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REMOVAL OF HEXAVALENT CHROMIUM FROM WATER BY USING NATURAL BROWN CLAY

Latifa Bentchikou*[1,2], Fatma-Zohra Mechelouf[2], Fayza Neggaz[2] and Abdelhamid Mellah [3]

1. Faculty of Mechanical and Process Engineering, University of Sciences and Technology Houari-Boumediene, Department of Environment, Algiers, Algeria
2. National School of Marine Science and Coastal Planning, ENSSMAL, Algiers, Algeria
3. Nuclear Research Center of Algiers, CRNA, Algiers, Algeri

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Abstract: The present study investigates the removal of chromium from aqueous solution, by natural Algerian brown clay, in batch mode, at different temperatures. Kinetic experiment showed that the adsorption process can be simulated by pseudo-second order model. In order to determine the best-fit-isotherm, the experimental data were analyzed by the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich equation, at different temperatures of 20, 30, 40 and 50°C. The mean deviation obtained from the four models revealed that Freundlich is the most suitable one. The results showed that natural brown clay is effective to remove chromium (VI) about 90% at 20°C.

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***Corresponding author. E-mail:** bentchikoul@yahoo.fr.

INTRODUCTION

Hexavalent chromium is a commonly identified contaminant because of its high toxicity and mobility [Hsu *et al.*, 2010]. It is occuring to the environment from different industrial applications such as electroplating, leather tanning, wood preservation, stainless steel, textile dyeing, industrial water-cooling, wood preservation, paper pulp production, and petroleum refining.

Several techniques like electro-coagulation [El-Taweel *et al.*, 2015], ion-exchange [Rengaraj *et al.*, 2001], reverse osmosis [Hafez and El-Manharawy, 2004] and solvent extraction [Alonso *et al., 1999*] have been studied for removing Cr(VI) from polluted water or wastewater. However, some disadvantages, such as high cost or inadequate efficiencies at low metal concentrations have led to a problem in the application of these methods.

Adsorption has been proven to be one of the most important and effective processes of metal uptake especially when it concerns the removal of metallic trace pollutants in solutions.

Different organic and mineral materials were used as adsorbents. Because of low production cost of clays, there is no need to regenerate them, which provides more advantages in using clays as an adsorbent [Kashıf Uddin, 2017].

The main objective of the present work was to show the effectiveness of the application of such raw, abundant and low cost material for water purification. This paper reports the use of a natural Algerian brown clay for the uptake of Cr(VI) ions from aqueous solution. Equilibrium at different temperatures and kinetic were studied in accordance with different models and their parameters were also evaluated to help provide a comprehensive explanation of the batch adsorption process.

MATERIALS AND METHODS

Adsorbent material

Natural local brown clay from Maghnia (north western Algeria) used in this work was sieved to a particle size of 1000-2000 µm, dried in an oven at 105°C for 24 h and maintained in a desiccator until used.

Reagents

All chemicals used in this study were of analytical grade reagents. A synthetic stock solution of 1000 mg L^{-1} of hexavalent chromium was prepared using potassium dichromate ($K_2Cr_2O_7$) in double distilled water. The acidic (HCl) and basic (NaOH) solutions were prepared respectively at 2 M and 5 M and used into adjust the pH of the solution.

Batch experiments

Batch adsorption experiments were carried out at room temperature using 50 mg of adsorbent in conical flasks with 50 mL of Cr(VI) ion solution at 50 mg L^{-1} and temperature of 20±0.2°C. The mixture was mechanically agitated in an oscillatory shaker for 240 min, under pH adjusted to 5±0.2. The supernatant was then centrifuged with a Sigma 1-6P centrifuge at 5000 rpm for 10 min. The concentrations of metal ions were determined using previously calibrated UV-Vis spectrophotometer (Shimadzu UV-1800) at 540 nm [Yuan *et al.*, 2010].

The amount of Cr(VI) adsorbed per unit mass of the adsorbent at equilibrium time, q_e (mg g^{-1}), was determined by using the following equation:

$$q_e = (C_0 - C_e)v/m \quad (1)$$

where C_0 and C_e are the initial and the equilibrium concentration (mg L^{-1}) of Cr(VI) in the solution respectively, v is the volume (mL) of the solution and m is the weight of the adsorbent (g).

The removal efficiency of Cr(VI) was calculated using the following equation:

$$\%\ Removal = [(C_0 - C_e)/C_0]\times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of time contact

The removal efficiency (%) of Cr(VI) as a function of time contact is summarized in Figure 1. The metal uptake was very fast in the beginning (the first 5 minutes), then it increased lightly and slowly until reaching the equilibrium at 60 min with an efficiency of about 90%. This can be explained on the basis that, initially a large number of vacant surface sites may be available for adsorption of metal ions and by time the surface sites become exhausted [Zhan, 2000].

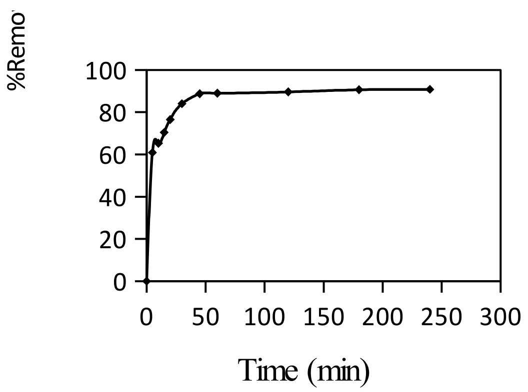

Figure 1: Kinetic of adsorption of Cr(VI) onto natural brown clay (C_0, 50 mg L^{-1} ; adsorbent dose, 0.5 g; pH 5±0.2 ; temperature, 20°C)

Adsorption isotherm studies

The adsorption isotherms for Cr(VI) on the natural brown clay were obtained at various metal concentrations from 25 to 200 mg L^{-1}, at pH adjusted to 5±0.2 for different temperatures of 20°C, 30°C, 40°C and 50°C. The adsorption isotherm models of Langmuir, Freundlich, Temkin and Dubinin-Radeshkevich were used.

For Langmuir model, the linear form could be expressed by the following equation:

$$\frac{C_e}{q_e}=\frac{1}{q_m}C_e+\frac{1}{K_L q_m} \tag{3}$$

Where q_m is the maximum adsorption capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}). The Langmuir constants q_m and K_L (Table 1) were obtained graphically by plotting versus C_e. From the results, the low regression coefficient (R^2) of this model did not fit the equilibrium data. This might suggest that the surface of the adsorbent is heterogeneous and not homogenous in nature. Furthermore, in order to investigate if the adsorption of Cr(VI) is a favorable one, an important separation factor R_L was calculated as follows:

$$R_L=\frac{1}{1+\ K_L C_0} \tag{4}$$

The values of R_L found for all temperatures of this study ($0<R_L<1$) indicate that the adsorption is favorable.

The Freundlich adsorption isotherm model has been applied. The linearized equation of this isotherm model is given by:

$$\ln q_e = K_f + \frac{1}{n} lnC_e \tag{5}$$

K_f and *n* are Freundlich constants, related to adsorption capacity and adsorption intensity, respectively. These constants can be determined by the plot of $ln(q_e)$ versus $ln(C_e)$ as shown in Figure 2 for the different temperatures.

From the results (Table 1), the highest regression coefficients for the four temperatures (0.987-0.998) suggest that the adsorption of Cr(VI) can be modeled by Freundlich model. Similar results were found by some authors [Arfaouia *et al.*, 2008] for trivalent chromium ions adsorbed onto natural and modified clay. The adsorption process was also favorable according to the values of 1/n which are less than 1 for all temperatures.

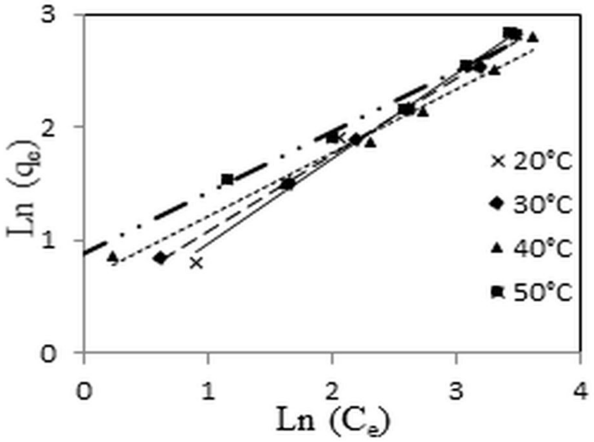

Figure 2: Freundlich equilibrium isotherm at different temperatures.

Table 1: Isotherm constants and correlation coefficients by linear regression.

Isotherm model	**Temperatures (°C)**			
	20	30	40	50
Langmuir				
Q_m (mg g^{-1})	32.78	27.855	22.321	21.505
R_L	0.399	0.344	0.277	0.205
R^2	0.936	0.883	0.842	0.857
Freundlich	0.754	0.676	0.561	0.535
1/n	0.754	0.676	0.561	0.535
K_f (g^{-1})	1.251	1.502	1.929	2.444
R^2	0.987	0.998	0.988	0.989
Temkin				
b_T	454.68	519.37	643.68	277.09
A_T (L mg^{-1})	0.487	0.609	0.894	1.298
R^2	0.945	0.896	0.852	0.863
D-R				
$K_{D\text{-}R}$ (10^6) (mol^2 KJ^{-2})	2.000	1.000	0.700	0.700
$q_{m\ D\text{-}R}$ (mg g^{-1})	10.782	9.774	9.166	9.673
R^2	0.809	0.706	0.649	0.684

The Temkin isotherm has been used in the following form:

$$q_e=\frac{RT}{b_T}\ln(A_T)+\frac{RT}{b_T}\ln(C_e) \tag{6}$$

b_T and *A_T* are Temkin isotherm constants and *R_T/b_T* is constant related to the heat of adsorption. The values of these constants (Table 1) were determined by plotting *q_e* versus *$ln(C_e)$*.

The Dubinin-Radushkevich (D-R) equation is given by:

$$\ln q_e=\ln q_m-K_{D-R}\,\varepsilon^2 \tag{7}$$

Where $K_{D\text{-}R}$ is the activity coefficient related to mean sorption energy and ε is the Polanyi potential, which is equal to:

$$\varepsilon = RT\ln\left(1+1/C_e\right) \tag{8}$$

The calculated values of D-R isotherm parameters from the plot of *ln(Ce)* versus ε^2 are summarized in Table 1.

Adsorption kinetics

In order to evaluate the kinetic mechanism which controls the process, the pseudo-first-order and pseudo-second-order models were tested.

The Pseudo-first-order equation [Lagergren, 1898] given by Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linearized form is:

$$\ln\left(q_e - q_t\right) = \ln q_e - \frac{K_1}{2.303}t \tag{9}$$

Where *t* (min) is a time, K_1 (min^{-1}) is the pseudo-first-order rate constant. The values of K_1 and R^2 calculated from a linear plot of $\ln(q_e - q_t)$ vs. *t* are given in Table 2. The calculated value of q_e does not match with the experimental one and R^2 value is also low, so it does not follow the pseudo-first-order kinetic model.

The kinetic data were further analyzed by using form pseudo-second-order equation. The linearized form of the equation [Ho and Mckay, 1999] is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{10}$$

Where K_2 is the pseudo-second-order rate constant (g $\mathrm{mg}^{-1}\mathrm{min}^{-1}$). A plot of t/q_t vs. *t* is shown in Figure 3. The results were compared with the correlation coefficient *(R^2)* and are given in Table 2.

Table 2: Adsorption kinetic parameters.

Kinetic model	**Parameters**
Pseudo- first-order	
q_e (cal)	1.0379
q_e (exp)	4.54
K_1	0.0629
R^2	0.881
Pseudo-second-order	
q_e (cal)	4.6082
q_e (exp)	4.54
K_2	0.0668
R^2	1

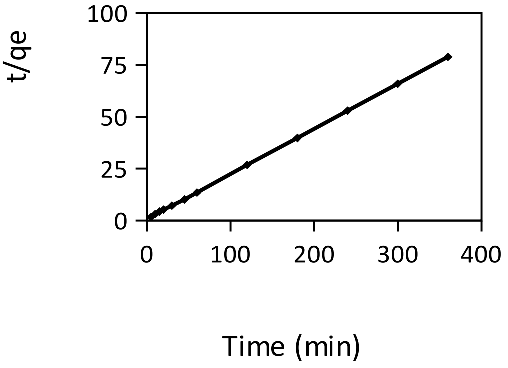

Figure 3: Pseudo-second-order plot for Cr(VI) adsorption onto the natural brown clay (C_0, 50 mg L^{-1}; adsorbent dose, 0.5 g; pH 5±0.2; temperature, 20°C)

The pseudo-second-order equation gives a higher regression value ($R^2 = 1$) compared to the pseudo-first-order kinetic and the experimental value of q_e of pseudo-second-order equation also agreed well with the calculated value. So, it can be concluded that the pseudo-second-order model is the appropriate one for the adsorption kinetic of Cr(VI) onto natural brown clay. Similar results were also obtained for the uptake of this metal ion from aqueous solution using natural clay adsorbents [Wanees *et al.*, 2013, Barkat *et al.*, 2014].

CONCLUSION

This study evaluated the efficiency of a readily available Algerian brown clay used without any chemical modification or treatment as adsorbent for the removal of Cr(VI) ions from aqueous solution in order to keep the decontamination process cost low. About 90% of Cr(VI) metal ions were adsorbed from the used raw material at 20°C under pH: 5, using C_0: 50 mg L^{-1} and

10 g L^{-1} of adsorbent. The adsorption depended on time of contact. The isotherm data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms at temperatures of 20, 30, 40, and 50 °C, and the results revealed that the adsorption process was favorable, confirmed by the Freundlich isotherm model which gave the best fit to the experimental data for all temperatures. The pseudo-first-order and the pseudo-second-order kinetic models were used. The adsorption kinetic followed the pseudo-second-order equation provided by the best correlation for the adsorption of Cr(VI) onto the natural brown clay.

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