

Adsorption Behaviour of Cr(III) Ions on Sepiolite

Y. ASÇI* and P. BERKAN

Department of Chemical Engineering, Eskisehir Osmangazi University,
Bati Meselik-26480, Eskisehir, Turkey

Fax: (90)(222)2349718; Tel: (90)(222)2393750

E-mail: yelizbal26@hotmail.com

Removal of Cr(III) ions from waste waters is essential due to their toxicity. In the present study, batch sorption experiments were carried out to evaluate the performance of sepiolite in the removal of Cr(III) from aqueous solution. The sorption of Cr(III) from aqueous solution with sepiolite was studied at varying Cr(III) concentration, adsorbent dose, pH, contact time and temperature. The results obtained from equilibrium adsorption studies are fitted in various adsorption models such as Langmuir and Freundlich and the adsorption was well described by the Freundlich adsorption isotherm model. Thermodynamic parameters, free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were also calculated. Furthermore, the Lagergren-first-order, pseudo-second-order and the intraparticle diffusion models were used to describe the kinetic data. The experimental data fitted well the Lagergren-first-order.

Key Words: Chromium(III), Adsorption isotherm, Sepiolite, Thermodynamics, Kinetics.

INTRODUCTION

Heavy metals (Pb, Cd, Zn, Ni, Cr, Mn, Co, *etc.*) have been discharged to the environment as industrial wastes, causing serious water, air and soil pollutions and they were also threaten to the human health¹. Due to their toxicity even at low concentrations, the maximum levels allowed of metals are regulated by legislation in each country².

Applications designed to improve analytical determinations and to improve the environment by metal removal have recently emerged. There are many methods for the removal of wastewater pollution from aqueous solutions such as adsorption, chemical precipitation, ion exchange, membrane processes, *etc.*³. Among several removal technologies, adsorption and ion exchange with natural clays have great importance due to the ease of operation and comparable low cost of application. Different adsorbents have been used for removal of various materials from aqueous solutions. These include perlite, activated carbon, bentonite, silica gels, flyash, lignite, peat, silica, *etc.*⁴. The most generally used sorbent is activated carbon. Although activated carbon is effective in removal of metal ions from wastewaters, it is expensive and requires chelating agents to enhance its performance, thus increasing treatment cost⁵. For this reason, this research is focused on new, efficient, low-cost and easily

obtainable natural materials, *e.g.*, clay materials. The wide usefulness of these kinds adsorbents is a result of their high specific surface area, high chemical and mechanical stability and variety of surface and structural properties. Sepiolite [$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})\cdot 6\text{H}_2\text{O}$], a zeolite like clay mineral, is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels. Sepiolite contains a continuous two-dimensional tetrahedral sheet of T_2O_5 ($\text{T} = \text{Si}, \text{Al}, \text{Be}, \text{etc.}$) but has no continuous octahedral sheets. Sepiolite has molecular sized channels ($3.6 \times 10^6 \text{ \AA}$) and large specific surface area with more⁶⁻⁹ than $200 \text{ m}^2 \text{ g}^{-1}$. Because of this excellent fibrous structure, organic and inorganic ions can penetrate into the structure of sepiolite and this makes it an important industrial raw material in sorptive, rheological and catalytic applications. Most of the world's sepiolite reserves are found in Turkey.

As Cr(VI) is carcinogenic, in wastewater a maximum permissible concentration for total Cr of 0.5 mg L^{-1} and for Cr(VI) of 0.05 mg L^{-1} is legally prescribed. In present studies, Cr(III) was chosen because it is an important environmental pollutant. Therefore, the control of the chromium level in wastewater is essential¹⁰. Also, a lot of work is present in literature on Cr(VI) removal but limited research work is done on the removal of Cr(III) from aqueous solutions by clay materials^{11,12}. The present study, thus, reports a detailed investigation of Cr(III) removal from aqueous solutions using sepiolite under different experimental conditions. The effects of pH, contact time, adsorbent dosage and temperature were studied. Well-known isotherm models were applied to the equilibrium data. Kinetic and thermodynamic parameters were also calculated to describe the adsorption mechanism.

EXPERIMENTAL

Sepiolite characterization: Sepiolite was obtained from sepiolite mines of Eskisehir region of Turkey. The sepiolite samples were ground and sieved to 0.038-0.053 mm size. Chemical analysis of the sepiolite sample was performed using X-ray fluorescence spectroscopy technique (XRF, Rigaku ZSX Primus model). The sepiolite was ground and then sieved to a particle size of less than $65 \mu\text{m}$ and prepared by fluxing of powder samples with $\text{Li}_2\text{B}_4\text{O}_7$ for XRF measurements. The chemical composition of sepiolite is also shown in Table-1. It contains mainly SiO_2 , MgO , which they constitute 76.7 % of the total weight.

Effect of sepiolite dosage: A Cr(III) stock solution of 1000 mg/L was obtained by dissolving $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ in distilled water 0.10, 0.25, 0.50, 0.75 and 1 g of sepiolite was added to 25 mL of 100 mg/L metal ion solutions in 50 mL centrifuge tubes. The pH of metal ion solutions was kept at 3.0. The centrifuge tubes were agitated on a shaker at $25 \text{ }^\circ\text{C}$, at 150 rpm for 150 min, then the tubes were centrifuged at $19,000 \times g$ for 10 min and the supernatant was acidified to pH 2.0 with 1 % HNO_3 for atomic absorption analysis (Perkin-Elmer atomic absorption spectrophotometer). Sorbed Cr(III) concentration by the sepiolite was calculated from the difference between initial Cr(III) concentration in solution and Cr(III) concentration remained in the supernatant after sorption.

TABLE-1
CHEMICAL PROPERTIES OF THE SEPIOLITE IDENTIFIED BY XRF

Composition	Content (wt.%)
CO ₂	21.200
Na ₂ O	0.0427
MgO	24.600
Al ₂ O ₃	0.1950
SiO ₂	52.100
P ₂ O ₅	0.0149
SO ₃	0.0291
K ₂ O	0.0338
CaO	1.4600
Fe ₂ O ₃	0.1530
NiO	0.0866
CuO	0.0153

Effect of pH: 25 mL portions of 100 mg/L of metal ion solutions were added to 0.25 g of sepiolite samples. The pH values of the suspensions were adjusted as 1.0, 2.0, 3.0, 4.0, 5.0 and 5.6 using either 0.1 M NaOH or 0.1 M HNO₃. The centrifuge tubes were agitated on a shaker at 25 °C, at 150 rpm for 150 min, then the tubes were centrifuged at 19,000 × g for 10 min and the supernatant was acidified to pH 2.0 with 1 % HNO₃ for atomic absorption.

Effect of contact time: 25 mL of 100 mg/L metal ion solutions was added to 0.25 g of sepiolite samples in 50 mL tubes. The pH of the solutions was adjusted to 5.0 and then they were agitated on a shaker at 25 °C, at 150 rpm. Sorption of Cr(III) onto sepiolite was measured in the time intervals varying from 5-300 min. Thereafter the same procedure as above was followed.

Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism of the adsorption process and to test the experimental data. In present investigation, the adsorption data were analyzed using three kinetic models, the Lagergren-first-order, pseudo-second-order and the intraparticle diffusion models. The Lagergren-first-order rate equation is the most popular kinetic equation. The form is,

$$dq/dt = k_1 (q_e - q_t) \quad (1)$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eqn. 1 becomes:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_t (mg/g) is the amount of Cr(III) adsorbed in time t (min); k_1 is the rate constant of the equation (min^{-1}) and q_e is the Cr(III) amount at adsorption equilibrium (mg/g). The adsorption rate constant k_1 can be determined experimentally by plotting $\ln (q_e - q_t)$ versus t .

Pseudo-second-order equation is in the following form:

$$dq/dt = k_2 (q_e - q_t)^2 \quad (3)$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eqn. 3 becomes:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (4)$$

where k_2 (g/mg min) is the rate constant of the second-order equation; q_t (mg/g), the amount of Cr(III) adsorbed in time t (min) and q_e is the Cr(III) amount at adsorption equilibrium (mg/g). Values of k_2 and q_e can be calculated from the plot of t/q_t against t .

The Lagergren first-order and pseudo-second-order cannot identify the diffusion mechanism. For this reason, the kinetic results were then subjected to analyze by the intraparticle diffusion model. The intraparticle diffusion equation can be written as follows^{1,13,14}.

$$q_t = k_{id}t^{1/2} + C \quad (5)$$

where q_t (mg/g) is the amount of Cr(III) adsorbed in time t (min) and k_{id} (mg/g min^{1/2}) is the rate constant of intraparticle diffusion. If the plots of q_t versus $t^{1/2}$ yield straight lines passing through the origin, intra-particle diffusion is likely to control the kinetics of the adsorption process. The slope gives the rate constant k_{id} .

Adsorption equilibrium studies: A 0.25 g of the sepiolite placed into 50 mL centrifuge tubes was treated in 25 mL of metal ion solutions in the concentrations 25, 50, 100, 150, 200, 250 and 300 mg/L at pH 5. The centrifuge tubes were agitated on a shaker at 25 °C, at 150 rpm for 150 min, then the tubes were centrifuged at 19,000 × g for 10 min and the supernatant was analyzed by atomic absorption analysis.

To investigate the sorption equilibrium of Cr(III) onto sepiolite, the sorption equilibrium results were fitted to the Langmuir and Freundlich sorption models to obtain the characteristic parameters of each model. The Langmuir adsorption isotherm has been successfully applied to many pollutants adsorption processes and has been the most widely used sorption isotherm for modeling of the sorption equilibrium data. The Langmuir adsorption isotherm model assumes that adsorption takes place at specific homogeneous sites within the adsorbent¹³, that sorbed molecules are organized as a monolayer and that all sites are energetically equivalent and that there is no interaction between sorbed molecules.

Langmuir isotherm is commonly presented as^{15,16}:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (6)$$

q_e is the amount of solutes sorbed per unit weight of sorbent at equilibrium concentration, C_e is the metal concentration in solution, q_m is the maximum amount of sorbed material required to give a complete monolayer on the surface and K is a measurement of relative sorption affinity and it is a constant related to the energy of sorption. A large value of the Langmuir constant, K , implies strong bonding.

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface¹⁷:

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

In this expression K_F and $1/n$ are characteristic constants relating to temperature, pH, sorbate and sorbent. K_F is an indication of the sorption capacity of the sorbent while $1/n$ indicates the effect of concentration on the sorption capacity and represents the sorption intensity. If sorption is favourable¹⁸, then $n > 1$.

The sorption model constants were estimated from the sorption data of Cr(III) ions on sepiolite by using a curve expert 1.3 computer program (biological software).

Temperature studies: To investigate the effect of temperature on the adsorption of Cr(III) onto sepiolite, 0.25 g of sepiolite was added to 25 mL of 100 mg/L metal ion solutions at pH 5.0. The above procedure was carried out at 298, 308, 318 and 328 K.

The thermodynamic parameters, the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the adsorption of Cr(III) to sepiolite are calculated using the following equations.

$$K_d = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (11)$$

The distribution coefficient, K_d (L/g), was calculated at the temperatures of 298, 308, 318 and 328 K by using eqn. 8. The values of ΔH° and ΔS° were determined from the slope and the intercept of the linear plot¹⁹ of $\ln K_d$ versus $1/T$. Gibbs free energy (ΔG°) values were calculated by using eqn. 10.

RESULTS AND DISCUSSION

Effect of sepiolite dosage: Sepiolite dosage is an important parameter because this determines the retention capacity of sepiolite for a given initial metal concentration. As shown in Fig. 1, the adsorption of the Cr(III) increased with increasing sepiolite dosage from 0.1-0.5 g and the adsorption was constant at higher dosages than 0.5 g as 100 %. With increasing sepiolite dosage, more surface area is available for adsorption due to increase in active sites on the sepiolite and thus making easier retention of metal ions onto the sorption sites²⁰.

Effect of pH: The pH of solution has been identified as the most important variable affecting metal adsorption onto adsorbent. To determine the effect of pH on the adsorption efficiencies of Cr(III) ions, pH was varied between 1.0-5.6. The effect of pH on adsorption efficiency is shown in Fig. 2. The removal efficiency was found to be highly dependent on H^+ concentration of solution. The maximum adsorption efficiency was 72 % at pH 5.0-5.6 and pH 5.0 value was selected as optimum pH for further studies. At higher pH values than 5.6, metal precipitation was observed.

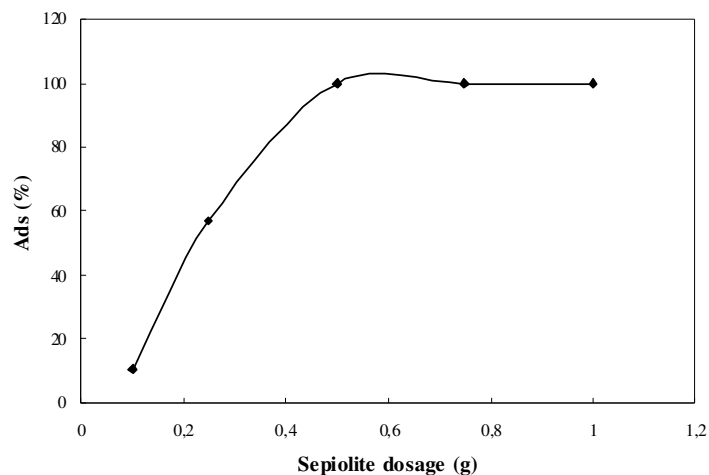


Fig. 1. Effect of sepiolite dosage on Cr(III) sorption efficiencies by sepiolite (C_i , 100 mg/L; temperature, 25 °C; pH, 3.0; stirring rate, 150 rpm)

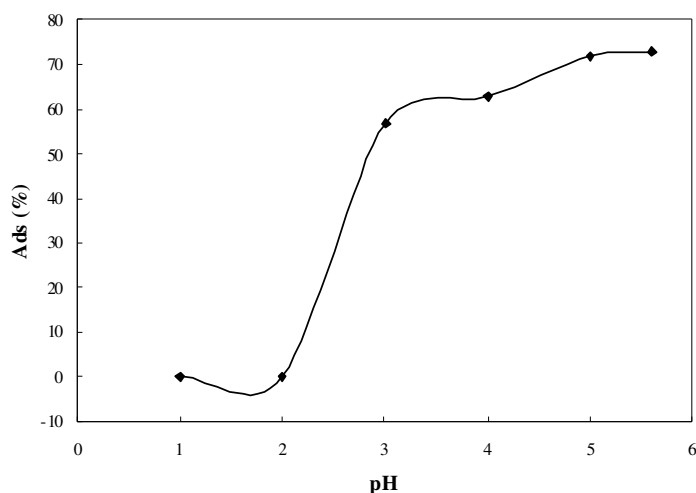


Fig. 2. Effect of pH on Cr(III) sorption efficiencies by sepiolite (C_i , 100 mg/L; amount of sepiolite, 0.25 g temperature, 25 °C; stirring rate, 150 rpm)

The effect of pH can be explained considering the surface charge on the adsorbent material. The increase of the suspension pH results in an increase in the negative charge of sepiolite. This can be ascribed to either the adsorption of OH^- ions onto the positive charge centers of sepiolite or the deprotonation of surface hydroxyl groups. As a result, we can say that the removal of Cr(III) ions increases since interaction of Cr(III) ions with sepiolite surface occurs more easily. At low pH values, hydrogen ions at active sites on the sepiolite surface compete with Cr(III) ions for adsorbing each other, resulting in lower level of Cr(III) uptake and at pH values above six, Cr(III) ions might precipitate. At higher pH values greater than six, the presence of OH^- ions forms the hydroxyl complexes of chromium $\text{Cr}(\text{OH})_3$ ^{10, 20,21}.

Effect of initial Cr(III) ion concentration: To determine the sorption isotherms, initial Cr(III) ion concentrations were varied between 25-300 mg/L. At an initial Cr(III) ion concentration of 25 mg/L, 96.22 % of the Cr(III) was bound to the sepiolite. The sorption efficiencies of Cr(III) decreased with increasing initial Cr(III) concentration (Fig. 3). The relative number of binding sites available to the metal ion would reduce as the concentration of the metal ion was increased. The sepiolite became nearly saturated at high initial concentrations¹⁸.

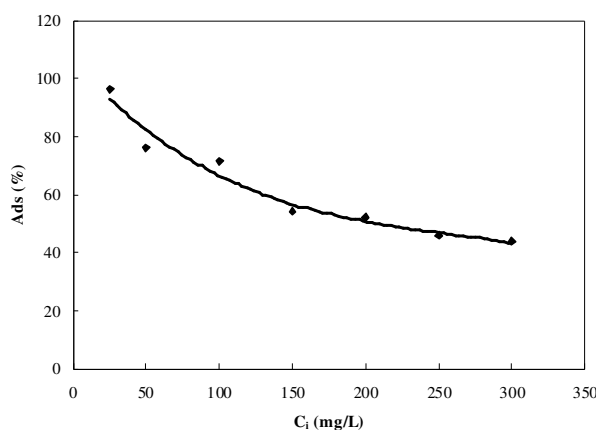


Fig. 3. Effect of initial Cr(III) concentration on Cr(III) sorption efficiencies by sepiolite (pH, 5.0; amount of sepiolite, 0.25 g; temperature, 25 °C; stirring rate, 150 rpm)

Sorption equilibrium of Cr(III) ions onto sepiolite: Langmuir and Freundlich sorption isotherms obtained at pH 5 for Cr(III) ions are shown in Fig. 4. Langmuir and Freundlich constants, the coefficient of multiple determination (R^2) between the experimental values and the predicted values using the models are given in Table-2. As seen from the Table, the R^2 values for both Langmuir and Freundlich isotherm models were above 0.95, suggesting that both models closely fit the experimental results. However, the R^2 values indicate that the Freundlich isotherm fit the experimental data better than Langmuir isotherm. Langmuir adsorption maxima (q_m) was quite high with the value of 14.626 mg/g. Langmuir equilibrium constant (K) had value of 0.0279 L/mg.

TABLE-2
ISOTHERM CONSTANTS FOR THE ADSORPTION OF
Cr(III) IONS ONTO SEPIOLITE AT 25 °C

q_m (mg g ⁻¹)	K (L mg ⁻¹)	R^2
Langmuir model		
14.626	0.0279	0.9726
K_f (mg ⁿ g ⁻¹ L ⁿ)	n	R^2
Freundlich model		
1.751	2.58	0.9908

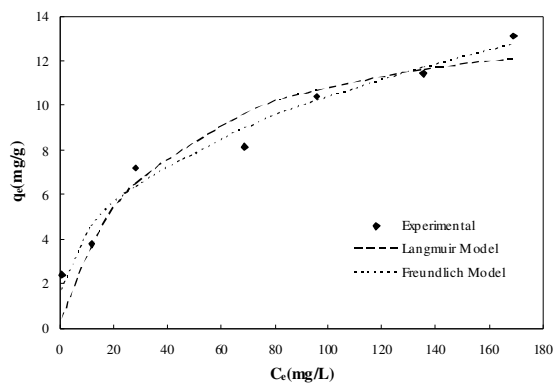


Fig. 4. Comparison of the Langmuir and Freundlich sorption isotherms for Cr(III) sorption onto sepiolite at 25 °C

Freundlich adsorption capacity, K_F , was found to be $1.751 \text{ mg}^n \text{ g}^{-1} \text{ L}^n$. Moreover, Freundlich coefficient ($1/n$) was smaller than 1 and indicating that the adsorption of Cr(III) on sepiolite under studied conditions was favourable². n is a constant representing the mutual interaction of sorbed species. Experimental values of n are usually greater than unity and this means that the forces between the sorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equation is the zero, the more heterogeneous is the system²².

Thermodynamic studies: The ΔH° parameter obtained from the $\ln K_d$ versus $1/T$ plot (Fig. 5) had a value of 67.26 kJ/mol and the ΔS° parameter was found to be 0.190 kJ/mol K (Table-3). The positive value of the enthalpy change indicates that the adsorption is endothermic and the large ΔH° value that there are strong interactions between the metal ions and the functional group (Si-O-) on the surface of sepiolite^{13,14,23}. The positive entropy change value corresponds to an increase in randomness at the solid-liquid interface and significant changes possibly occur in the internal structure of the sepiolite through the adsorption of Cr(III) on sepiolite^{13,14}.

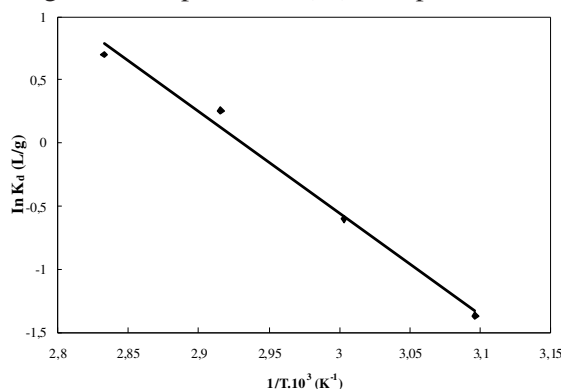


Fig. 5. Plot of $\ln K_d$ versus $1/T$ for the estimating of thermodynamic parameters for the adsorption of Cr(III) ions onto sepiolite (C_i , 100 mg/L; pH, 5.0; amount of sepiolite, 0.25 g; stirring rate, 150 rpm)

TABLE-3
THERMODYNAMIC PARAMETERS CALCULATED FOR THE ADSORPTION OF
Cr(III) IONS ONTO SEPIOLITE AT VARIOUS TEMPERATURES

T(K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
298	5.89	–	–
308	3.99	–	–
–	–	67.26	0.19
318	2.09	–	–
328	0.19	–	–

From eqn. 10, Gibbs free energy change of adsorption (ΔG°) was calculated for different temperatures. It was found as +5.89, +3.99, +2.09, and +0.19 kJ/mol for the adsorption of Cr(III) onto sepiolite at 298, 308, 318 and 328 K, respectively.

The positive ΔG° values indicated that the adsorption of Cr(III) on sepiolite was non spontaneous thermodynamically. This is further supported by the positive ΔH° value obtained for the adsorption of Cr(III)^{24,25}.

Kinetics of adsorption: Fig. 6 shows the effect of reaction time on the removal of Cr(III) by sepiolite. The percentage of metal removal increased rapidly up to approximately 150 min and a further increase in contact time had a negligible effect on the per cent removal. Therefore, in all subsequent experiments, the equilibrium time was maintained at 150 min, which was considered as sufficient for the removals of Cr(III) ion by sepiolite.

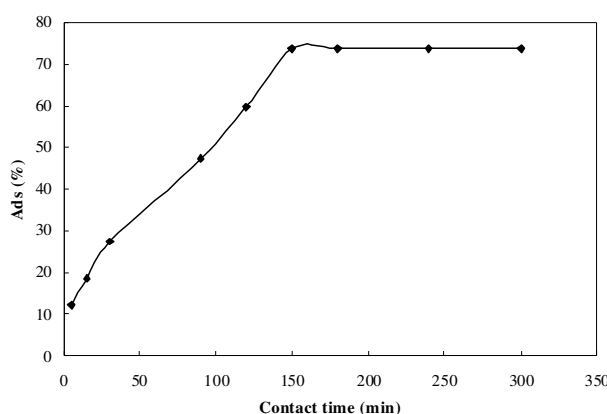


Fig. 6. Effect of contact time for the adsorption of Cr(III) ions onto sepiolite (C_i , 100 mg/L; pH, 5.0; amount of sepiolite, 0.25 g; temperature, 25 °C; stirring rate, 150 rpm)

The plots of linear form of the Lagergren first-order (Fig. 7), pseudo-second-order (Fig. 8) and intraparticle diffusion (Fig. 9) models for the adsorption of Cr(III) ions were obtained at the temperature of 25 °C. The kinetic parameters for the adsorption of Cr(III) ions onto sepiolite are summarized in Table-4. It is seen that the correlation coefficient of pseudo-second-order kinetic are lower than in the case

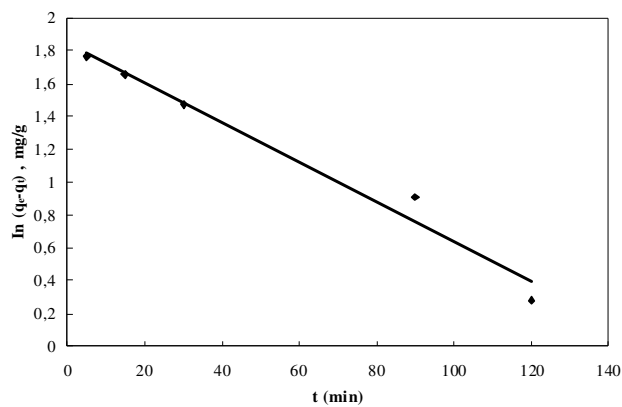


Fig. 7. Lagergren-first-order model plot for the adsorption of Cr(III) ions onto sepiolite at 25 °C

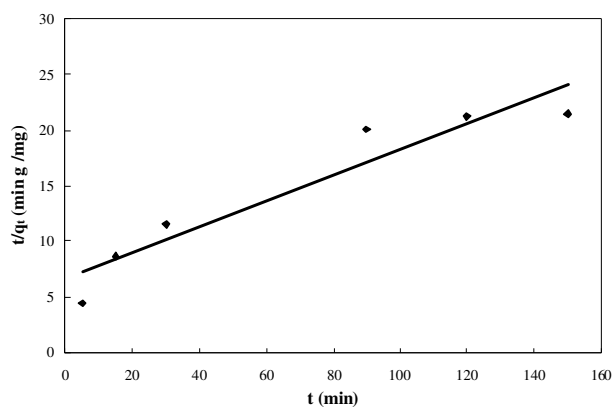


Fig. 8. Pseudo-second-order model plot for the adsorption of Cr(III) ions onto sepiolite at 25 °C

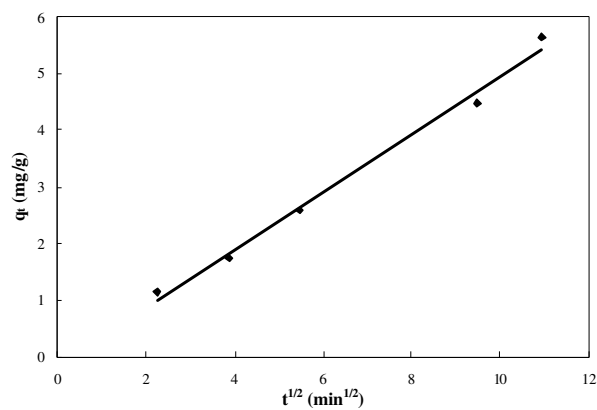


Fig. 9. Intraparticle diffusion model for the adsorption of Cr(III) ions onto sepiolite at 25 °C

TABLE-4
KINETIC PARAMETERS FOR THE ADSORPTION OF Cr(III) IONS
ONTO SEPIOLITE AT 25°C

k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R ²
Lagergren-first-order 0.0121	6.342	0.9756
k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R ²
Pseudo-second-order 0.00204	8.591	0.9044
k_{id} (mg g ⁻¹ min ^{-1/2})		R ²
Intraparticle diffusion 0.509		0.9918

case of Lagergren-first-order kinetic model. This finding shows that kinetics of Cr(III) adsorption by sepiolite are better described by Lagergren-first-order kinetic model rather than pseudo-second-order model. Whether the process of adsorption is controlled by intraparticle diffusion was tested by plotting q_t versus $t^{1/2}$ as in eqn. 5. The correlation coefficient obtained were very high (0.9918). This value indicates substantial diffusion of Cr(III) ions into the intraparticle of the sepiolite. However, the plot does not pass through the origin. Although intraparticle diffusion might have considerable influence on the adsorption process, it may not be the controlling factor in determining the kinetics of the process¹⁹.

Conclusion

In this study, batch adsorption experiments for the removal of Cr(III) from aqueous solution by using sepiolite clay of Eskisehir region of Turkey have been carried out. The obtained results can be summarized as follows: (1) For reaching the maximum adsorption efficiency, the pH and contact time was selected as 5-150 min, respectively, as the optimal operating parameters. (2) The sorption efficiency of Cr(III) to the sepiolite varied between as 96.2 and 43.7 % in the range of 25 and 300 mg/L. Sorption of Cr(III) to the sepiolite was non-linear and the sepiolite-Cr(III) isotherms fitted well the Freundlich model and have similar shapes (n-values > 1, showing favorable sorption). The highest Cr(III) sorption capacity, K_F (1.751 mgⁿ g⁻¹ Lⁿ) and intensity, n (2.58), were obtained for the sepiolite. (3) The positive value of the enthalpy change indicates that the adsorption is endothermic. The positive ΔG values indicated that the adsorption of Cr(III) on sepiolite was non-spontaneous thermodynamically. The positive entropy change value corresponds to an increase in randomness at the solid-liquid interface and may be significant changes occur in the internal structure of the sepiolite through the adsorption of Cr(III) on the sepiolite. (4) By applying the kinetic models to the experimental data, it was found that the adsorption of Cr(III) onto sepiolite follows the Lagergren-first-order rate kinetics.

ACKNOWLEDGEMENT

The authors wish to thank Asistant Prof. Duygu Kavak for supplying the materials.

REFERENCES

1. O. Gok, A.S. Ozcan and A. Ozcan, *Desalination*, **220**, 1 (2008).
2. S. Kocaoba and G. Akcin, *Desalination*, **180**, 1 (2005).
3. M. Dogan, Y. Turhan, M. Alkan, H. Namli, P. Turan and O. Demirbas, *Desalination*, **230**, 1 (2008).
4. M. Alkan, O. Demirbas, S. Celikcapa and M. Dogan, *J. Hazard. Mater.*, **116**, 1 (2004).
5. Y. Wu, S. Zhang, X. Guo and H. Huang, *Biores. Techn.*, **99**, 16 (2008).
6. A. Garcia-Sanchez, A. Alastuey and X. Querol, *Sci. Environ.*, **242**, 1 (1999).
7. E. Sabah, M. Turan and M.S. Celik, *Water Res.*, **36**, 16 (2002).
8. L.I. Vico, *Chem. Geo.*, **198**, 3 (2003).
9. S. Kocaoba and T. Akyuz, *Desalination*, **181**, 1 (2005).
10. F. Gode and E. Pehlivan, *J. Hazard. Mater.*, **100**, 1 (2003).
11. S. Mustafa, K.H. Shah, A. Naeem, M. Waseem and M. Tahir, *J. Hazard. Mater.*, **160**, 1 (2008).
12. S.S. Tahir and R. Naseem, *Sep. Purif. Technol.*, **53**, 312 (2007).
13. A.S. Ozcan, O. Gok and A. Ozcan, *J. Hazard. Mater.*, **161**, 1 (2009).
14. N. Dizge, B. Keskinler and H. Barlas, *J. Hazard. Mater.*, **167**, 915 (2009).
15. L. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).
16. R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao and M. Tang, *Chem. Eng. J.*, **145**, 496 (2009).
17. H. Freundlich, *Zeitsch. Physik. Chem.*, **57A**, 385 (1907).
18. Y. Asçi, M. Nurbas and Y. Sag Acikel, *J. Hazard. Mater.*, **139**, 1 (2007).
19. S.S. Gupta and K.G. Bhattacharyya, *J. Hazard. Mater.*, **128**, 2 (2006).
20. A. Sari, M. Tuzen, D. Citak and M. Soylak, *J. Hazard. Mater.*, **149**, 2 (2007).
21. M. Dogan, A. Turkyilmaz, M. Alkan and O. Demirbas, *Desalination*, **238**, 1 (2009).
22. Y. Asçi, M. Nurbas and Y. Sag Acikel, *J. Hazard. Mater.*, **154**, 1 (2008).
23. R. Donat, A. Akdogan, E. Erdem and H. Cetisli, *J. Colloid. Interface Sci.*, **286**, 1 (2005).
24. E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang and L.X. Kong, *Hydrometallurgy*, **93**, 1 (2008).
25. A. Sari, M. Tuzen and M. Soylak, *J. Hazard. Mater.*, **144**, 1 (2007).

(Received: 23 July 2009;

Accepted: 1 December 2009)

AJC-8126