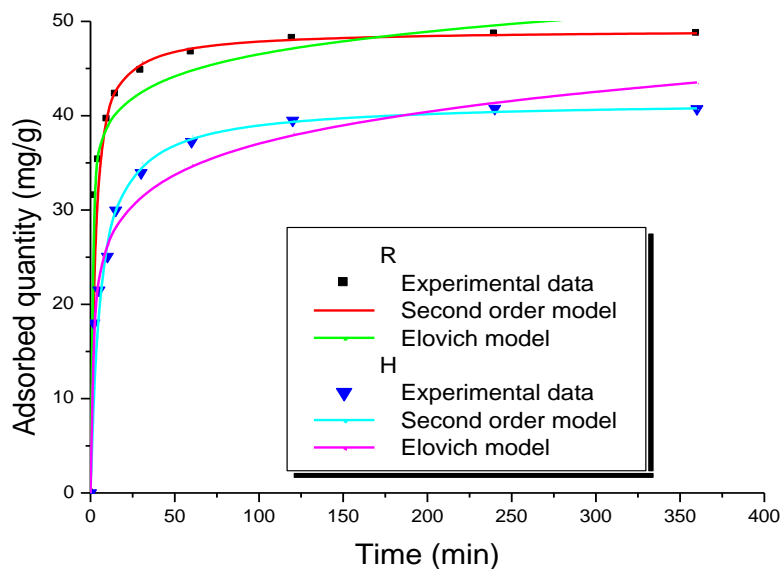


Figure 5: Kinetics of adsorption of chromium on sediments - Experimental data and kinetics models (C_0 : 50 mg/L, sediment dose: R (1g/L); H (1.2g/L))

In the Pseudo-first order model, chromium adsorption speed is proportional to $(Q_e - Q_t)$; it is described by the relation: $\ln(Q_e - Q_t) = \ln Q_e - Kt$, where, Q_e and Q_t are the adsorption capacity (mg/g) at equilibrium and at time t respectively and K is the adsorption rate constant. The obtained results are presented in Figure 6.

The pseudo-second order model obeys the equation: $\frac{t}{Q_t} = \frac{1}{KQ_e^2} + \frac{1}{Q_e} t$, where, K is the rate constant of adsorption (g/mg/min), Q_t is the adsorption capacity at time t , Q_e is the adsorption capacity at equilibrium. The Figure 7 illustrates the obtained results.

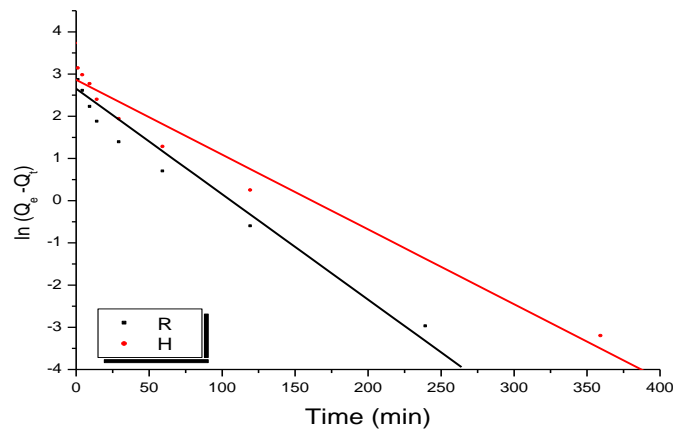


Figure 6: Pseudo-first order plots for Cr(III) adsorption on sediments

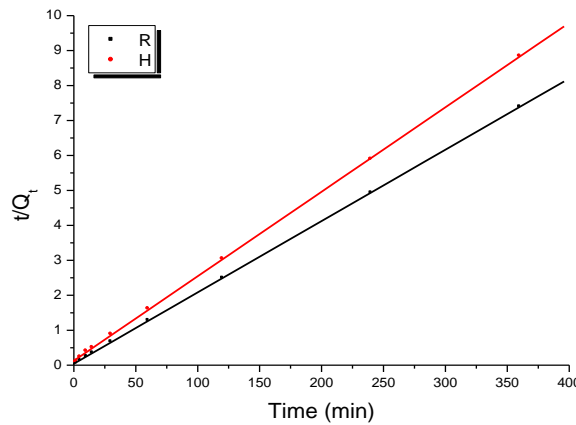


Figure 7: Pseudo-second order plots for Cr(III) adsorption on sediments

The Elovich model is represented by the equation:

$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln t ;$$

where α is the initial adsorption rate (mg/g.min) and β is a constant in a relation to the activation energy of chemisorption (g/mg). The obtained results are illustrated in Figure 8.

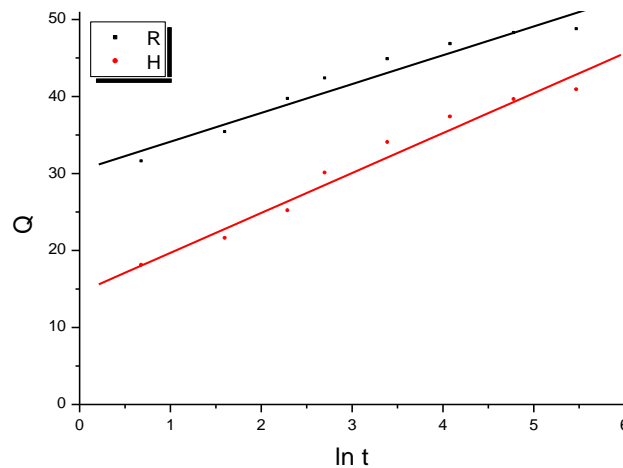


Figure 8: Elovich plots for Cr(III) adsorption on sediments

The calculated apparent rate constants of the kinetics models and the other parameters are listed in Table 1. According to the correlation coefficients ($R^2 > 0.95$), the three models can describe the kinetics. However, the equilibrium adsorption capacities calculated by the first model equation are not acceptable by comparison with the experimental ones; consequently this model is ruled out. The two other models can describe the kinetics data but the second order model is more suitable (Figure 5); the adsorbed quantities at equilibrium are in agreement with the experimental data for the two sediments. In this model, the rate limiting step is chemical adsorption. Adsorption of copper, zinc, cadmium and lead on river sediments have been also successfully described by the second order and Elovich models [12].

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

Sediment	Kinetic model	R	K	Q_e
Rhumel (R)	First order	0.963	0.0249	14.19
	Second order	0.999	0.0098	49.02
	Elovich	0.959	-	-
Hemmimim (H)	First order	0.976	0.0177	17.54
	second order	0.999	0.0045	41.39
	Elovich	0.976	-	-

3.2.3. Effect of chromium concentration - Adsorption isotherms

The chromium uptake increases with the increase of the initial concentration. The adsorption capacity increases from 4.6 mg/g to 86.4 mg/g when the initial chromium concentration increases from 5 mg/L to 110 mg/L for the Rhumel sediment (R) and 3.9 mg/g to 57.7 mg/g from 5 mg/L to 90 mg/L for Hemmimim sediment (H) (Figure 9). Experimental data are fitted using the Langmuir, Freundlich and Temkin isotherms (Figures 10, 11, 12).

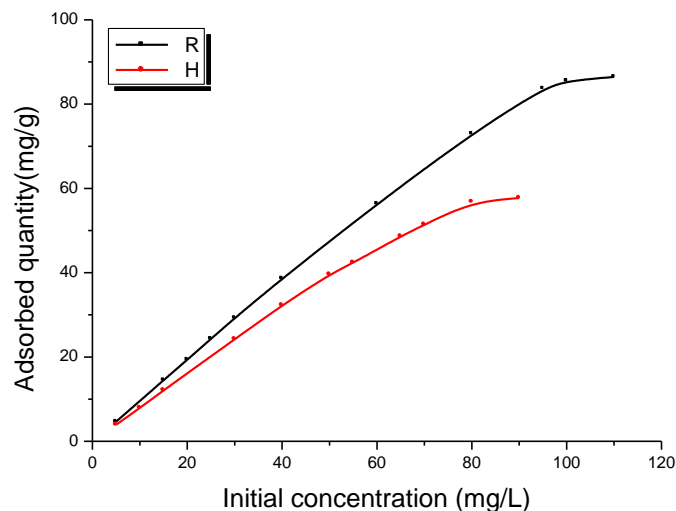


Figure 9: Effect of chromium concentration on chromium adsorption on sediments (t= 60 min; sediment dose: R (1g/L), H (1.2g/L))

The Langmuir equation assumes that the adsorbent surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed. The linear form of the Langmuir isotherm is given by the equation: $\frac{1}{Q} = \frac{1}{Q_{max} K} \times \frac{1}{C_r} + \frac{1}{Q_{max}}$ where K ($L \cdot mg^{-1}$) is the Langmuir constant related to the free adsorption energy and Q_{max} ($mg \cdot g^{-1}$) is the maximum adsorption capacity; C_r is the equilibrium concentration (mg/L). The obtained results (Figure 10) reveal that this isotherm is not convenient for describing the chromium sorption on the two sediments.

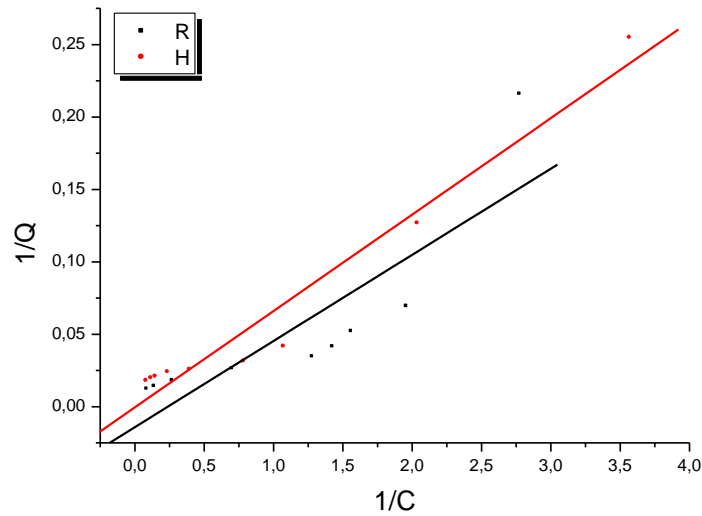


Figure 10: Langmuir plots for Cr (III) adsorption on sediments

The Freundlich expression is an empirical equation based on sorption on heterogeneous surfaces, suggesting that binding sites are not equivalent. The linear equation is given by: $\ln Q = \frac{1}{n} \ln C_r + \ln K$ where K and n are constants related to adsorption capacity and adsorption intensity respectively. The obtained correlation coefficients for the two sediments are less than 0.92, implying that the Freundlich equation can not be used for describing the sorption isotherm.

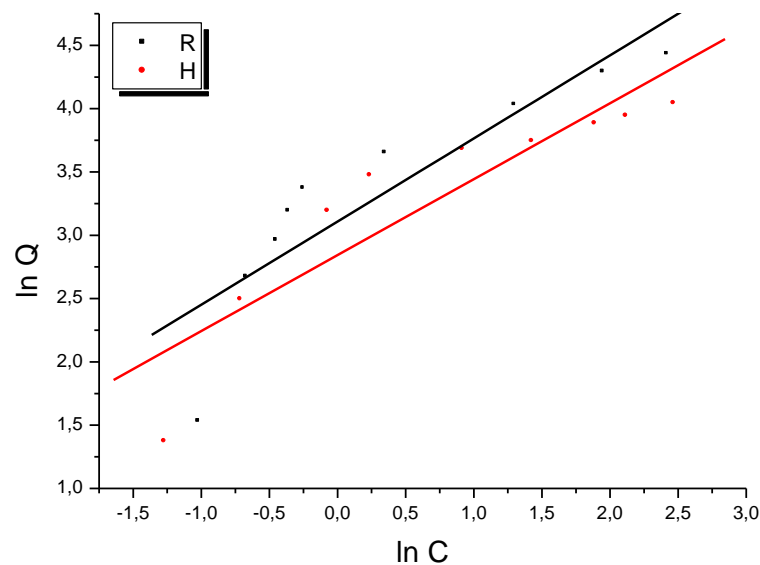


Figure 11: Freundlich plots for Cr(III) adsorption on sediments

The Temkin model assumes that the adsorption heat decreases linearly with coverage. It is described by the equation: $q_e = q_{max} \cdot \left(\frac{RT}{\Delta Q}\right) \ln K_T + q_{max} \cdot \left(\frac{RT}{\Delta Q}\right) \ln C_e$ where ΔQ represents the variation in adsorption energy ($J \cdot mol^{-1}$) and K_T the Temkin constant ($L \cdot mg^{-1}$) (R: universal gas constant ($8.314 J/mol/K$), T: Temperature ($298K$)). With correlation coefficients greater than 0.98 only the Temkin model is suitable for describing the

adsorption of chromium onto the two sediments. The Temkin constants are 4.36 and 5.59 respectively. From the Figure 13, it can be seen that effectively this model describes well the experimental data for the two sediments. This result is not in agreement with that found for metals adsorption on river sediments where the isotherms were best described by Langmuir and Freundlich models [13].

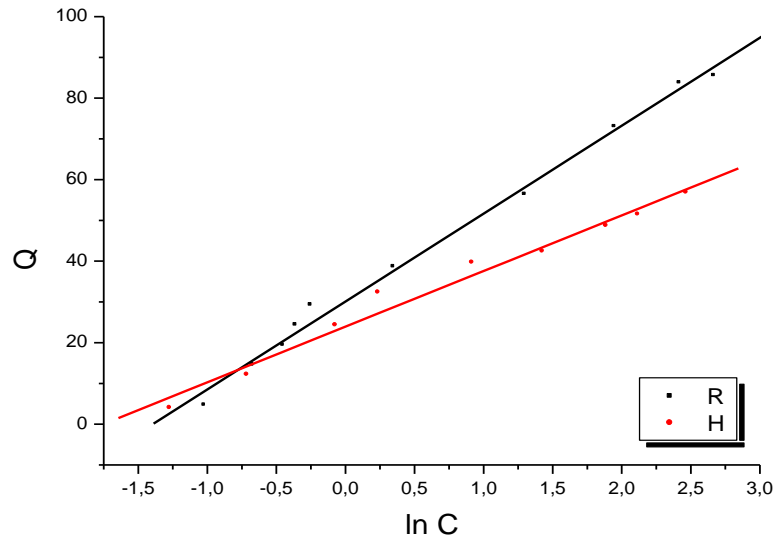


Figure 12: Temkin plots for Cr(III) adsorption on sediments

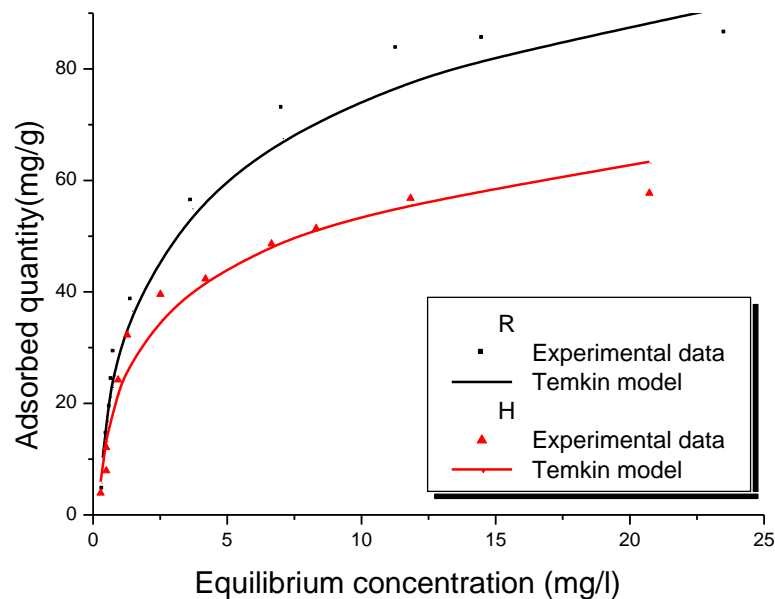


Figure 13: Chromium (III) sorption isotherms (t: 60 min; sediment dose: R (1g/L), H (1.2g/L))

3.2.4. Effect of pH

The solution pH is an important factor controlling the surface charge of the adsorbent and the speciation of the adsorbate in aqueous solution. The effect of initial solution pH on Cr(III) removal by the two sediments is shown in Figure 14. The pH-dependent behavior for Cr(III) adsorption is explained by sorption at surface hydroxyl sites. It appears that the removal efficiency increases significantly with the elevation of solution pH in the two cases. As pH increases from 2.5 to 6.0, the removal efficiency of Cr(III) is doubled. At higher pH, precipitation of Cr(III) can be considered as the main mechanism for the removal of Cr(III) by the sediments.

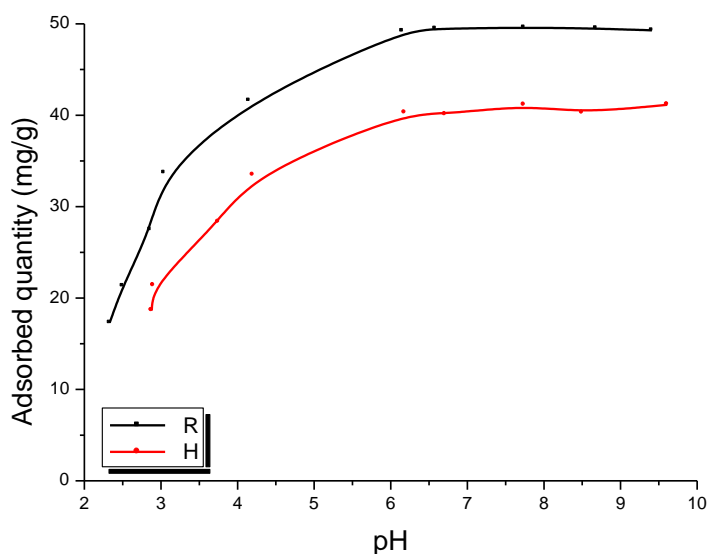


Figure 14: Effect of solution pH on chromium adsorption on sediments (C_0 :50 mg/L, t: 60 min; sediment dose: R (1g/L), H (1.2g/L))

Conclusion

On the basis of the present study results, the following conclusions may be drawn:

1. The sediments of Rhumel and Boumerzoug rivers can be considered as high effective natural adsorbents for chromium removal from aqueous solutions.
2. The kinetics and isotherms modeling showed that the chemisorption is the more probable process in chromium adsorption.

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