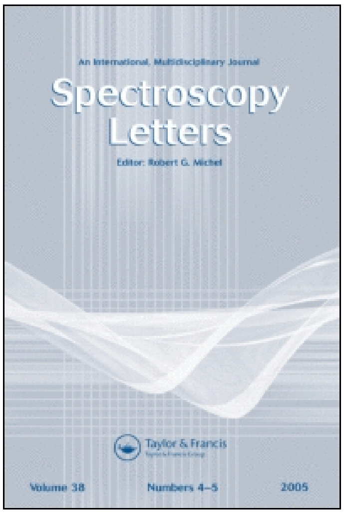

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Adsorption of Cr(VI) from Aqueous Solutions Onto Raw and Acid-Activated Reşadiye and Hançılı Clays

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To cite this Article Göde, Fethiye , Öztürk, Nuri , Sert, Yusuf and Bahçeli, Semiha(2010) 'Adsorption of Cr(VI) from Aqueous Solutions Onto Raw and Acid-Activated Reşadiye and Hançılı Clays', Spectroscopy Letters, 43: 1, 68 — 78
To link to this Article: DOI: 10.1080/00387010903261164
URL: http://dx.doi.org/10.1080/00387010903261164

Spectroscopy Letters, 43:68–78, 2010
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ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903261164

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Adsorption of Cr(VI) from Aqueous Solutions Onto Raw and Acid-Activated Reşadiye and Hançılı Clays

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ABSTRACT The adsorption of Cr(VI) from aqueous solutions onto raw and acid-activated clays—namely, Reşadiye region clay (R, raw Reşadiye region clay; R-H_2SO_4, acid-activated with H_2SO_4 Reşadiye region clay; R-HCl, acid-activated with HCl Reşadiye region clay) and Hançılı region clay (H, raw Hançılı region clay; H-H_2SO_4, acid-activated with H_2SO_4 Hançılı region clay; H-HCl, acid-activated with HCl Hançılı region clay)—was studied in a batch system. For optimization of the Cr(VI) adsorption on raw clays and acid-activated clays, the effect of pH, temperature, initial Cr(VI) concentration, time, and adsorbent dosage were investigated. X-ray diffraction analyses of raw and acid-activated clays were used to determine the effects of acid-activating on the layer structure of the clays. The surface characterizations of clays and modified clays were performed by using FT-IR spectroscopy. The Langmuir and Freundlich adsorption models were employed to describe the equilibrium isotherms, and thus the isotherm constants were determined. The data obtained from our investigations were well described by the Langmuir model. The adsorption capacity of the adsorbents Reşadiye and Hançılı clays were found to be 0.0269, 0.0144, and 0.0170 mmol/g for H, H-HCl, and H-H_2SO_4 and 0.0356, 0.0276, and 0.0422 mmol/g for R, R-HCl, and R-H_2SO_4, respectively. The results show that the adsorption was strongly dependent on pH of the medium, initial Cr(VI) concentration and temperature. The removal of Cr(VI) reached saturation in about 120 min, and the adsorption process of Cr(VI) was observed as exothermic. A maximum removal of 73% was noted at 1.0×10^{-4} M concentration of Cr(VI) in solution for H-HCl. Furthermore the enhancement of removal of Cr(VI) was observed from pH 3 to 4. The results are discussed to highlight the influence of acid activation on Cr(VI) adsorption characteristics of the clays.

KEYWORDS acid-activated clay, adsorption, Cr(VI), isotherms, montmorillonite clay

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INTRODUCTION

For the environment, the removal of heavy metal from aqueous solutions has been a considerable necessity because of unregulated applications and inappropriate waste-disposal practices in various industries. In this framework, chromium contamination has become a significant environmental problem. Chromium has two oxidation states in water system, Cr(VI) and Cr(III), whose mobilities and toxicities are different. Cr(VI) species are known as mutagens and potential carcinogens, whereas Cr(III) is somewhat less toxic.[1–5]

A number of technologies for the removal of Cr(VI) ions from aqueous solutions have been developed over the years. Adsorption is of prime importance as a procedure for the removal of heavy metal traces from aqueous solutions.[2,3] Recently, in order to minimize processing costs, several investigations have focused on the use of low-cost adsorbents,[3,6–8] for example, sawdust,[9,10] pumice,[11] coal,[12] and clay materials.[13–17]

Adsorbents, especially clay minerals, are readily available inexpensive materials[18] and natural, fine-grained materials composed largely of a group of crystalline minerals.[19] Clays, that are hydrous alumino-silicates, are broadly defined as those minerals that dominantly make up the colloid fraction of soils, sediments, rocks, and water.[20] The high specific surface areas, chemical and mechanical stabilities, layered structures, high cation exchange capacities, etc., have made the clays excellent adsorbent materials. Presence of both Bronsted and Lewis types of acidity in clays boosts the adsorptive capacities of clays.[21–23]

The specific surface area and surface acidity of the clay samples can be greatly increased by acid activation. Treatment of clay minerals with concentrated inorganic acids usually at high temperature is known as acid activation. Acid treatments of clay minerals are important controls over mineral weathering and genesis.[23] Such treatments can often replace exchangeable cations with H ions and release Al and other cations out of both tetrahedral and octahedral sites, but leave the SiO_4 groups largely intact. It was reported that acid activation followed by thermal treatment increases the adsorbent capacity to a good extent.[21]

The aim of the present work is to report the use of locally available Reşadiye and Hançılı region clays that are from Middle-East Anatolia (Tokat, Turkey) and acid-activated clays as adsorbents for the removal of Cr(VI) from aqueous solution, as an alternative to existing commercial adsorbents. The effect of adsorbent dosage, initial solution pH, shaking time, initial Cr(VI) concentration, and temperature was also investigated. The Freundlich and Langmuir isotherms models were employed to find the equilibrium data. On the other hand, the use of the acid-activated Reşadiye and Hançılı clays for the adsorption of Cr(VI) from aqueous solution has not been documented in literature.

MATERIALS AND METHODS

Preparation of Acid-Activated Clays

The two natural samples used in this study were obtained from Reşadiye and Hançılı regions of Anatolia (Turkey). First, the raw Reşadiye and Hançılı clays were heated at 623 K for 4 hr, and then 10 g of each clay were mixed with 100 mL of concentrated HCl (Riedel-de Hain, 37%) and H_2SO_4 (Merck, 96.5%) acids in 100 mL of distilled water. The reaction mixtures were stirred vigorously at 80°C for 2 hr. The suspensions were cooled in air and filtered off and then washed several times with distilled water. The resulting materials were dried in a convection oven at 80°C for 2 hr prior to use.

Adsorption Studies

In order to determine the influence of acid activation, the clay samples obtained by activation with two different acids were subjected to Cr(VI) adsorption test. In adsorption experiments, the analytical grade $K_2Cr_2O_7$ (Merck, 99.5%) was used without further purification. First, 0.5 g of each of raw and acid-activated clays was placed into 1.0×10^{-3} mol/L of $K_2Cr_2O_7$ solution in distilled water, and the whole was stirred during 2 hr at $25 \pm 1°C$. Then, the supernatant solution was analyzed by atomic absorption spectrometry (AAS) for its residual Cr(VI) content. The amount of adsorbed Cr(VI) was calculated from the difference between their initial and final concentrations. The PerkinElmer AA800 model atomic absorption spectrometer (PerkinElmer; U.S.A.) was used in this work.

pH Measurements

The pH of the aqueous solution is a crucial controlling parameter in the adsorption process. In our study, the pH values of the samples were measured by using a HI9321 model pH meter with a glass electrode. About 0.5 g of each raw and acid-activated clay was added to 30 mL of Cr(VI), which has 1.0×10^{-3} M. The mixture was shaken for 2 hr at 25 ± 1°C and then was filtered.

The pH of each solution was adjusted to the desired value by addition of 0.1 M HCl or NaOH solutions. The solutions were shaken for 2 hr (except when the effect of time was studied) to reach equilibrium. The pH was adjusted from 2.0 to 8.0.

Furthermore, effects of contact time, temperature, and dosage were also studied. In our experiments, the initial Cr(VI) concentration, the amount of adsorbent, time, and temperature were varied from 1.0×10^{-4} to 1.0×10^{-3} M, from 0.1 to 1 g, from 5 to 2880 min, and from 25°C to 55°C, respectively.

X-Ray Diffraction

XRD patterns of the clay samples were recorded using Pananalytical BV (PW 3050/60 model) powder diffractometer with CuKα (1.54060 Å, 40 mA, 45 kV) at 0.02 steps at the rate of 0.5 per second over the range $5° < 2\theta < 75°$.

Infrared Spectroscopy

IR spectra were recorded at room temperature on a PerkinElmer Spectrum One FT-IR (Fourier Transformed Infrared) Spectrometer (PerkinElmer; U.S.A.) with a resolution of 4 cm^{-1} in the transmission mode. The prepared samples were compressed into self-supporting pellets and introduced into an IR cell equipped with KBr windows.

Zeta Potential Measurements

Zeta potential measurements of raw and acid-activated with HCl and H_2SO_4 Reşadiye and Hançılı clays in the presence of Cr(VI) ions was determined by using a ZEN 3600 Model Zetasizer Nano-ZS connected with MPT-2 multipurpose automatic titrator (Malvern Inst. Ltd.; U.K.).

The optical device contains a 5 mW He–Ne (638 nm) laser. The samples of 0.1 g of suspensions of clays were sonicated for 10 min. The suspension was then kept still for 5 min to let larger particles settle. About 10 mL of clear supernatant was placed into the vial, which was connected with automatic titrator. The desired pH of the solution was kept constant during conditioning by introducing appropriate amounts of HCl or NaOH.

RESULTS AND DISCUSSIONS

X-Ray Structure Determination

Powder X-ray diffraction patterns of the raw Hançılı and Reşadiye clays heated at 350°C for 4 hr and activated with HCl and H_2SO_4 are shown in Fig. 1, Parts a and b, respectively.

As seen in Fig. 1, the acid treatment followed by calcinations affects the crystal structure of the Hançılı and Reşadiye clays.[24] In the figures, all changes at different θ values have been marked on the graphics. For instance, while the raw Hançılı clay heated at 350°C has a illite layer, the Hançılı acid-activated with HCl and H_2SO_4 exhibits the presences of beidellite and montmorillonite, respectively.[24] On the other hand, the raw Reşadiye heated at 350°C has the properties of illite–montmorillonite at 2 θ of 9–7° and 26.5°, but these properties transform to beidellite property for both Reşadiye acid-activated clay with HCl and Reşadiye acid-activated clay with H_2SO_4. Furthermore, the graphite property at 2 θ of 45° of Reşadiye heated at 350°C modifies to albite for Reşadiye acid-activated clay with HCl.

Infrared Spectra

FT-IR spectroscopy is very sensitive to modification of the clay structure upon acid activations.[25] The IR spectra of the raw and acid-activated Hançılı and Reşadiye clays are given for two frequency ranges in Fig. 2 (3800–3200 cm^{-1}) and Fig. 3 (1650–550 cm^{-1}). The assignments of IR vibrational frequencies of the raw Hançılı and acid-activated Hançılı clays and the raw Reşadiye and acid-activated Reşadiye clays followed by calcinations can be explained as follows. For the assignments of IR vibrational frequencies of the raw clay, we referred to the works of Majedova, Kati and Katti, Esmer and Tarcan, and Shoval.[26–29]

In Fig. 2a, the arrows denote the OH deformation of water vibrational bands for acid-activated Hançılı

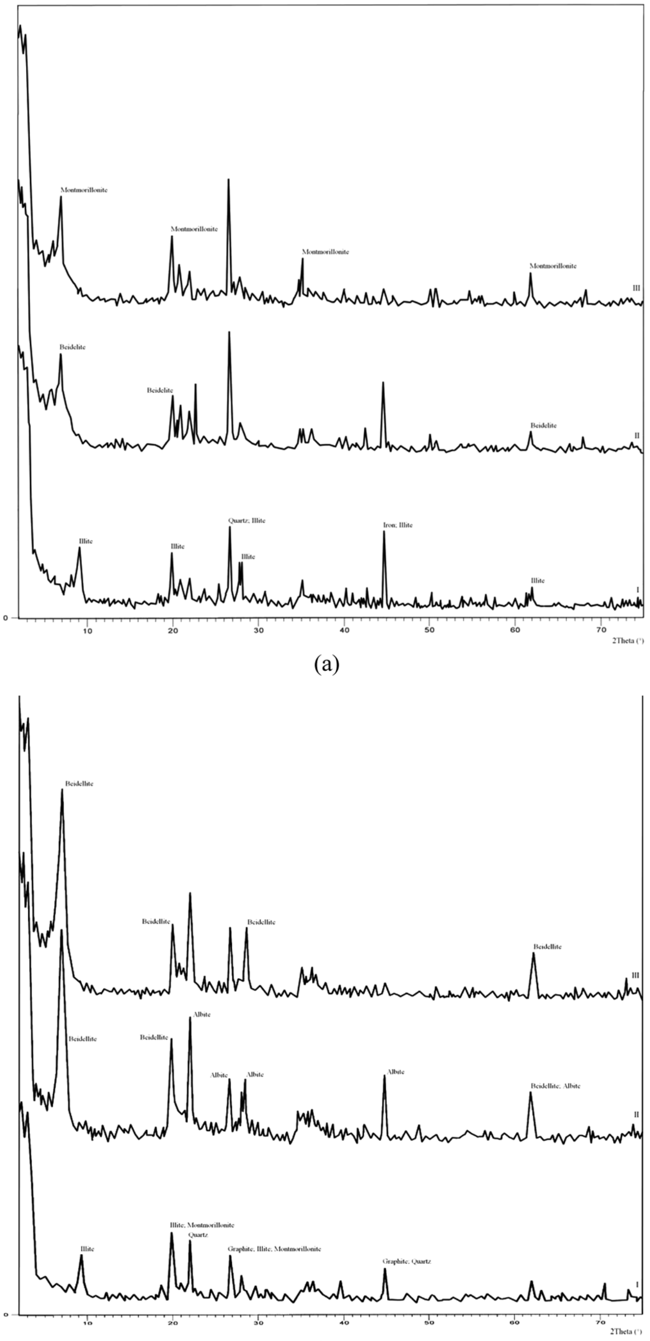


FIGURE 1 (a) Powder X-ray diffraction pattern of Hançılı (heated at 350°C) clays and (b) Reşadiye (heated at 350°C) clays where I, II, III show the raw, activated with HCl and activated with H_2SO_4.

clays. Similarly, the weak bands at 3382 and 3389 cm^{-1} that are shown with arrows indicate the OH deformation of water for the Reşadiye clays acid-activated with HCl and H_2SO_4, respectively, in Fig. 2b. As seen in Fig. 2b, the weak bands at 3740–3750 cm^{-1} for Reşadiye clays can be assigned to the attractions of K^+ ions from the KBr that disturb the orientation of the hydroxyl groups because of highly localized negative charge on the Si-O surface resulting from Al(III) for Si(IV) substitution.[26] The broad bands (shown with arrows) at 3382 and 3389 cm^{-1} in Fig. 2a and at 3401 and 3403 cm^{-1} in Fig. 2b can be attributed to the OH deformation vibrational mode of water for Hançılı and Reşadiye acid-activated with HCl and H_2SO_4, respectively. This deformation band is not observed for raw Hançılı and raw Reşadiye clays. This situation can be explained by considering the existence of the effect of acid activation on clays. Similarly, the broad medium band at 1455 cm^{-1} for raw Hançılı clay that is assigned to the CH_2 symmetric and CH_3 asymmetric bending vibrational mode can be only observed at 1426 cm^{-1} as very weak band shown with an arrow

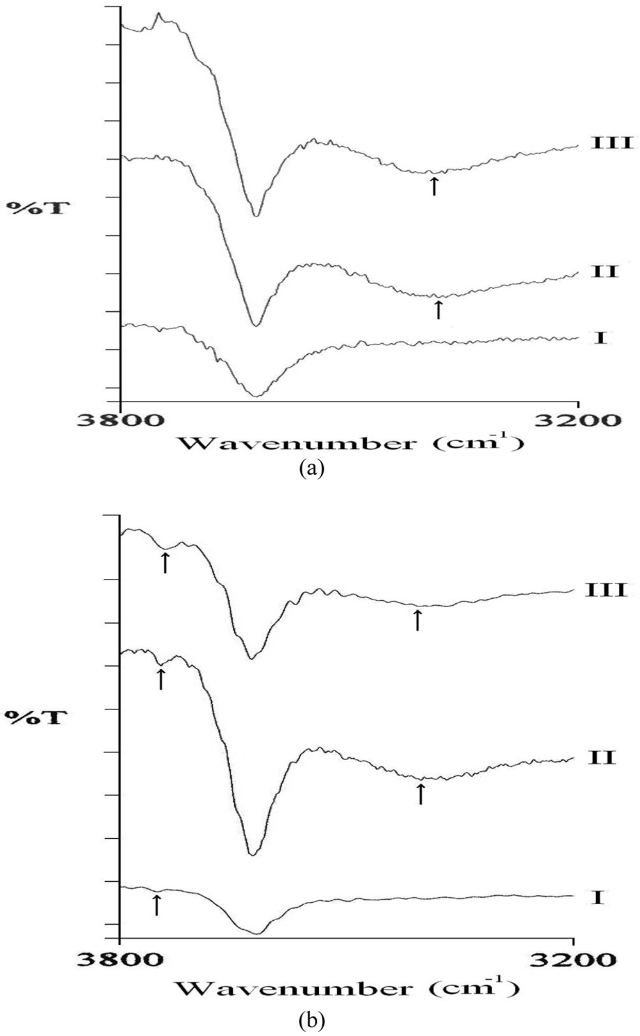
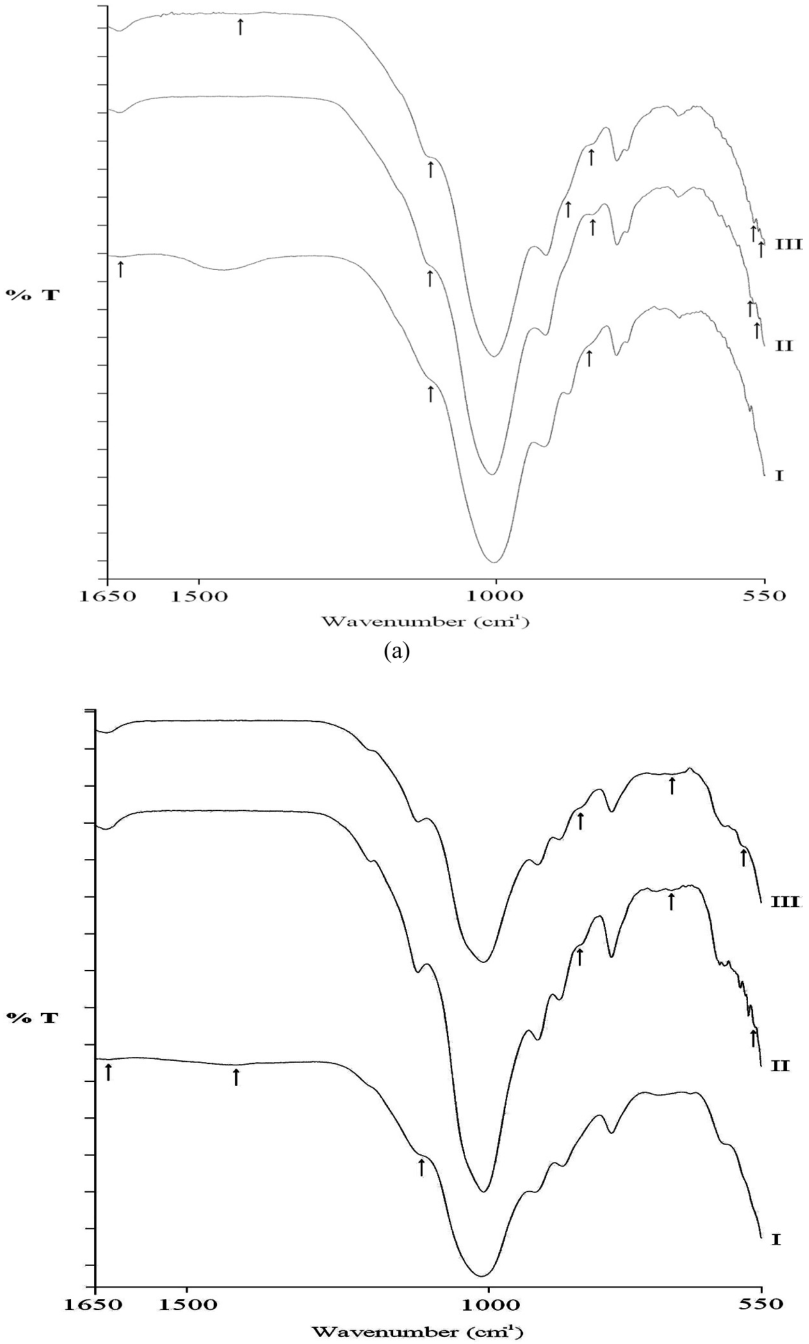


FIGURE 2 Infrared spectra of (a) Hançılı and (b) Reşadiye clays in the interval 3800–3200 cm^{-1} [(I) raw clay (heated at 350°C), (II) acid-activated with HCl clay, and (III) acid-activated with H_2SO_4 clay].



(a)

(b)

FIGURE 3 Infrared spectra of (a) Hançılı and (b) Reşadiye clays in the interval 1650–550 cm^{-1} [(I) raw clay (heated at 350°C), (II) acid-activated with HCl clay, and (III) acid-activated with H_2SO_4 clay].

in Fig. 3a. This band in Fig. 3b is only observed as a broad band at 1416 cm^{-1} (shown with an arrow) for raw Reşadiye clay. But it is not exhibited for acid-activated Reşadiye clays. This situation can be also based on the effect of acid activation on clay.

The other examples of influence of acid activation on clay are the weak bands at 1627 cm^{-1} (shown with arrows) in Fig. 3, Parts a and b, for both raw clays, respectively. But this band is getting stronger in terms of intensity for the acid-activated clays.

On the other hand, as seen in Figs. 2 and 3, the other bands (mostly shown with arrows) are in very good agreement with those in the literature.[26–28] For instance, the Si-O stretching bands can be assigned to the some shoulder weak and very strong bands at the interval 1112–990 cm^{-1} for raw and acid-activated Hançılı clays and at the interval 1200–990 cm^{-1} for raw and acid-activated Reşadiye clays. On the other hand, the several bands at the interval 600–559 cm^{-1} for both clays can be attributed to the Si-O-Al (octahedral Al) and Si-O-Si bending vibrations.[27–29]

Adsorption of Cr(VI)

Adsorption measurements were made by a batch technique at room temperature. The batch technique was selected because of its simplicity and reliability. In order to determine the influence of acid activation, the clay samples obtained by activating with different acids were subjected to adsorption tests.

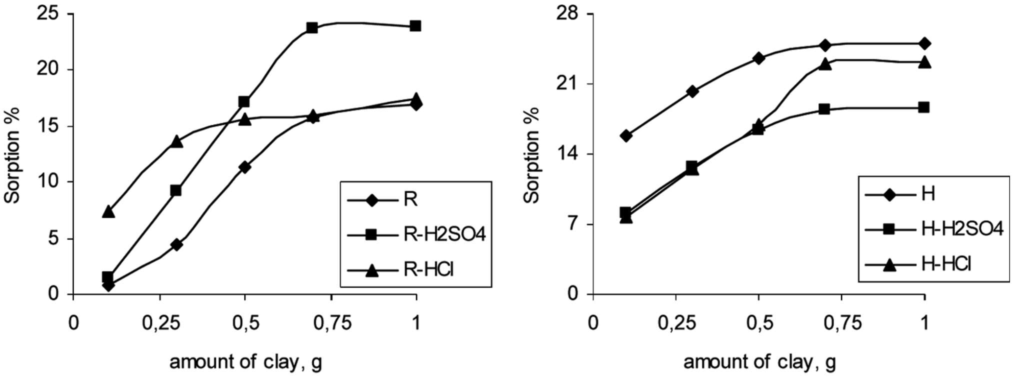
When the adsorption efficiency of the clay heated at 350°C and followed by acid-activated clay with HCl and H_2SO_4 acids is compared with that of the raw clay, it can be seen that it decreases by heating and acid-activating. According to Erdem et al.,[1] it has been reported that the major factor governing the heat activation of bauxite is dehydration which causes an increase in specific surface area and porosity depending on temperature. In the present study, the heat activation and then acid activation of clays changed the specific surface area and porosity.

Effects of Adsorbent Dosage

Adsorbent dosage is an important parameter. It determines the capacity of an adsorbent. The results of the dependence of Cr(VI) on the amount of Hançılı and Reşadiye region clays are shown in Fig. 4. The adsorption of Cr(VI) slightly increased with increasing dosage of the clays up to 0.5 g, after which it stayed constant at about 0.75 g. This is an expected result because as the amount of adsorbent increases, the number of adsorbent sites increases; therefore, these particles attach more ions to their surfaces.[8] For heavy metals, removal from aqueous solution by using Celtek clay[19], tripolyphosphate-impregnated Kaolinite,[30] and palygorskite clays,[18] respectively, as an adsorbent has been reported in similar findings.

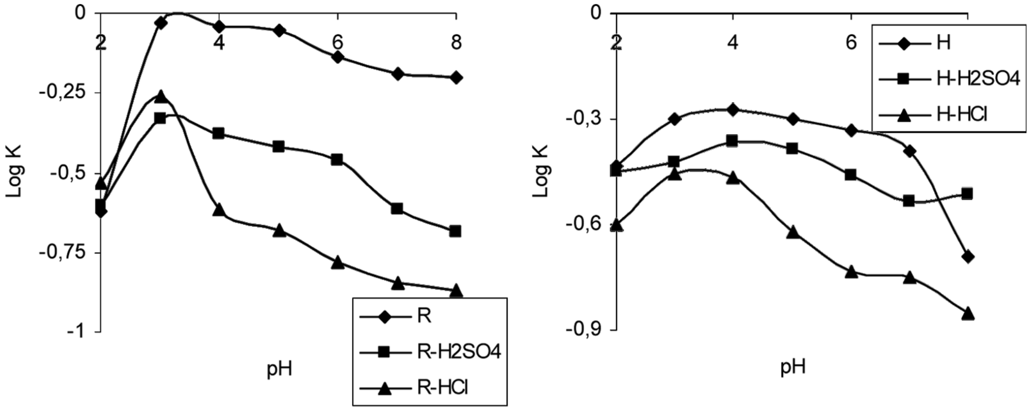
Effects of pH

The point of zero charge of the adsorbent is necessary in order to choose the optimum pH for the adsorption study, as well as to understand the adsorption mechanism. The zeta potentials of raw and acid-activated clays were determined. Regarding obtained data, raw clays have no point of zero charge (pHpzc) and exhibit negative zeta potential values at all studied pH values. This result agrees with the data given by Özcan et al. and Gök et al.[31,32] According to Özcan et al. (2009),[31] this situation can be explained as pHpzc arising from isomorphic transactions, defects in the crystal lattice, broken particle edges, and structural hydroxyl groups. The zero point could not obtain for both of the clays because the neutrality of the clay particles could not be obtained. But, we observed the same data toward more positive values for both clays that are activated with HCl and H_2SO_4. For instance, in raw Reşadiye clay and Reşadiye clay activated with H_2SO_4, IEP (isoelectrical point) points exhibit the same amounts in positive direction.



(a) (b)

FIGURE 4 Sorption graph of Cr(VI) ions on adsorbents as a function of amount of adsorbent dosage (a) Reşadiye Region Clay (b) Hançılı Region Clay (Adsorption conditions; initial concentration of chromium: 1.0×10^{-3} mol/L, amount of adsorbents: 0.1 g, temperature: 25 ± 1°C).



(a) (b)

FIGURE 5 Sorption graph of Cr(VI) ions on adsorbents as a function of pH (a) Reşadiye region clay (b) Hançılı region clay.

The pH of the aqueous solution is an important controlling parameter in the adsorption process.[1,22] The results of the effect of pH on adsorption of Cr(VI) on Hançılı and Reşadiye region clays in the pH range 2.0–8.0 are shown in Fig. 5. The effect of initial solution pH on the Cr(VI) adsorption on activated clays was studied at the conditions of contact time, 120 min; adsorbent dosage, 0.5 g; and temperature, 25 ± 1°C. In addition, raw clays were also studied. The pH of the solution was kept constant by the addition of 0.1 M HCl and 0.1 M NaOH as needed. It was found that the total amount of adsorption of Cr(VI) onto Hançılı and Reşadiye region clays increases with an increase of pH from 2.0 to 3.0. It reached a maximum at pH 3.0 and decreased with an increase of pH from 3.0 to 8.0.

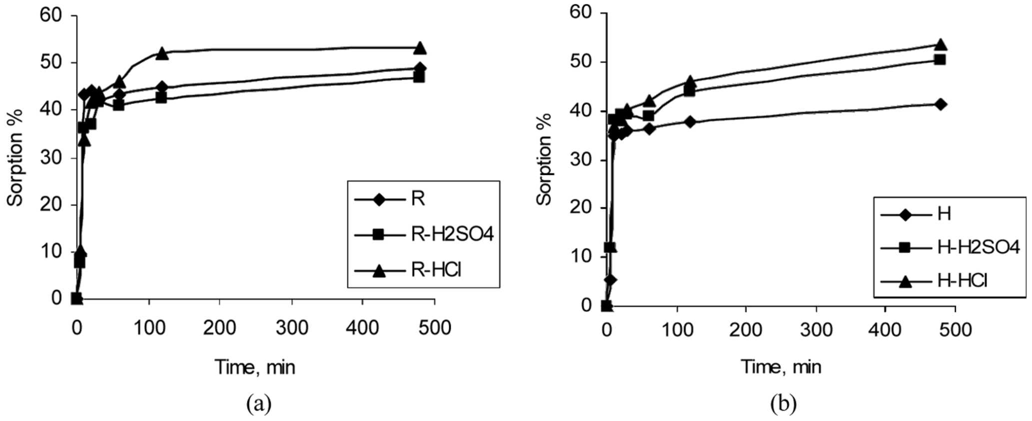
It is widely believed that the mechanism for the adsorption of anions onto oxidic surfaces involves a surface complexation phenomenon in the adsorption process. Depending on the type of connection of an anion to an active surface site, the surface complexes formed are classified as inner-sphere or outer-sphere complexes.[1] If the number of protonated surface groups is more than that of dissociated groups, the surface is positively charged and becomes suitable for anion adsorption.[1] The pH effect was also attributed to the different complexes that Cr(VI) can form in aqueous solution. The hexavalent Cr(VI) forms are $Cr_2O_7^{2-}$ and CrO_4^{2-}. The two forms of Cr(VI) are pH dependent. The predominant form of Cr(VI) below a pH of 6.0 is $Cr_2O_7^{2-}$. Increasing the pH will shift the concentration from the $Cr_2O_7^{2-}$ form to CrO_4^{2-}.[1,18,33–35] It can be concluded that the most effective form of Cr(VI) that is adsorbed by Hançılı and Reşadiye region clays in the present study is $Cr_2O_7^{2-}$. This mechanism is in agreement with the findings of previous studies on palygorskite such as those by Potgieter et al. (2006).[18]

For highly acidic media of pH 2–3, it can be stated that the adsorbent surfaces might be highly protonated and favor the uptake of Cr(VI). With a further increase in the pH from 3 to 9, the degree of protonation of the surface reduces gradually, and hence decreased adsorption is observed.[1] The oxygen atoms present on the clay surface interact with water in an acidic medium, forming some aqua complexes, which result in positive charge formation as follows[22]:

$$\text{-MO} + \text{H-OH} \rightarrow \text{M-OH}^{2+} + \text{OH}^-$$

Effect of Time

The influence of shaking time for the adsorption of Cr(VI) on Hançılı and Reşadiye region clays was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 5–2880 min at 25 ± 1°C. The results were drawn in Fig. 6. The obtained results show that the equilibrium is reached quickly and indicate that the adsorption sites are well exposed. The results from Potgieter et al. (2006)[18] were similar to those found in this investigation. The removal of Cr(VI) increases rapidly with time, and then it continues at a slower rate and reaches saturation in about 120 min, as shown in Fig. 6. A further increase in contact time has a negligible effect on the removal. This finding is in agreement with recent work by other



(a) (b)

FIGURE 6 Sorption graph of Cr(VI) ions on adsorbents as a function of time (a) Reşadiye region clay (b) Hançılı region clay.

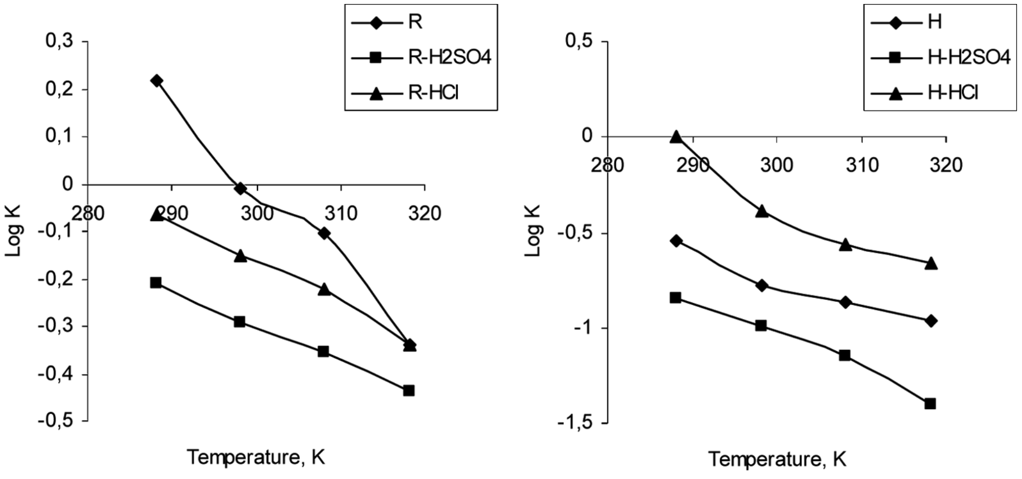
authors[19] who found the same behavior. The shaking time of 120 min was found suitable for maximum adsorption and used in all subsequent measurements.

Effect of Temperature

Figure 7 shows the effect of temperature on the Cr(VI) adsorption. In order to investigate the effect of temperature on the adsorption of Cr(VI) on clays, the distribution coefficient, *K*, was calculated at the temperatures of 288.15, 298.15, 308.15, and 318.15 K. Cr(VI) adsorption efficiency on Hançılı and Reşadiye region clays decreases by increasing the temperature. The decreases in Cr(VI) adsorption by increasing the temperature suggest that the mechanism governing the adsorption process may be physical.[1,19,36] The results showed that the *K* value decreased with increasing temperature and that the adsorption of Cr(VI) on the clay was exothermic. This finding is in agreement with Sari and Tuzen's work.[37] The adsorption process for Turkish vermiculite was also found to be exothermic.

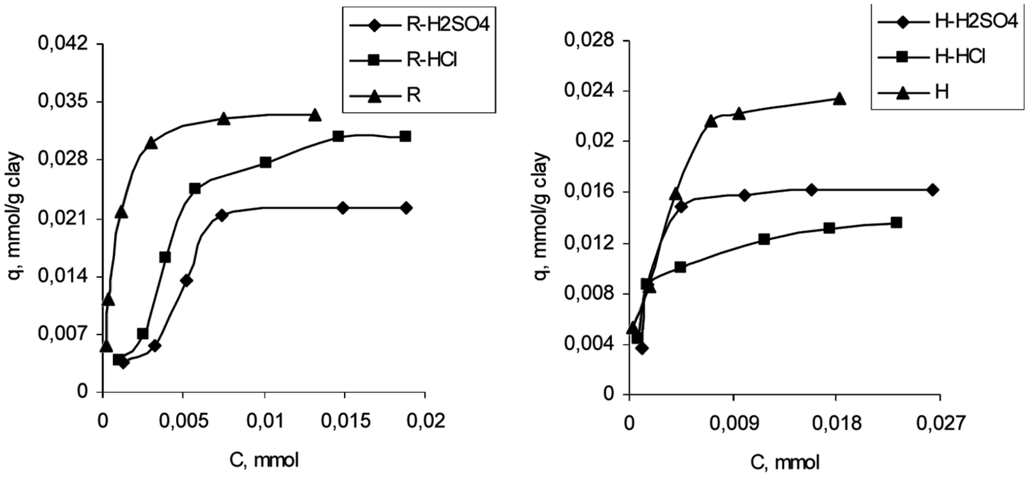
Effect of Initial Cr(VI) Concentration and Adsorption Isotherms

The concentration of Cr(VI) ions was varied from 1.0×10^{-4} to 1.0×10^{-3} M. Figure 8 illustrates the equilibrium adsorption of Cr(VI) on Hançılı and Reşadiye region clays. It shows that increases in initial Cr(VI) concentration increased the amount of Cr(VI) uptake per unit weight of Hançılı and Reşadiye region clays as was expected. This finding is in agreement with the results of Potgieter et al.



(a) (b)

FIGURE 7 Sorption graph of Cr(VI) ions on adsorbents as a function of temperature (a) Reşadiye region clay (b) Hançılı region clay.



(a) (b)

FIGURE 8 The effects of initial Cr(VI) concentration on removal Cr(VI) from aqueous solutions (a) Reşadiye region clay (b) Hançılı region clay (Adsorption conditions; initial concentration of chromium: 1.0×10^{-4}–1.0×10^{-3} mol/L, amount of clays: 0.1 g, temperature: $25 \pm 1°C$).

(2006)[18] and Erdem et al. (2004),[1] who investigated heavy metals' removal from aqueous solutions by using palygorskite clay and heat-activated bauxite.

The adsorption isotherms for Cr(VI) removal were studied using initial concentrations of Cr(VI) between 1.0×10^{-4} and 1.0×10^{-3} M at adsorbent mass of 0.1 g at $25 \pm 1°C$. The adsorption isotherm—that is, the plot of the equilibrium solid-phase concentration (q) versus the equilibrium liquid-phase concentration (C)—is often described by the two-parameter Langmuir and Freundlich equations. Langmuir and Freundlich isotherm models were applied to establish the relationship between the amount of Cr(VI) adsorbed by Hançılı and Reşadiye region clays and their equilibrium concentration in aqueous solution. The data obtained from the various plots are summarized in Table 1. Adsorption capacity decreased by our using acid-activated clays with HCl and H_2SO_4 acids. According to the data of the Langmuir adsorption isotherm, while the adsorption capacity of Hançılı clay has 0.0269 mmol/g clay, acid-activated clays adsorption capacities are 0.0144 and 0.0170 mmol/g clay. Similar findings were also observed in the Reşadiye clay. The adsorption pattern of the Cr(VI) on Hançılı and Reşadiye region clays well fit the Langmuir model because the correlation coefficient values were in the range of 0.96–0.99 (Table 1). The Langmuir model was more applicable than the Freundlich model since the correlation coefficient values evaluated from that the Langmuir model were higher than those determined from the Freundlich model. The Langmuir equation was originally developed to describe individual chemical adsorbents and is applicable to physical adsorption (monolayer) within a low concentration range.[38–41] The Freundlich equation is applicable to adsorption of a single-solute system within a fixed range of concentration. This model is generally suitable for

TABLE 1 Freundlich and Langmuir Adsorption Isotherm Parameters of Adsorbents

	Freundlich adsorption isotherm			Langmuir adsorption isotherm		
Clays	N	K_f	R^2	Q_m	a_L	R^2
H	2.2291	0.1806	0.9590	0.0269	422.1429	0.9813
H-HCl	3.4506	0.0438	0.8567	0.0144	587.9032	0.9983
H-H_2SO_4	4.6992	0.0392	0.7587	0.0170	1016.6380	0.9984
R	1.6795	0.9262	0.9654	0.0356	1261.2557	0.9992
R-HCl	1.1669	1.4508	0.9191	0.0276	255.8192	0.9554
R-H_2SO_4	1.3392	0.5473	0.8839	0.0422	186.4252	0.9690

Note. Q_m and K_f, adsorption capacity, mmol/g clay; a_L and n, constants; R^2, correlation coefficient.

TABLE 2 **Summary of Adsorption Capacity of Various Adsorbents**

	Adsorption capacity, mg g^{-1}		
Adsorbents	Cr(VI)	Cr(III)	References
Riverbed sand	6.34		42
Pumice		5.97×10^{-4}	43
Polyacrylonitrile/pumice composite		5.16×10^{-3}	43
Wollastonite	8.26×10^{-1}		44
Montmorillonite	15.3		45
Kaolinite		$74.37–127.55 \times 10^{5}$	46
Spent activated clay	0.743–1.422		47
Celtek clay		21.55	48
Turkish vermiculite	87.7		49
Limestone		1.61×10^{-2}	50
Zeolite		13.18	51
Surfactant-modified montmorillonite clay	7.6589×10^{-3}		34
Brazilian vermiculite		9.25×10^{-3}	14
Reşadiye clay	3.4297×10^{-4}		In this study
R-H_2SO_4	4.0655×10^{-4}		In this study
R-HCl	2.6589×10^{-4}		In this study
Hançılı clay	2.5915×10^{-4}		In this study
H-HCl	1.3873×10^{-4}		In this study
H- H_2SO_4	1.6378×10^{-4}		In this study

high- and middle-concentration environments and is not suitable for low-concentration environments because it does not meet the requirements of Henry's law.[41]

A comparison and an interesting review between the adsorption capacities of the Reşadiye and Hançılı clays and other adsorbents are presented in Table 2. When comparing our results with the results of others, it can be concluded that the Reşadiye and Hançılı clays adsorbed Cr(VI) as effectively as the other adsorbents.

CONCLUSIONS

The following conclusions can be drawn from this investigation:

1. The XRD and IR techniques are complementary methods of investigating clays and clay minerals. Our studies are in very good agreement with the previous work in the literature.
2. The increase in initial Cr(VI) concentration decreased the percentage adsorption and increased the amount of Cr(VI) uptake per unit weight of the sorbent.
3. The equilibrium data well followed the linear Langmuir model.
4. The decrease in *K* value with increasing temperature depicted that the adsorption of Cr(VI) on the clays was an exothermic process.
5. On the basis of all results, it can be concluded that Hançılı and Reşadiye region clays can effectively be used for the removal of Cr(VI) from wastewater by the adsorption method. These clays present a major advantage of giving low-cost recovery processes, making them suitable for use in water purification.

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