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Comparison of kinetics of Cr (III) ions removal from wastewater using raw and activated montmorillonite minerals

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Abstract

In this study, kinetics of the removal of Cr (III) from the waters by adsorption have been investigated using montmorillonite natural clay that was obtained from the vicinity of Narman, Erzurum in Turkey. Activation energy, thermodynamic values and adsorption kinetics were determined. In addition, the trials were repeated by subjecting to the same adsorbent activation process. The values found for these two adsorbents were compared. As a result of the experiments, the parameters affecting the adsorption kinetics were examined. It was determined that the adsorption process could be best depicted by pseudo second order reaction kinetics. Using pseudo second order reaction rate constants, $\Delta H° = -25.791$ kJ mol^{-1} and $\Delta S° = 106.19$ joule mol^{-1} were calculated for raw adsorbent. For the activated adsorbent, $\Delta H° = -18{,}806$ kJ mol^{-1} and $\Delta S° = 79.37$ joule mol^{-1} were calculated. That $\Delta G°$ increases as temperature increases indicates; adsorption is more spontaneous at high temperatures. Negative $\Delta H°$ values show that the reaction is exothermic. The positive values of $\Delta S°$ indicate increased randomness at the adsorbent/solution interface during the adsorption of chrome.

Keywords
activated adsorbent, adsorption, Chrome removal, heavy metal removal

Introduction

Wastewaters can be contaminated as physical, chemical and biological. Wastewaters of various industrial such as textile, paper, leather, paint and metal good industries contains large amounts of heavy metals and synthetic dyes. Heavy metals are mixed to the water source with industrial wastewater or acid rains. When considering natural diffusion of heavy metals, it seems to quite highly concentrations of heavy metals caused by human factors in the ecological system (Taştan et al., 2010). Both metallic chromium and chromium compounds have been used widely in industry. Thus, they cause significant pollution in the industrial wastewater. Chromium in the industrial wastewaters present as both +3 and +6. In the removal of chromium from wastewaters are used commonly process such as chemical precipitation, adsorption, ion exchange, recovering by evaporation, solvent extraction and reverse osmosis process. The adsorption process in the treatment of wastewater containing at low concentrations chromium draws attention as a viable method. Many experiments have been done in the literature using different adsorbents such as soil (Barlett and Kimble,1976; Jiant et al., 2008), ash (Griffin et al., 1977), activated carbon (Chen et al., 2007; Huang and Wu, 1975), silica titania gel (Koneko et al., 1978), bentonite (Majdan et al., 2005), activated clinoptilolite (Toprak and Girgin, 2000), clay (Krishna et al., 2001), zinc extraction wastes (Günaydın et al., 1999), activated bauxite (Erdem et al., 2004). Commercial activated carbon is an ideal adsorbent used in environmental engineering for chromium adsorption in wastewater treatment. However, because of the expensive material, studies are carried out to find a lower cost adsorbent.

Chromium that has an atomic weight of 51.9961 g mol^{-1} and atomic number of 24 is silvery metallic element at room temperature. Chrome is among the most important heavy metal. The reason for this is that chromium is widely used in developing countries due to its durable structure. Due to the toxic effects on living systems, the US EPA has determined maximum contaminant concentrations for chromium in wastewaters (Bueno et al. 2008). Chromium has been wanted to be present at a maximum concentration of 0.1 mg L^{-1} in air and a maximum of 1 mg L^{-1} in water. Chromium affects protein, carbohydrate and water metabolism by providing the body's insulin movement. Some of the uses of chromium include leather refinement, corrosion control, pigment production and nuclear weapon production.

In this study, the kinetics of chromium (III) removal from wastewater by the adsorption process using montmorillonite was investigated. Both raw montmorillonite and activated montmorillonite by acid treatment was used as adsorbents.

Materials and Methods

Materials

Obtained from the vicinity of Narman in Erzurum and used as adsorbent in this study, characteristics of montmorillonite mineral and chemical analysis is given in Table 1 (Bayram, 2012).

Table 1. *Micronized montmorillonite's minerals and chemical analysis.*

Contents of minerals	%	Chemical analysis	% (average)
Smectites	68-78	Na_2O	1.20
Kaolin	15-20	MgO	5.01
Clay	94	Al_2O_3	17.15
Quartz	4	SiO_2	51.60
Others	2	K_2O	1.61
		CaO	4.50
		TiO_2	0.52
		Fe_2O_3	5.91
		LOI	12.5

Methods

The raw montmorillonite used was washed with distilled water and dried at 105°C for 4 hours. To activate adsorbent, montmorillonite was first washed and dried. The dried adsorbent was saturated using concentrated phosphoric acid (85% by weight) in ratio of 1:1 adsorbent/acid. This adsorbent was kept in the incubator at 500°C for 1 hour and washed with hot distilled water up to pH 6. The shells were again dried at 105°C for 4 hours.

The experiments were carried Edmond Buhler KS-15 brand shaker incubator. Cr (III) analysis was performed with the Shimadzu model AA6800 atomic absorption spectrometry. In order to determine the reaction degree and reaction rate constant in the studies, the pseudo first-order and pseudo-second-order reaction kinetics were used by Eq. [1] and [2], respectively (Agarwal et al. 2016; Regazzoni 2020; Ezzati 2020).

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1.t \qquad [1]$$

$$\frac{t}{q_t} = \frac{1}{q_e^2.k_2} + \frac{t}{q_e} \qquad [2]$$

where, q_e is the amount of substance adsorbed per unit mass of adsorbent at equilibrium concentration (mg g^{-1}, $(C_0\text{-}C_e)/m$) q_t is th aount of adsorbed substance per unit mass of adsorbent (mg g^{-1}, $(C_0\text{-}C_t)/m$), C_o is the initial Cr (III) concentration (mg L^{-1}), C_e is the equilibrium Cr (III) concentration, C_t is the Cr (III) concentration at time (mg L^{-1}) and m is adsorbent concentration (gr L^{-1}).

To find the Gibbs free energy, enthalpy and entropy in the adsorption process are used Eq. [3] and [4] (Lima et al. 2020).

$$\Delta G° = -R.T.\ln K_c\,,\ K_c = \frac{C_a}{C_e} \qquad [3]$$

$$\ln K_c = \frac{\Delta S°}{R} + \frac{\Delta H°}{R.T} \qquad [4]$$

where, ΔG° is the Gibbs free energy, R is the ideal gas constant (0.082 L atm mol^{-1} K^{-1}), K_c is the equilibrium constant, C_a is the amount of substance that can be retained in the adsorbent (mg L^{-1}), C_e is equilibrium concentration of adsorbate (mg L^{-1}), ΔS° is enthalpy and ΔH° is entropy.

Classical adsorption models have been used to describe the equilibrium between amount of adsorbed metal ions per unit weight of biosorbent (q_e) and metal ions in solution (C_e) at a constant temperature. These models (Freundlich, Langmuir, BET and Temkin) are given in Eq. [5], [6], [7] and [8] respectively (Freundlich 1907; Langmuir 1918; Branauer et al. 1938; Temkin and Pyzhev 1940).

$$\log q_e = \log K_F + \frac{1}{n}.\log C_e \qquad [5]$$

$$\frac{1}{q_e} = \frac{1}{a.K_L}.\frac{1}{C_e} + \frac{1}{a} \qquad [6]$$

$$\frac{C_e}{(C_s - C_e).q_e} = \frac{1}{K_B.q_s} + \frac{K_B - 1}{K_B.q_s}.\frac{C_e}{C_s} \qquad [7]$$

$$q_e = \frac{R.T}{b_T}.\ln K_t + \frac{R.T}{b_t}.\ln C_e;\ B = \frac{R.T}{b_T} \qquad [8]$$

Where:

K_F = the Freundlich adsorption constant (adsorption capacity) (mg g^{-1})

N = the Freundlich adsorption constant adsorption intensity (L mg^{-1})

A = the maximum amount of the adsorbate adsorbed per unit weight of adsorbent (mg g^{-1})

K_L = constant related to the affinity of adsorbent attachment areas (L mg^{-1}),

C_s = saturation concentration of the solute on the adsorbent (mg L^{-1})

K_B = BET constant expressing the energy of interaction with the surface (L mg^{-1})

q_s = the amount of adsorbate required to form a single layer on the adsorbent's surface (mg g^{-1}),

b_T = the Temkin constant related to the heat of adsorption (J mol^{-1}),

K_T = the Temkin isotherm equilibrium binding constant (L g^{-1}),

R = the gas constant (8.3145 J mol^{-1} $°K^{-1}$)

T = the temperature (°K).

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Results and Discussion

In a study made by İrdemez et al., Cr^{3+} removal from wastewater using raw and activated montmorillonite was studied and optimum values were found for adsorption. In the study, the most suitable pH = 5, the most suitable temperature 30 °C and the optimum stirring speed were found to be 300 rpm [24]. In this study, the kinetic behavior of adsorption, adsorption isotherms, and thermodynamic values were studied by using these optimum values.

Investigation of adsorption kinetics

To investigate the adsorption kinetics during the removal of chromium using montmorillonite mineral was used 5 g L^{-1} of adsorbent concentration, 100 mg L^{-1} of Cr (III) concentration and experiments were performed at 300 rpm stirring speed and pH 5. The study was conducted at 20° temperature. At this temperature, pseudo first-order and pseudo second order kinetic constants were found for both raw adsorbent and activated adsorbent. The data obtained are shown schematically in Fig. 1. Reaction rate constants calculated from these results are given in Table 2.

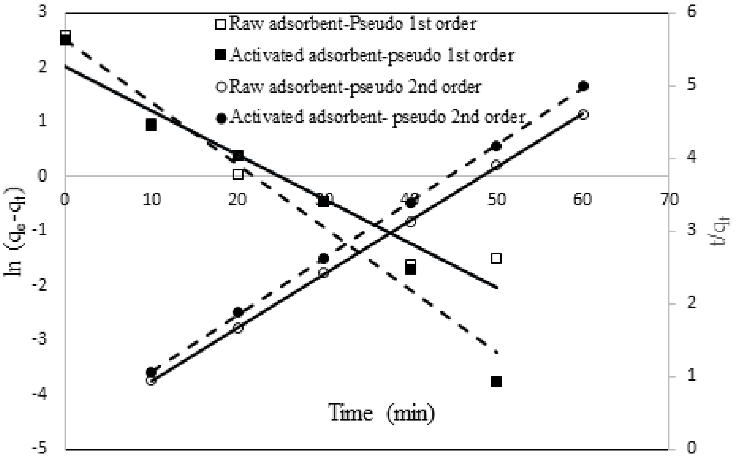

Figure 1. *Adsorption kinetics of Cr^{3+} removal using raw and activated adsorbent.*

$y = -0{,}0815x + 2{,}0303$	$R^2 = 0{,}9255$	Raw adsorbent- pseudo 1st order
$y = -0{,}1146x + 2{,}5161$	$R^2 = 0{,}9638$	Activated adsorbent-pseudo 1st order
$y = 0{,}0733x + 0{,}2118$	$R^2 = 0{,}9998$	Raw adsorbent-pseudo 2nd order
$y = 0{,}0776x + 0{,}3005$	$R^2 = 0{,}9996$	Activated adsorbent-pseudo 2nd order

Table 2. *Kinetic constants calculated for Cr (III) removal using montmorillonite at 20°C*

	Raw adsorbent			Activated adsorbent		
Parameters		Pseudo first order	Pseudo second order		Pseudo first order	Pseudo second order
k		0.0815 min^{-1}	0.0253 gr mg^{-1} min^{-1}		0.1146 min^{-1}	0.0201 gr mg^{-1} min^{-1}
q_e (mg g^{-1})	13.04	7.61	13.64	12.03	12.38	12.87

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The q_e values for raw adsorbent and activated adsorbent based on the experimental results respectively have been calculated 13.04 and 12.03 mg g^{-1}. Since these values are closer to the values in the Table 2, the reaction rate has been considered to progress with respect to pseudo second order.

When Table 2 is examined, it is seen that the adsorption rate of raw montmorillonite is a little faster than activated montmorillonite. The same is true for pseudo-1st order kinetics. These results show that the activation process does not increase the rate in inorganic adsorbents such as montmorillonite, but rather decreases it. It is understood from the q_e values that the removal efficiency is lower as well as the speed.

Thermodynamic constants

To test for the effects of temperature on removal of chromium, 5 g L^{-1} of adsorbent concentration and 100 mg L^{-1} of chromium concentration was used and experiments were performed. The data obtained for 20, 30, 40 and 50° are also shown schematically in Figure 2.

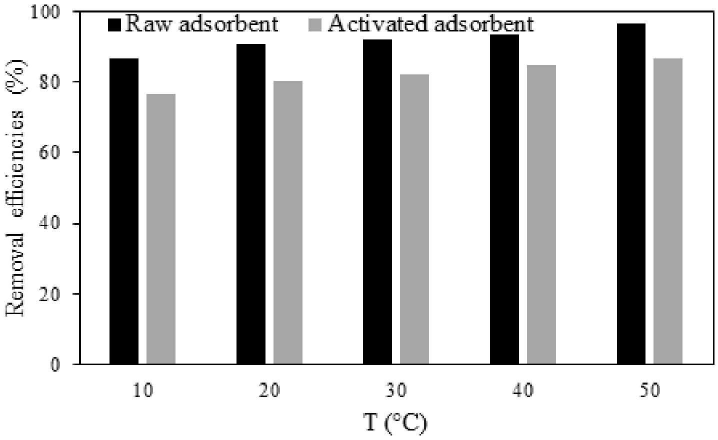


Figure 2. *The effects of temperature on the removal of Cr^{3+} for raw adsorbent and activated adsorbent.*

When Figure 2 is examined, it can be said that the equilibrium concentration increases a little with the increase of temperature for both pure and activated adsorbent. This state can be seen from the q_e values in Table 3. Again, it is seen that the efficiency is lower in the activated adsorbent. Pseudo-second-order rate graphs drawn with the data obtained as a result of temperature tests are given in Figure 3 and 4. In addition, using data given in Fig. 3 and Fig. 4, pseudo second-order kinetic reaction rate constants were calculated. These values are shown in Table 3.

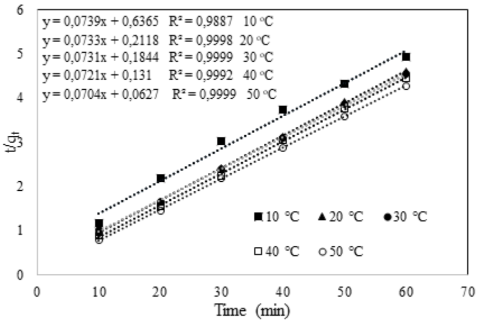


Figure 3. *Pseudo-second-order rate graphs plotted for raw montmorillonite at different temperatures.*

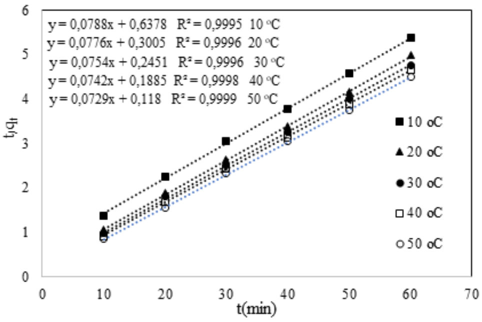


Figure 4. *Pseudo-second-order rate graphs plotted for activated montmorillonite at different temperatures.*

Table 3. *Cr (III) removal using montmorillonite pseudo second-order kinetic constants.*

	Raw adsorbent			Activated adsorbent		
Temperature (K)	Pseudo second-order (g mg^{-1} min^{-1})	$q_{e, reel}$ (mg g^{-1})	$q_{e, calculated}$ (mg g^{-1})	Pseudo s econd-order (g mg^{-1} min^{-1})	$q_{e, reel}$ (mg g^{-1})	$q_{e, calculated}$ (mg g^{-1})
283	0,00858	12.57	13,53	0,0913	11.49	12.61
293	0,0253	13.04	13,64	0,0201	11.89	12.56
303	0,0289	13.17	13,68	0,0232	12.14	12.56
313	0,0396	13.48	13,87	0,0292	12.59	12.95
323	0,0791	14.02	14,2	0,0451	12.74	12.90

When Table 3 is examined, it is seen that the increase in temperature causes the q_e values to increase. This means that as the temperature increases, the amount of Cr^{3+} captured per unit adsorbent increases. also, the higher the temperature, the higher the reaction rate.

Equilibrium constants was calculated using data obtained from these graphics, and They are drawn (1/T) versus ln (K_c) graphics as seen in Fig 6.

The graphs drawn to find the activation energies and thermodynamics constants using the values given in Table 3 is given in Fig.5.

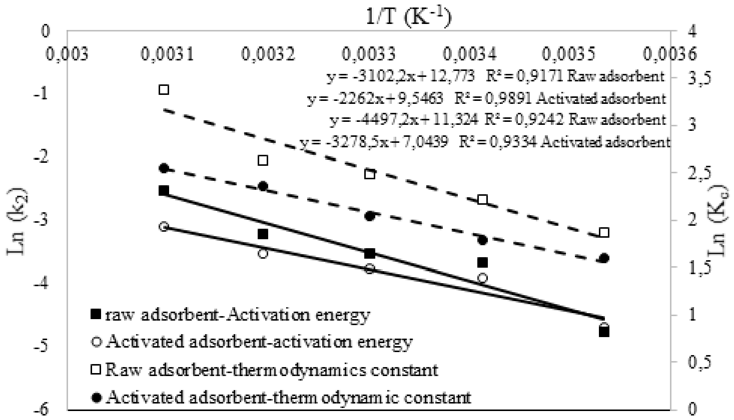


Figure 5. *The graphics of activation energies and thermodynamics constants for Cr (III) adsorption using raw adsorbent and activated adsorbent.*

Using data obtained from Figure 5, the activation energies have been found respectively as 37.389 kJ mol^{-1} and 27.257 kJ mol^{-1}, for raw adsorbent and activated adsorbent. If the activation energy is between 5 kJ mol^{-1} and 40 kJ mol^{-1}, adsorption is defined as physical adsorption (Wu 2007). These values indicate that the adsorption process takes place physically. These values indicate that the adsorption process takes place physically.

Enthalpy, entropy and Gibbs free energy values are calculated from the data obtained in Fig 4 and these are given in Table 4. When Table 4 is examined, It is seen that the Gibbs free energy values are negative and the maximum value is -0.606 kJ mol^{-1} and the smallest value is -8.999 kJ mol^{-1}. If the Gibbs free energy is between (-20)-(0) kJ mol^{-1}, there is physical adsorption, if between (-80)-(-400) kJ mol^{-1}, there is chemical adsorption (Jaycock and Parfitt 1981). The lower Gibbs free energy for the activated adsorbent means the greater the equilibrium constant K_c. In this case, it means that the equilibrium concentration decreases and the removal efficiency increases. Negative ΔH° values show that the reaction is exothermic and the negative ΔG° values show that adsorption progress spontaneously. Also, the positive ΔS° values show high rates of coincidental.

Table 4. *Equilibrium constant, enthalpy, entropy and Gibbs free energy changes for Cr (III) removal using raw adsorbent and activated adsorbent.*

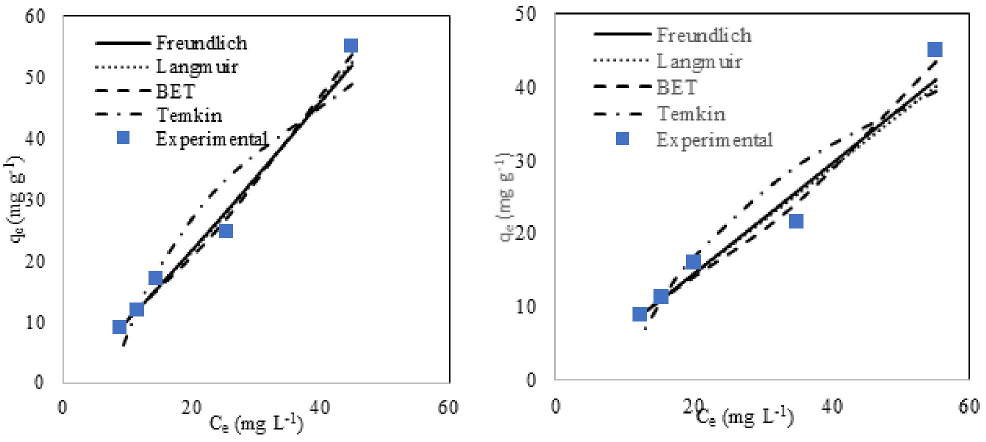
	Temperature (K)	K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (joule mol^{-1} K^{-1})
Raw adsorbent	283	6,472	-4.394	-25.791	106.19
	293	9,18	-5.401		
	303	11,93	-6.244		
	313	13,82	-6.834		
	323	29,13	-9.055		
Activated Adsorbent	283	4,91	-3.745	-18.806	79.37
	293	5,97	-4.354		
	303	7,67	-5.133		
	313	10,63	-6.150		
	323	12,72	-6.829		

Gibbs free energy indicates the degree of spontaneity of an adsorption process and a higher negative value means better adsorption with higher energy (Jia et al. 2019). In this case, it appears that crude montmorillonite is a more suitable adsorbent.

Adsorption isotherm

Isotherm studies to remove Cr (III) using montmorillonite mineral have been performed at 100 mg L^{-1} of Cr (III) concentration, 300 rpm of mixing speed, 20°C of temperature and pH 5. Langmuir, Freundlich, BET and Temkin isotherm graphics are shown schematically in Fig. 7. The isotherm constants calculated from this graph are given in Table 5.

When Figure 7 is examined, it can be said that the adsorption is more suitable for the Langmuir isotherm than the others. This situation shows that adsorption proceeds in a monolayer and the adsorption rate is directly proportional to the adsorbate concentration and active sites on the surface (Langmuir 1918).



(a) (b)

Figure 7. *Adsorption isotherms of* Cr^{3+} *removal using (a) raw montmorillonite and (b) activated montmorillonite.*

When the isotherm coefficients are compared, it is seen that the raw adsorbent coefficients are higher than the activated adsorbent. High "K_L" values indicates that the raw adsorbent adsorp more pollutants per unit mass, and high "a" values indicates that the binding sites of the raw adsorbent are more affinity to the contaminant.

Table 5. *Isotherm constants for chromium adsorption using both raw montmorillonite and activated montmorillonite*

	Raw adsorbent			Activated adsorbent		
Freundlich isotherm	n	K_F	R^2	n	K_F	R^2
	0.930	0.868	0.9857	0.978	0.682	0.9701
Langmuir isotherm	a	K_L	R^2	a	K_L	R^2
	-322	$-3.11*10^{-3}$	0.9808	-5000	$-1.44*10^{-4}$	0.9873
BET isotherm	K_B	q_s	R^2	K_B	q_s	R^2
	6.205	22.076	0.9219	39.79	10.47	0.9596
Temkin isotherm	b_T	K_T	R^2	b_T	K_T	R^2
	109.69	0.1345	0.9065	109.20	0.106	0.8836

Conclusions

In this study, Cr (III) removal from wastewaters prepared synthetically by adsorption using the montmorillonite had been examined the adsorption kinetics. The Montmorillonite natural clay used in this study is extracted from Erzurum, a city in Turkey. In studies, montmorillant natural clay was used both in its raw form and applying the activation process. Adsorption kinetics, thermodynamic constants and isotherms were determined from results of experimental studies. Data obtained in this study have been analyzed according to the pseudo-first and pseudo-second order kinetic model and kinetic constants have been calculated. The adsorption isotherms have been determined from the obtained data.

Because the optimum pH is 5 and the optimum stirring speed is 300 rpm in the studies previously, experiments have been performed under such conditions(İrdemez et al. 2017). Due to precipitation of chromium hydroxide above the pH 6, It had not been studied the high pH.

The data obtained in studies had been applied to pseudo first and pseudo second order reaction kinetics and reaction degree has been determined. A result of these studies, the reaction was concluded that in the accordance pseudo second order reaction kinetics. Pseudo second order reaction rate constant for raw adsorbent have been calculated 0.021 g mg^{-1} min^{-1} at 20°. Pseudo second order reaction rate constant for activated adsorbent have been also found as 0.01 gr mg^{-1} min^{-1} at 20°. These results show that the activation process is not suitable for the montmorillant mineral. The same results have been reached in other experiments.

In the trials to the effects of temperature, adsorption rates and removal efficiencies have increased increasing temperature. In studies examining the effect of temperature, the reaction rate constants, equilibrium constants and the activation energies were calculated. For raw adsorbent and activated adsorbent, $\Delta H°$ values have been found as -25.791 kJ mol^{-1}, -18.806 kJ mol^{-1} and $\Delta S°$ values have been found as 106.19 joule mol^{-1} K^{-1}, 79.37 joule mol^{-1} K^{-1}, respectively. The negative values of $\Delta G°$ at tested temperatures reveal that the adsorption is spontaneous process. The increase of $\Delta G°$ with temperature indicates that adsorption is more spontaneous at high temperatures. Negative **$\Delta H°$** values show that the reaction is exothermic. The positive values of $\Delta S°$ indicate increased randomness at the adsorbent/solution interface during the adsorption of chrome.

The data obtained on experiments have been applied to Freundlich, Langmuir, BET and Temkin isotherms and kinetic constants were determined for these isotherms. From the results obtained, it can be said that the Langmuir isotherm is more valid for both types of adsorbents. If the two adsorbents are compared, it is understood from the isotherm constants that the

adsorption capacity of the raw adsorbent is higher.
In this study, found abundantly in nature and low cost-effective montmorillonite natural clay has showed could be used as adsorbent for removal of chromium from the waters.

Conflicts of interest

The authors declare no conflicts of interest

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