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Removal of Cr(VI) From Aqueous Solution by Turkish Vermiculite: Equilibrium, Thermodynamic and Kinetic Studies

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Abstract: The adsorption of Cr(VI) from aqueous solution by Turkish vermiculite were investigated in terms of equilibrium, kinetics, and thermodynamics. Experimental parameters affecting the removal process such as pH of solution, adsorbent dosage, contact time, and temperature were studied. Equilibrium adsorption data were evaluated by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Langmuir model fitted the equilibrium data better than the Freundlich model. The monolayer adsorption capacity of Turkish vermiculite for Cr(VI) was found to be 87.7 mg/g at pH 1.5, 10 g/L adsorbent dosage and 20°C. The mean free energy of adsorption (5.9 kJ/mol) obtained from the D–R isotherm indicated that the type of sorption was essentially physical. The calculated thermodynamic parameters (ΔG° , ΔH° and ΔS°) showed that the removal of Cr(VI) ions from aqueous solution by the vermiculite was feasible, spontaneous and exothermic at 20–50°C. Equilibrium data were also tested using the adsorption kinetic models and the results showed that the adsorption processes of Cr(VI) onto Turkish vermiculite followed well pseudo-second order kinetics.

Keywords: Adsorption, Cr(VI), kinetics, removal, thermodynamics, Turkish vermiculite

INTRODUCTION

Environmental pollution resulting from heavy metal pollution is increasing throughout the world with the growth of industrial activities (1). The removal of heavy metals from waters and wastewaters is important in terms of protecting of public health and the environment due to their

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accumulation in living tissues throughout the food chain as nonbiodegradable pollutants (1,2).

Chromium, a known heavy metal, has widespread industrial applications; hence, large quantities of chromium are discharged into the environment. The chromium metal and its compounds have been involved in many applications such as making alloys, chrome plating, leather tanning, batteries, refractories, dyes, paints, welding, and catalysis (3–4). The wastewaters of all of these industries causes major environmental problems. Chromium exists in several oxidation states (–2 to +6), the most stable and common forms are hexavalent Cr(VI) and trivalent Cr(III) (5). For example, hexavalent chromium compounds are known to be very toxic although trivalent ones are somewhat less toxic. The International Agency for Research on Cancer has determined that Cr(VI) is carcinogenic to both humans and animals (6). This has led to the concern over the environmental effects of chromium present in surface water and groundwater. Therefore, several methods are utilized to remove chromium from industrial wastewater. These include: reduction followed by chemical precipitation, ion exchange, membrane separation, reduction, adsorption, biosorption, electrochemical precipitation, solvent extraction (7–13). Among these methods, adsorption is an effective method for removing chromium from aqueous solution, particularly when combined with appropriate regeneration steps (2,14–16). The removal of chromium ions from the industrial effluents can be achieved using natural and low-cost adsorbents. However, the literature is still insufficient to solve this problem, and more work and investigations are needed to deal with other locally available and cheap adsorbents.

Vermiculite is a clay mineral with 2:1 crystalline structure. It consists of unit layers composed from two silica tetrahedral sheets attached to a central magnesium octahedral sheet. Al^{3+} substitution for Si^{4+} in tetrahedral layers, and Al^{3+} and/or Fe^{3+} substitutions for Mg^{2+} in octahedral layers are responsible for the negative charge of the structure (17). Moreover, high surface area makes this material suitable adsorbent for adsorption studies and therefore, it has been successfully used as adsorbent to remove heavy metals from wastewaters (18–23). However, based on the authors' literature survey there is no study on the removal of Cr(VI) using Turkish vermiculite in literature. In addition, vermiculite is a natural and low-cost adsorbent and thus easily available in Turkish markets. In this regard, the present work focused on the potential use of Turkish vermiculite for Cr(VI) removal from aqueous solution. Experimental parameters affecting the removal process such as pH, contact time, adsorbent dosage, and temperature were studied. The equilibrium adsorption data were evaluated by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models. The removal mechanisms were also investigated in terms of thermodynamics and kinetics.

EXPERIMENTAL

Adsorbent, Reagents, and Equipments

The adsorbent used in this work was obtained from DRT Company (Antalya, Turkey). The mineralogical composition of the dried vermiculite supplied by the company is 42% SiO₂, 11.5% Al₂O₃, 22.5% MgO, 8% Fe₂O₃, 4% K₂O, 2% CaO, 1.4% TiO₂, 0.4% MnO, 0.2% Cr₂O₃, 0.7% Na₂O, and 7.3% H₂O. The adsorbent was ground in a laboratory type ball-mill and sieved to give 30–300 μm size fractions using ASTM standard sieves.

All chemicals used in this work, were of analytical reagent grade and were used without further purification. A Perkin Elmer A Analyst 700 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame.

FT-IR Analysis

The FT-IR spectra of Turkish vermiculite were taken before and after adsorption by JASCO-430 model spectrophotometer in order to obtain information on the nature of interactions between the functional groups of the adsorbent and metal ions. The results are shown in Fig. 1. The broad band observed at 3415 cm⁻¹ is due to the O–H stretching vibration of the Si–OH and Al–OH groups. The spectral band at 1646 cm⁻¹ reflects the bending vibration of water molecules retained in the silica or alumina matrix. The peak at 996 cm⁻¹ may be attributed to bending vibration of Si–OH and Al₂OH. The band at 676 cm⁻¹ assigns to the deforming modes of the –Si–O groups of the tetrahedral sheet. After Cr(VI) adsorption, especially the bands observed at 3412, 996 and 676 cm⁻¹ were shifted to 3401, 992, and 664 cm⁻¹. The significant changes in the wave number of specific bands indicated that the Si–OH and Al–OH groups on the surface of vermiculite mainly involved in the adsorption.

Batch Adsorption Procedure

Adsorption experiments were carried out at the optimum pH value, contact time, and adsorbent dosage level using the necessary adsorbent in a 100 mL stoppered conical flask containing 25 mL of test solution. Cr(VI) stock solutions were prepared from K₂Cr₂O₇. Initial solutions with different concentrations of Cr(VI) were prepared by proper dilution from stock 1000 mg/L Cr(VI) standards. 0.1 mol/L HCl was used for pH 1. 0.03 mol/L HCl was used for pH 1.5. Sodium phosphate buffer

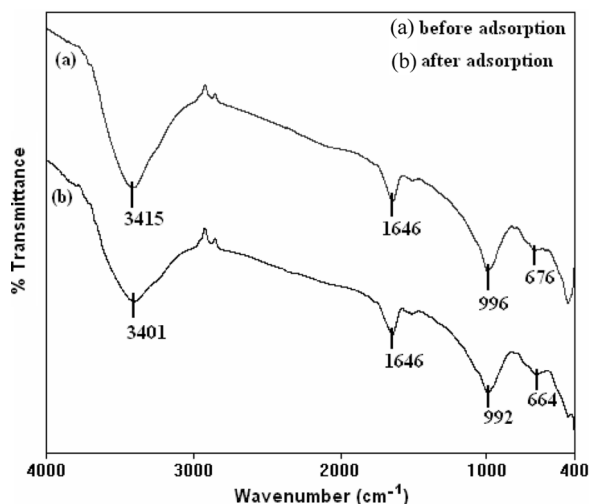


Figure 1. FT-IR spectra of Turkish vermiculite before and after adsorption.

(0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to obtain a solution of pH 2–3. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to obtain solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to obtain solutions of pH 8.

Necessary amount of the adsorbent was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 100 rpm. The experiments were repeated at 20, 30, 40, and 50°C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through blue band filter paper and the filtrate was analyzed for metal concentration by using flame AAS. The percent removal of metal ion was calculated as follows:

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively. Adsorption experiments for the effect of pH were conducted by using a solution having 25 mg/L of Cr(VI) concentration with a adsorbent dosage of 10 g/L. Throughout the study, the contact time was varied

from 10 to 180 min, the pH from 1.5 to 8, the initial metal concentration from 25 to 400 mg/L, and the adsorbent dosage from 2 to 40 g/L. All adsorption tests have been done in triplicate and the average results were taken into consideration.

Desorption and Reusability Studies

A sample volume of 25 mL, containing 10 mg/L of Cr(VI), was transferred into a beaker; 10 mL of buffer solution was added. After a fast shaking, 4 g/L of Turkish vermiculite was added and the mixture was shaken again for 120 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. In order to elute the adsorbed analyte onto Turkish vermiculite, 8–10 mL of 1 mol/L HCl was used. The final volume was completed to 25.0 mL with 1 mol/L HCl. Analyte contents of the final solution were determined by flame AAS. The same procedure was applied to the blank solution. In order to use the Turkish vermiculite for next experiment, the Turkish vermiculite was washed with excess of 1 mol/L HCl and distilled water, sequentially. All desorption tests have been done in triplicate and the average results were taken into consideration.

RESULTS AND DISCUSSION

Effect of pH

One of the most important factors affecting adsorption of metal ions is acidity of solution. The effect of pH on the removal efficiency of Cr(VI) onto Turkish vermiculite was studied by changing pH values in the range of 1.5–8 and the results were presented in Fig. 2. From this figure it is clear that the percent removal of Cr(VI) is maximum for all the concentrations at pH 1.5 and thereafter decreases with further increase in pH. This result directly related with competition ability of hydrogen ions with metal ions to active sites on the adsorbent surface.

Different mechanisms, such as electrostatic forces, ion exchange, and chemical complexation, must be taken into account when examining the effect of pH on Cr(VI) sorption. One of the commonly proposed mechanisms is electrostatic attraction/repulsion between sorbent and sorbate. Adsorption of hexavalent Cr(VI) varies as a function of pH, with H_2CrO_4 , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} ions present as dominant species. At pH 1–3, HCrO_4^- was the dominant species. At low pH, there is presence of a large number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface thereby reducing

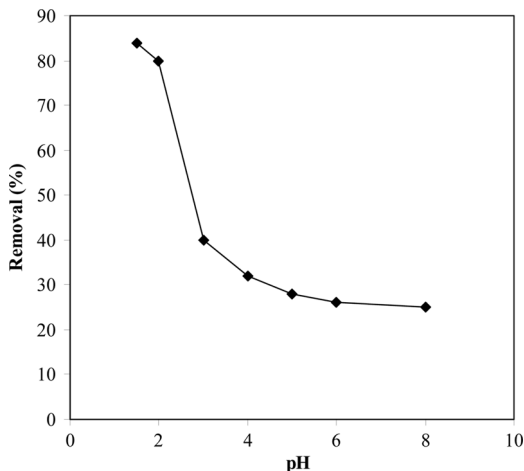


Figure 2. Effect of pH on the removal efficiency of Cr(VI) by the vermiculite (metal concentration: 25 mg/L; adsorbent dosage: 10 g/L; temperature: 20°C).

hindrance to the diffusion of HCrO_4^- ions (24). As the pH rises, the concentration of OH^- ions increases and overall charge on surface of the sorbent becomes negative which causes repulsion effect against the negatively charged Cr(VI) species like $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc., results in the decreased sorption of hexavalent chromium ions (15,25). Almost the same pH results were reported for the adsorption of Cr(VI) on different adsorbents and biosorbents (15,26–28). Moreover, at higher pH values (6–8), decrease in removal efficiency is due to the formation of soluble hydroxylated complexes of the chromium and their competition with the active sites, and as a consequence, the retention would decrease (7).

Effect of Adsorbent Dosage

To determine the effect of the adsorbent dosage on the removal efficiency of Cr(VI) by Turkish vermiculite the amounts of adsorbent in solution were varied from 2 to 40 g/L and the results are presented in Fig. 3. The removal efficiency of Cr(VI) increased with increasing of the adsorbent dosage as expected. The maximum removal efficiency was attained at 10 g/L and reached a saturation level at higher dosages. This trend could be explained as a consequence of a partial aggregation of adsorbent at higher concentration, which results in a decrease in effective surface area for the adsorption (29).

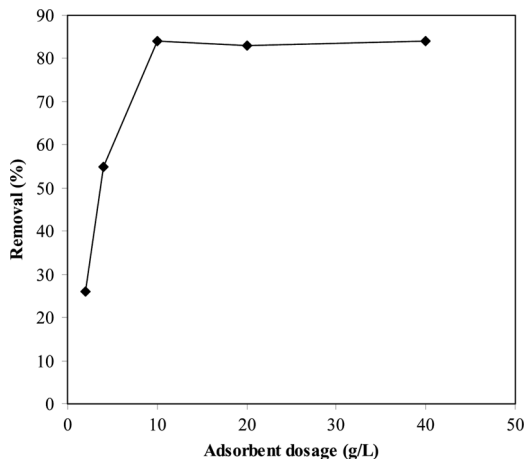


Figure 3. Effect of adsorbent dosage on the removal efficiency of Cr(VI) by the vermiculite (metal concentration: 25 mg/L; pH: 1.5; temperature: 20°C).

Effects of Contact Time and Temperature

Contact time is one of the important parameters for successful use of an adsorbent for practical application and rapid sorption is among desirable parameters. Figure 4 shows the effect of contact time and temperature on the removal efficiency of Cr(VI) using 10 g/L of Turkish vermiculite at

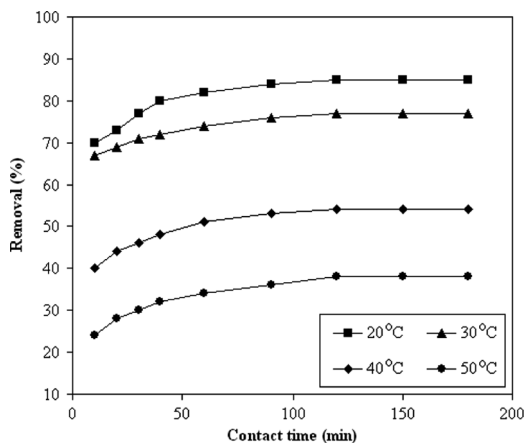


Figure 4. Effect of contact time and temperature on the removal efficiency of Cr(VI) by the vermiculite (metal concentration: 25 mg/L; adsorbent dosage: 10 g/L; pH: 1.5).

pH 1.5. The removal efficiency increases with increase of contact time till equilibrium. As shown in Fig. 4, the removal efficiency increased gradually up to 85% with increasing contact time between 10 and 120 min and it becomes almost constant. Therefore, the optimum contact time was selected as 120 min for further experiments.

Figure 4 also shows the experimental results obtained from a series of contact time studies in which temperature was varied from 20 to 50°C. The removal efficiency decreased from 85% to 38% with increasing temperature from 20 to 50°C during a 120 min-contact time. The decrease in adsorption capacity of the vermiculite with temperature indicates an exothermic process. The increase in adsorption with temperature may be attributed to increasing tendency to desorb metal ions from the interface to the solution (30–33). The optimum solution temperature was selected as 20°C for further adsorption experiments.

Adsorption Isotherm Models

An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacity of the adsorbent for different pollutants (34). Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models.

Langmuir isotherm models the single coating layer on adsorption surface. This model supposes that the adsorption takes place at a specific adsorption surface. This model can be written in linear form (35).

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L} \right) \frac{1}{C_e} \quad (2)$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer adsorption capacity of the adsorbent (mg/g), g, and K_L is the Langmuir adsorption constant (L/mg) relating the free energy of adsorption.

Figure 5 indicates the linear relationship between the amount (mg) of Cr(VI) sorbed per unit mass (g) of vermiculite against the concentration of Cr(VI) remaining in solution (mg/L). The coefficient of determination (R^2) was found to be 0.998, indicating that the adsorption of Cr(VI) onto vermiculite fitted well the Langmuir model. In other words, the sorption

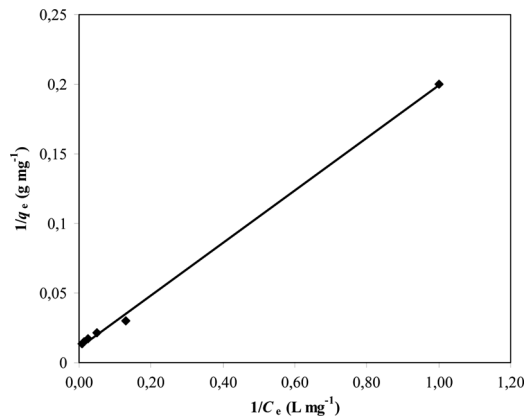


Figure 5. Langmuir isotherm plots for the adsorption of Cr(VI) by the vermiculite (adsorbent dosage: 10 g/L; pH: 1.5; contact time: 120 min; pH: 1.5; temperature: 20°C).

of Cr(VI) ions onto vermiculite was taken place at the functional groups/binding sites on the surface of the adsorbent which is regarded as monolayer sorption. The maximum adsorption capacity (q_m) was found to be 87.7 mg/g and the K_L value was found as 0.06 L/mg. In addition,

Table 1. Comparison of adsorption capacity of Turkish vermiculite for Cr(VI) with that of different sorbents

	pH	q_m (mg/g)	Reference
<i>Brown coal (YK)</i>	3	50.9	(3)
<i>Brown coal (KK)</i>	3	47.8	(3)
<i>Pseudomonas sp.</i>	1	95.0	(7)
<i>Staphylococcus xylosus</i>	1	143.0	(7)
Activated bentonite	5	91.7	(15)
Olive oil industry waste	2	13.9	(25)
Modified lignin	2	9.3	(27)
<i>Fucus vesiculosus</i>	2	42.7	(36)
<i>Fucus spiralis</i>	2	5.4	(36)
<i>Ulva lactuca</i>	2	27.6	(36)
<i>Ulva spp.</i>	2	30.2	(36)
<i>Palmaria palmate</i>	2	33.8	(36)
<i>Polysiphonia lanosa</i>	2	45.8	(36)
Tea waste	2 (60°C)	54.7	(37)
Modified oak sawdust	3	1.70	(38)
Turkish vermiculite	1.5	87.7	present study

Table 1 presents the comparison of adsorption capacity of Turkish vermiculite for Cr(VI) with those of various sorbents in literature (3,7,15,25,27,36–38). From this table, it can be resulted that the Turkish vermiculite is an effective and alternative sorbent to remove Cr(VI) from aqueous solution.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. The Freundlich model (39) is

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \quad (3)$$

where K_f is a constant relating the adsorption capacity and $1/n$ is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material.

Figure 6 shows the linear Freundlich isotherm obtained for the removal of Cr(VI) onto vermiculite. The values of K_f and $1/n$ were found to be 7.74 and 0.53 respectively. The $1/n$ values were between 0 and 1, indicating that the adsorption of Cr(VI) onto vermiculite was favourable at studied conditions. However, the R^2 value was found to be 0.909, showing that the Freundlich model was not able to adequately to describe the relationship between the amounts of sorbed metal ions and their equilibrium concentrations in the solution. In addition, the Langmuir

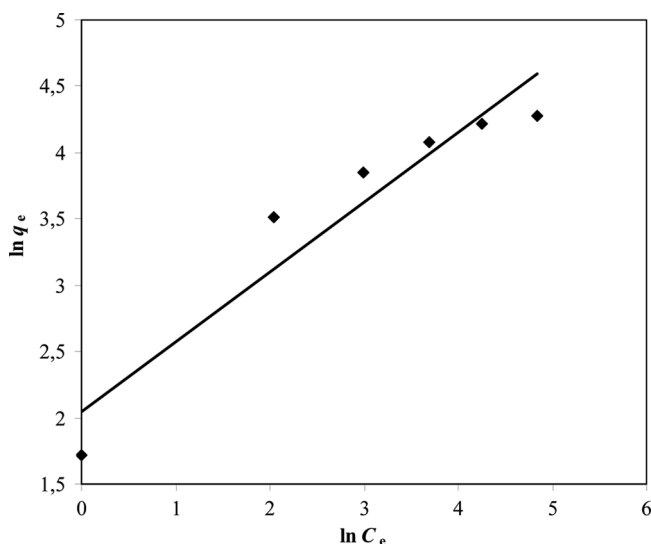


Figure 6. Freundlich isotherm plots for the adsorption of Cr(VI) by the vermiculite (adsorbent dosage: 10 g/L; pH: 1.5; contact time: 120 min; pH: 1.5; temperature: 20°C).

isotherm model best fitted the equilibrium data since it presents higher R^2 value than that determined from the Freundlich isotherm.

Another equation that has been used to determine the possible adsorption mechanism is the Dubinin–Radushkevich equation, which assumes a constant sorption potential. The linear form of the D-R isotherm equation (40) is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to mean adsorption energy (mol^2/J^2) and ε is the Polanyi potential which is equal to $\varepsilon = RT \ln(1 + 1/C_e)$, where R (J/mol K) is the gas constant and T (K) is the absolute temperature. Hence by plotting $\ln q_e$ against ε^2 it is possible to generate the value of q_m (mol/g) from the intercept, and the value of β from the slope.

The constant β gives an idea about the mean adsorption free energy E (kJ/mol) can be calculated using the relationship

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

The D-R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.991. (Fig. 7). From the intercept of the plots, the

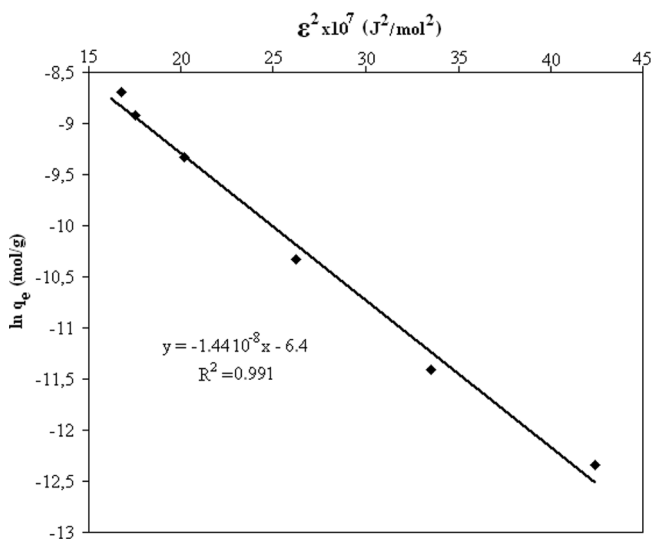


Figure 7. D-R isotherm plots for the adsorption of Cr(VI) by the vermiculite (adsorbent dosage: 10 g/L; pH: 1.5; contact time: 120 min; pH: 1.5; temperature: 20°C).

q_m value was found to be 1.610^{-3} mol/g. The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If this value is between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process is physical (41). The mean adsorption energy ($E = 5.9$ kJ/mol) indicated that the adsorption of Cr(VI) onto Turkish vermiculite has physical characteristics because the E value lies within 1–8 kJ/mol.

Desorption Efficiency

Desorption of adsorbed analyte ions onto Turkish vermiculite were also studied by using HCl and HNO_3 at various concentrations in Table 2. For these studies, 10 mL of each eluent was used. Analyte ions were desorbed from Turkish vermiculite with both 1 M HCl and 1 M HNO_3 . The highest recovery for both metal ions was found to be 96% using 1 mol/L HCl. The effects of volume of 1 mol/L HCl as eluent were also investigated in the range of 5.0–10.0 mL. Quantitative recovery values ($>95\%$) were obtained for both metal ions after 8.0 mL of 1 mol/L HCl. Subsequent elution with 10 mL 1 M HCl readily strips the sorbed metal ions from the Turkish vermiculite. The high stability of the Turkish vermiculite permitted six times of adsorption-elution process along the studies without a decrease about 10% in recovery of Cr(VI) ions. This result indicates that the Turkish vermiculite has a good reuse potential for adsorption of Cr(VI) from aqueous solution.

Adsorption Kinetics

Kinetics is another important aspect in any evaluation of sorption as a unit operation. Adsorption kinetics depends on the sorbate-sorbent interaction and operating condition and examined for their suitability for practical applications in water pollution control. Several kinetic models

Table 2. Influence of various eluents on the desorption of Cr(VI) ions from Turkish vermiculite

Eluent	Recovery, %
.5 mol L ⁻¹ HCl	75 ± 2
1 mol L ⁻¹ HCl	96 ± 3
0.5 mol L ⁻¹ HNO_3	60 ± 3
1 mol L ⁻¹ HNO_3	80 ± 3

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 this study, the adsorption equilibrium data were analyzed using two simplest kinetic models, pseudo-first-order and pseudo-second-order model.

The linear form of the pseudo-first-order rate equation by Lagergren (42) is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t and q_e (mg/g) are the amounts of the metal ions sorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The adsorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ vs t .

The plots of $\ln(q_e - q_t)$ vs t for the pseudo-first-order model were not shown as figure because of low R^2 values in Table 3 (0.954–0.979). It can be concluded from the R^2 values that the adsorption of Cr(VI) onto vermiculite does not follow the pseudo-first-order kinetic model. Moreover, it can be seen from Table 3 that the experimental values of $q_{e,\text{exp}}$ are not in good agreement with the theoretical values calculated ($q_{e1,\text{cal}}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Cr(VI) onto vermiculite.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form (43):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (7)$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of adsorption time t (min) and q_e is the amount of adsorption equilibrium (mg/g).

Table 3. Pseudo-first-order and pseudo-second-order parameters for the adsorption of Cr(VI) onto Turkish vermiculite at different temperatures

Temperature (°C)	$q_{e,\text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (l/min)	$q_{e1,\text{cal}}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e2,\text{cal}}$ (mg/g)	R^2
20	0.98	3.4×10^{-2}	0.21	0.954	0.35	0.87	0.999
30	0.92	2.8×10^{-2}	0.14	0.974	0.24	0.81	0.998
40	0.71	2.5×10^{-2}	0.11	0.979	0.18	0.60	0.995
50	0.63	1.8×10^{-2}	0.08	0.967	0.15	0.45	0.993

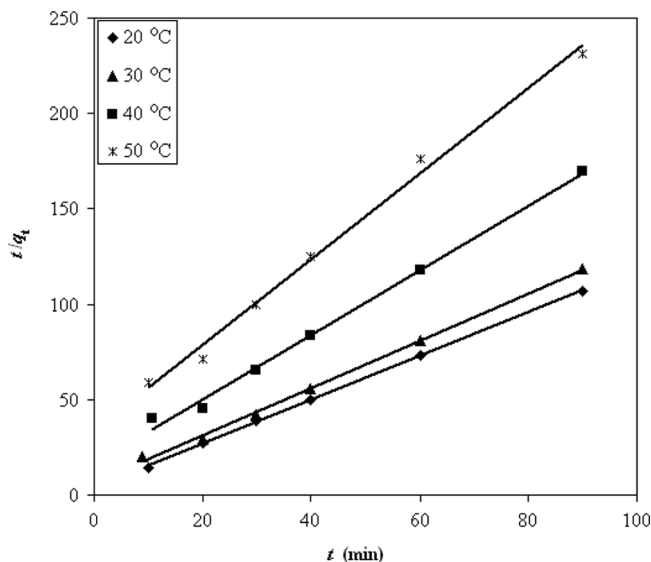


Figure 8. Pseudo-second-order kinetic plots at different temperatures.

The linear plots of t/qt vs t for the pseudo-second-order model for the removal of Cr(VI) by Turkish vermiculite at 20–50°C were shown in Fig. 8. The rate constants (k_2), the R^2 and the q_e values are given in Table 3. The R^2 values in the range, 0.993–0.999 suggested that the adsorption of Cr(VI) ions onto adsorption well follows the pseudo-second-order kinetic model. In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 3). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cr(VI) onto vermiculite in contrast to the pseudo-first-order model.

Adsorption Thermodynamics

The thermodynamic behavior of the adsorption of Cr(VI) onto vermiculite was evaluated by the thermodynamic parameters including the change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters were calculated from following equations

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

where, R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient (44).

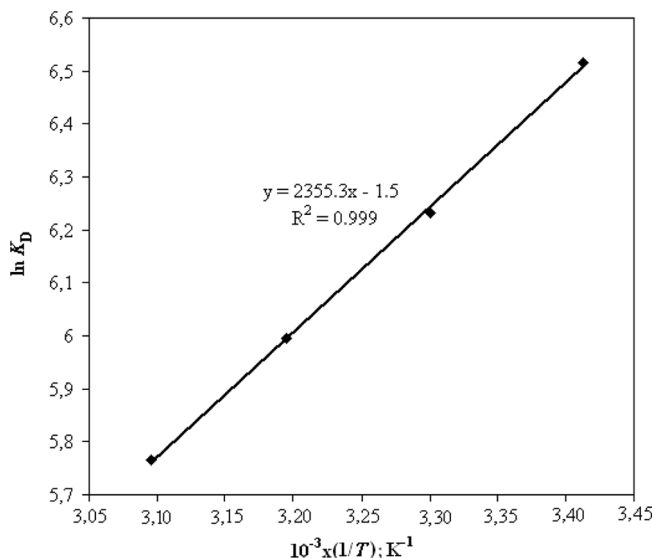


Figure 9. Plot of $\ln K_D$ vs $1/T$ for the estimation of thermodynamic parameters.

By considering Eq. (8), the enthalpy (ΔH°) and entropy (ΔS°) of adsorption were estimated from the slope and intercept of the plot of $\ln K_D$ vs $1/T$ yields, respectively (Fig. 9).

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Gibbs free energy change (ΔG°) was calculated to be -15.9 , -15.7 , -15.6 , and -15.5 kJ/mol for Cr(VI) adsorption at 20, 30, 40, and 50°C, respectively. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the adsorption. The decrease in ΔG° values with increase in temperature shows a decrease in feasibility of adsorption at higher temperatures. The enthalpy of adsorption (ΔH°) was found to be -19.6 kJ/mol. The negative ΔH° is an indicator of exothermic nature of the adsorption. Calculated ΔS° (-12.7 J/molK) parameter implying that Cr(VI) in solid phase (surface of adsorbent) were in a much less chaotic distribution compared to the relatively ordered state of bulk phase (aqueous solution). The negative entropy result can be also associated to decreasing of species in solution after adsorption such as solvation water when dichromate and chromate anions were adsorbed.

CONCLUSIONS

This study focused on the removal of Cr(VI) using Turkish vermiculite from aqueous solution. The operating parameters, pH of solution, adsorbent dosage, contact time, and temperature, were effective on the removal efficiency of Cr(VI). The maximum removal efficiency was found as 85% at the conditions of 10 g/L adsorbent dosage, pH 1.5, 120 contact time, and 20°C. Adsorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer adsorption capacity of Turkish vermiculite for Cr(VI) was found to be 87.7 mg/g ions. The mean energy (5.9 kJ/mol) determined from the D-R model showed that the adsorption Cr(VI) onto Turkish vermiculite may be carried out by physical sorption. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the adsorption process at 20–50°C. Kinetic examination of the equilibrium data showed that the adsorption of Cr(VI) onto Turkish vermiculite followed well the pseudo-second-order kinetic model. Based on all results, it can be also concluded that the Turkish vermiculite is an effective and alternative adsorbent for the removal of Cr(VI) ions from aqueous solution because of its considerable adsorption capacity, being of its natural and low-cost.

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REFERENCES

1. Sakaguchi, T.; Nakajima, A.; Horikoshi, T. (1981) Studies on the accumulation of heavy metal elements in biological systems. *Appl. Microbiology Biotechnol.*, 12: 84–89.
2. Lau, S.; Mohamed, M.; Tan Chi Yen, A.; Su'ut, S. (1998) Accumulation of heavy metals in freshwater molluscs. *The Sci. The Total Environ.*, 214: 113–121.
3. Gode, F.; Pehlivan, E. (2006) Chromium(VI) adsorption by brown coals. *Energy Sour. Part A*, 28: 447–457.
4. Malik, U.R.; Hasany, S.M.; Subhani, M.S. (2005) Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile. *Talanta*, 66: 166–173.

5. Baral, A.; Engelken, R.D. (2002) Chromium-based regulation and greening in metal finishing industries in the USA. *Environ. Sci. Pollut.*, 5: 121–133.
6. IARC (International Agency for Research on Cancer). (1997) IARC Monographs on the evaluation of Carcinogenic Risks to Humans. Chromium, Nickel and Welding, Volume 49, World Health Organization.
7. Ziagova, M.; Dimitriadis, G.; Aslanidou, D.; Papaioannou, X.; Litopoulou Tzannetaki, E.; Liakopoulou-Kyriakides, M. (2007) Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosus* and *Pseudomonas* sp. in single and binary mixtures. *Biores. Technol.*, 98: 2859–2865.
8. Gode, F.; Pehlivan, E.A. (2003) Comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution. *J. Hazard. Mater.*, 100: 231–243.
9. Rengaraj, S.; Joo, C.K.; Kim, Y.; Yi, J. (2003) Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. *J. Hazard. Mater.*, 102: 257–275.
10. Ramos, R.L.; Martinez, A.J.; Coronado, R.M.G. (1994) Adsorption of Chromium(VI) from aqueous solutions on activated carbon. *Water Sci. Technol.*, 30: 191–197.
11. Raji, C.; Anirudhan, T.S. (1998) Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water Res.*, 32 (12): 3772–3780.
12. Chakravarti, A.K.; Chowdhury, S.B.; Chakrabarty, S.; Chakrabarty, T.; Mukherjee, D.C. (1995) Liquid membrane multiple emulsion process of chromium(VI) separation from wastewaters. *Colloids Surface A: Physicochem. Eng. Aspects*, 103: 59–71.
13. Tunalı, S.; Kiran, I.; Akar, T. (2005) Chromium(VI) biosorption characteristics of *Neurospora crassa* fungal biomass. *Miner. Eng.*, 18: 681–689.
14. Cimino, G.; Passerini, A.; Toscano, G. (2000) Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Res.*, 34: 2955–2962.
15. Bayrak, Y.; Yesiloglu, Y.; Gecgel, U. (2006) Adsorption behavior of Cr(VI) on activated hazelnut shell ash and activated bentonite. *Micropor. Mesopor. Mater.*, 91: 107–110.
16. Bailey, S.E.; Olin, T.J.; Bricka, R.M.; Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33: 2469–2479.
17. Liu, Y.; Xiao, D.; Li, H. (2007) Kinetics and thermodynamics of lead(II) adsorption on vermiculite. *Separ. Sci. Technol.*, 42: 185–202.
18. Abate, G.; Masini, J.C. (2005) Influence of pH, ionic strength and humic acid on adsorption of Cd(II) and Pb(II) onto vermiculite. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 262: 33.
19. Fonseca, M.G.; Oliveira, M.M.; Arakaki, L.N.H. (2006) Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral. *J. Hazard. Mater.*, 137: 288–292.
20. Stylianou, M.A.; Inglezakis, V.J.; Moustakas, K.G.; Malamis, S.P.; Loizidou, M.D. (2007) Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents. *Desalination*, 215: 133–142.

21. Mathialagan, T.; Viraraghavan, T. (2003) Adsorption of cadmium from aqueous solutions by vermiculite. *Separ. Sci. Technol.*, 38: 57–76.
22. Cxueyia, G.; Inoue, K. (2003) Elution of copper from vermiculite with environmentally benign reagents. *Hydrometallurgy*, 70: 9–21.
23. Malandrino, M.; Abollino, O.; Giacomino, A.; Aceto, M.; Mentasti, E. (2006) Adsorption of heavy metals on vermiculite: Influence of pH and organic ligands. *J. Colloid Interf. Sci.*, 299: 537–546.
24. Mohanty, K.; Jha, M.; Meikap, B.C.; Biswas, M.N. (2006) Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*. *Chem. Eng. J.*, 117: 71–77.
25. Malkoc, E.; Nuhoglu, Y.; Dundar, M. (2006) Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies. *J. Hazard. Mater.*, 138: 142–151.
26. Oliveira, E.A.; Montanher, S.F.; Andrade, A.D.; Nóbrega, J.A.; Rollemberg, M.C. (2005) Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. *Process Biochem.*, 40: 3485–3490.
27. Demirbaş, A. (2005) Adsorption of Cr(III) and Cr(VI) ions from aqueous solutions on to modified lignin. *Energy Sour.*, 27: 1449–1455.
28. Gokhale, S.V.; Jyoti, K.K.; Lele, S.S. (2008) Kinetic and equilibrium modeling of chromium (VI) biosorption on fresh and spent *Spirulina platensis*/*Chlorella vulgaris* biomass. *Bioresour. Technol.*, 99: 3600–3608.
29. Karthikeyan, S.; Balasubramanian, R.; Iyer, C.S.P. (2007) Evaluation of the marine algae *Ulva fasciata* and *Sargassum sp.* for the biosorption of Cu(II) from aqueous solutions. *Bioresour. Technol.*, 98: 452–455.
30. Özer, A.; Özer, D. (2003) Comparative study of the biosorption of Pb(II), Ni(II) and ions onto *S. cerevisiae*: determination of biosorption heats. *J. Hazard. Mater.*, 100: 219–229.
31. Sari, A.; Tuzen, M.; Citak, D.; Soylak, M. (2007) Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution. *J. Hazard. Mater.*, 148: 387–394.
32. Saltali, K.; Sari, A.; Aydin, M. (2007) Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality. *J. Hazard. Mater.*, 141: 258–263.
33. Sari, A.; Tuzen, M.; Çitak, D.; Soylak, M. (2007) Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite. *J. Hazard. Mater.*, 149: 283–289.
34. Dursun, G.; Cicek, H.; Dursun, A.Y. (2005) Adsorption of phenol from aqueous solution by using carbonized beet pulp. *J. Hazard. Mater.*, 125: 175–182.
35. Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1361–1403.
36. Murphy, V.; Hughes, H.; McLoughlin, P. (2008) Comparative study of chromium biosorption by red, green and brown seaweed biomass. *Chemosphere*, 70: 1128–1134.
37. Malkoc, E.; Nuhoglu, Y. (2007) Potential of tea factory waste for chromium (VI) removal from aqueous solutions: Thermodynamic and kinetic studies. *Separ. Purif. Technol.*, 54: 291–298.

38. Argun, M.E.; Dursun, Ş.; Ozdemir, C.; Karataş, M. (2007) Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *J. Hazard. Mater.*, 141: 77–85.
39. Freundlich, H.M.F. (1906) Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie (Leipzig)*, 57A: 385–470.
40. Dubinin, M.M.; Zaverina, E.D.; Radushkevich, L.V. (1947) Sorption and structure of active carbons. I. Adsorption of organic vapors. *Zhurnal Fizicheskoi Khimii*, 21: 1351–1362.
41. Cabuk, A.; Akar, T.; Tunali, S.; Gedikli, S. (2007) Biosorption of Pb(II) by industrial strain of *Saccharomyces cerevisiae* immobilized on the biomatrix of cone biomass of *Pinus nigra*: Equilibrium and mechanism analysis. *Chem. Eng. J.*, 131: 293–300.
42. Lagergren, S. (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, 24: 1–39.
43. Ho, Y.S.; McKay, G. (1999) Pseudo-second order model for sorption processes. *Process Biochem.*, 34: 451–465.
44. Aravindhnan, R.; Rao, J.R.; Nair, B.U. (2007) Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*. *J. Hazard. Mater.*, 142: 68–76.