

Uptake of trivalent chromium ions from aqueous solutions using kaolinite

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Abstract

The sorption of Cr(III) from aqueous solutions on kaolinite has been studied by a batch technique. We have investigated how solution pH, ionic strength and temperature affect this process. The adsorbed amount of chromium ions on kaolinite has increased with increasing pH and temperature when it has decreased with increasing ionic strength. The sorption of Cr(III) on kaolinite is endothermic process in nature. Sorption data have been interpreted in terms of Freundlich and Langmuir equations. The adsorption isotherm was measured experimentally at different conditions, and the experimental data were correlated reasonably well by the adsorption isotherm of the Langmuir, and the isotherm parameters (q_m and K) have been calculated as well. The enthalpy change for chromium adsorption has been estimated as 7.0 kJ mol^{-1} . The order of enthalpy of adsorption corresponds to a physical reaction.

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1. Introduction

Problems associated with the removal of heavy metals in effluent waters from several different industries have become controversial issues in the world. Especially, chromium is one of the undesirable heavy metals which affects human physiology, accumulates in the food chain, and causes several ailments [1]. It is an element which can exist in several oxidation states, the most common are the trivalent and hexavalent forms, with the latter is the more toxic. Chromium(VI) ion in natural waters has attracted much attention since it is known to be carcinogenic (even at low concentrations, e.g. ≤ 50 ppb), mutagenic and teratogenic. Chromium(VI) compounds are introduced to the environment through the wastes of a variety of industries like chrome plating, electronic, metallurgical, timber, and leather tanning [2]. Due to the toxicity and commercial value of heavy metals, it has become increasingly urgent to develop new technologies for its reuse. Numerous methods exist for removing heavy metals from aqueous solutions. The conventional physicochemical methods used for this purpose, such as chemical precipitation, electrowinning, membrane separations,

evaporation or resin ionic exchange, can be very expensive, and sometimes not very effective. However, this type of technology has a high energy and chemical requirement and removal efficiencies are not always good [3]. Adsorption is a process which has been examined as an alternative technology and activated carbon is usually considered to be the adsorbent against which others are assessed. Aggarwal et al. studied the adsorption of chromium by activated carbon from aqueous solution [4]. However the costs of the activated carbon can be high in recent years. There have been many studies into the acceptability and applicability of low-cost adsorbents [5]. There are a numbers of study related to the adsorption of metal and chromium ions in literature. Lie and Xue investigated the determination of Cr(III) and Cr(VI) species in natural waters by catalytic cathodic stripping voltammetry [6]; Weerasooriya and Tobschall the adsorption of chromate onto goethite as a function of pH, electrolyte and adsorbate loading [7]; Bayat the removal of Cr(VI) and Cd(II) from an aqueous solution using two different Turkish fly ashes [8]; Alkan and Doğan the adsorption of copper onto perlite surfaces from aqueous solutions [9]; Daneshvar et al. chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake [10]; Chojnacka et al. biosorption of Cr^{3+} , Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina* sp. [11]; Adebowale et al. the effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay [12].

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Table 1
Chemical composition of kaolinite

Constituent	%
SiO ₂	53.00
Al ₂ O ₃	26.71
Na ₂ O	0.62
K ₂ O	1.39
CaO	0.57
Fe ₂ O ₃	0.37
MgO	0.28
LoI	17.20

LoI, loss of ignition.

Kaolinite is a 1:1 alumina silicate comprising a tetrahedral silica sheet bonded to an octahedral alumina sheet through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheets. Kaolinite is found as a common constituent of soils and sediments. Successive 1:1 layers are held together by hydrogen bonding of adjacent silica and alumina layers [13–16]. When different types of pollutants in domestic sewage, industrial effluents, sludge and other solid wastes are dumped on the earth surface, the soil particles including clay minerals can interact with the pollutants. The clay minerals in soil may therefore play a role in scavenging pollutants from the environment. Kaolinite has a low CEC of the order of 3–15 mequiv./100 g and therefore it is not expected to be an ion-exchanger of high order. The small number of exchange sites is located on the surface of kaolinite and it has no interlayer exchange sites. Nevertheless, the small CEC and the adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water [17,18].

Therefore, the aim of this study was to determine chromium adsorption behavior on kaolinite over a range of physico-chemical conditions that are important to identify various natural environmental systems. Adsorption isotherms have been analysed in terms of Freundlich and Langmuir equations. Enthalpy of adsorption has also been calculated and interpreted.

2. Materials and methods

2.1. Materials

The kaolinite sample was obtained from Güzelyurt (Aksaray, Turkey). All chemicals used were of analytical reagent grade and were used without further purification. The chemical constituent of kaolinite analysed by XRF are given in Table 1 [19].

2.2. Instrumentation

The pH of the solution was measured using Orion 920A pH meter. The shaking was carried out in an orbital shaker incubator. The centrifugation was done with a Nuve Centrifuge machine at 4500 rpm. Chromium amount was spectrophotometrically determined using Carry 1E UV–vis spectrophotometer [20].

2.3. Method

The sorption of Cr(III) on kaolinite was studied by a batch technique. Stock and test solutions of chromium were prepared from Cr(NO₃)₃·9H₂O. Ultrapure water was used in the all experiments. All the solutions were stored in polyethylene bottles. The bottles were cleaned thoroughly with water, then soaked in 0.01 M nitric acid solution. Before use, the bottles were rinsed with ultrapure water. The experiments were conducted using a orbital shaker incubator at 303 K under natural pH conditions for a known period of time. Adsorption experiments were carried out in polyethylene flasks of 100 mL using kaolinite 0.5 g and chromium ions in a concentration range of 1.92×10^{-5} to 76.90×10^{-5} mol L⁻¹. The equilibration time was found to be 16 h but for practical reasons the adsorption experiments were run for 24 h. The flasks containing the weighed amounts of kaolinite and chromium solution were kept separately in the incubator before mixing for a sufficient period of time to attain the desired experimental temperature. pH of solutions was adjusted by using 0.1N HCl and 0.1N NaOH and without adding any buffer to control the pH constantly. Centrifugation was used to remove kaolinite from the aqueous medium. Chromium concentration was detected by the diphenylcarbazide colorimetric method at 542 nm wavelength [20]. It was investigated the effects of the following parameters to the adsorption capacity of kaolinite in the experiments.

2.3.1. Effect of pH

The effect of pH to the adsorption capacity of kaolinite was investigated in the pH ranges of 4.5–6.0. The pH of solution was adjusted with NaOH and HCl solutions using a Orion 920A pH meter.

2.3.2. Effect of ionic strength

Ionic strength of chromium solutions was adjusted using NaCl salt in the concentration range of 0–0.1 mol L⁻¹.

2.3.3. Effect of temperature

The effect of temperature to the adsorption capacity of kaolinite was investigated in the temperature ranges of 303–323 K. Temperature was kept constant using a orbital shaker incubator.

3. Results and discussion

3.1. Chromium adsorption

The adsorption trends of chromium on kaolinite in aqueous solutions were investigated as a function of pH, ionic strength and temperature.

3.1.1. Effect of pH

As the surface concentration of adsorbate increases, the changes in the surface charge may become important. The adsorption extent is affected by pH as well as the affinity of the adsorbate for the surface [5]. The pH or acid–base surface values played an important role in metal ion adsorption equilibrium. A change in pH of the solution, as a result of the change in

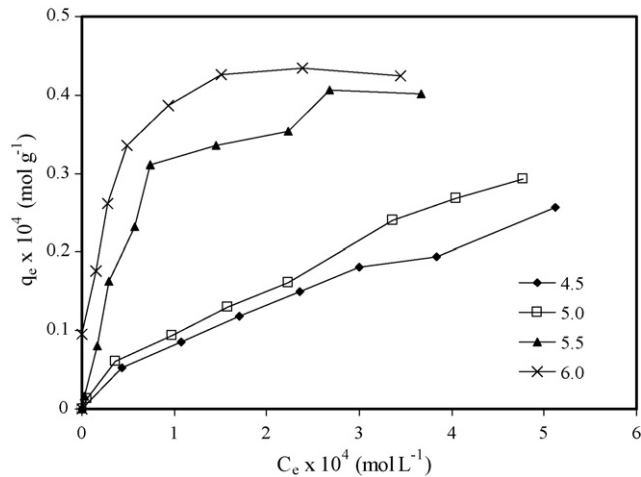
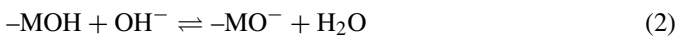


Fig. 1. Effect of pH for adsorption of chromium on kaolinite at $T=303$ K and ionic strength null.

amount of surface groups will change the extent of the positive charge on the chromic ion and kaolinite [4]. Fig. 1 represents the chromium sorption by kaolinite at different initial pH values. The pH effect on the adsorption are clearly seen. As the plot shows, in the range studied higher pH values resulted in higher chromium sorption.

Alkan et al. [19] found that the kaolinite surface in water had a net negative surface charge at natural pH and the iso-electrical point (IEP) of kaolinite was at about pH 2.35. The electrical charge at the oxide surface/aqueous phase to protonation/deprotonation of the surface hydroxyl can be ascribed as [21]:

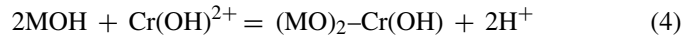


and at IEP

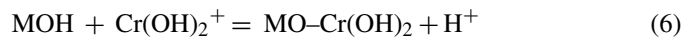


The fact that kaolinite has an IEP shows the reaction responsible for the surface charge of the solid is mainly the reaction in Eq. (1) below IEP and in Eq. (2) above IEP, respectively. Increase of solution pH hydrolyzes Cr^{3+} to $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_2^+$ [22]. The co-existence of these chromic species with decreasing charge is resulted in a decrease in the amount of protons released even when the uptake increases. The adsorption of Cr^{3+} on kaolinite at lower pH (2–3) is due to strong H^+ ion competition for the available exchange sites or a surface adsorption phenomenon in which the adsorbent surface does not favour the adsorption of positively charged ions at lower pH. The surface will be positively charged at lower pH and consequently will not favour the adsorption of positively charged ions. These changes in the charge on the kaolinite surface with increasing pH (4–6) and in the charge on the Cr(III) ions in solution favour the adsorption of Cr(III) ions because the electrostatic attractive interactions between the kaolinite surface and the chromium ions present in the solution are enhanced [22]. Hydrous species of Cr(III) in aqueous solutions calculated by a chemical equi-

librium programme, ChemEQL, has been given by Lie and Xue [6]. According to their results, the dominant species of Cr(III) at pHs about 5.0–6.0 is $\text{Cr}(\text{OH})_2^+$, while $\text{Cr}(\text{OH})_2^+$ at pHs about 6.5. The adsorption of Cr(III) can be expressed according to the following equations:



$$K_1 = \frac{[(\text{MO})_2\text{-Cr}(\text{OH})][\text{H}^+]^2}{[\text{MOH}]^2[\text{Cr}(\text{OH})_2^+]} \quad (5)$$



$$K_2 = \frac{[\text{MO-Cr}(\text{OH})_2][\text{H}^+]}{[\text{MOH}][\text{Cr}(\text{OH})_2^+]} \quad (7)$$

If $[\text{Cr}^{3+}]_{\text{ads}}$ represents the adsorbed amount of Cr(III) in terms of any one of the reactions (4) and (6), the equations below can be written:

$$\log \frac{[\text{Cr}^{3+}]_{\text{ads}}}{[\text{Cr}^{3+}]_e} = [\log K_1 + 2 \log(\text{MOH})] + 2\text{pH} \quad (8)$$

or

$$\log \frac{[\text{Cr}^{3+}]_{\text{ads}}}{[\text{Cr}^{3+}]_e} = [\log K_2 + \log(\text{MOH})] + \text{pH} \quad (9)$$

where $[\text{Cr}^{3+}]_e$ is the equilibrium concentration of Cr^{3+} in the solution and $[\text{MOH}]$ is the concentration of active site of the surface. A plot of the left-hand side of Eqs. (8) and (9) versus equilibrium pH of the solution should yield a linear relationship and the slope of which gives the stoichiometric coefficient of the reactions (4) and (6) [23]. The plots of $\log([\text{Cr}^{3+}]_{\text{ads}}/[\text{Cr}^{3+}]_e)$ versus equilibrium pH obtained adsorption experiments, which is called as a Kurbatov plot, are shown in Fig. 2. As can be seen from Fig. 2, the points up to about pH 6.0 has a slope of 1.9, whereas the slope is 0.9 after pH 6.0. This result means that the stoichiometry has changed from Eqs. (6)–(8) as equilibrium pH of the solution increases from 5.4 to 6.8.

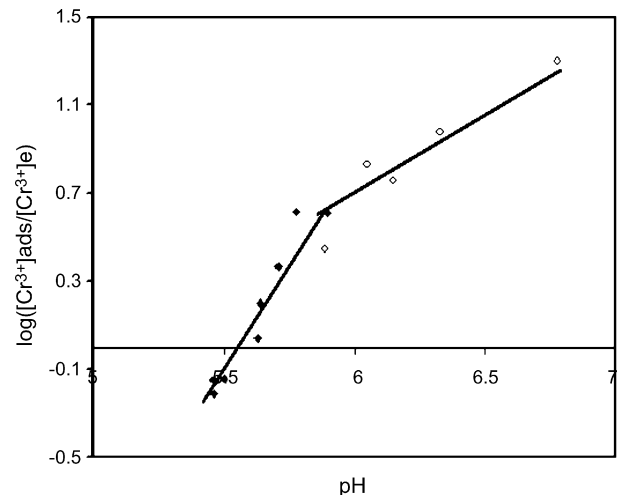


Fig. 2. Kurbatov plot.

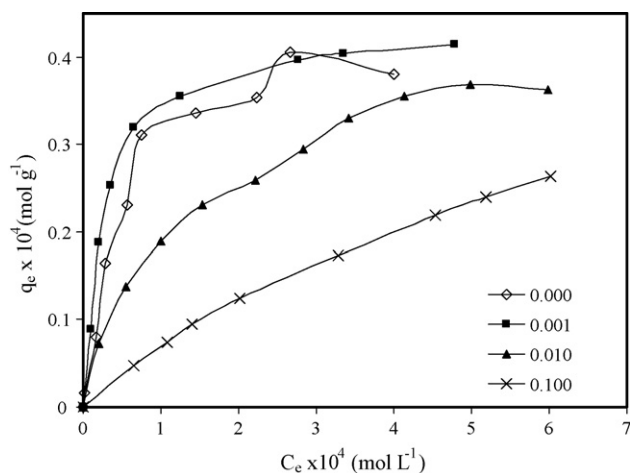


Fig. 3. Effect of ionic strength for adsorption of chromium on kaolinite at $T = 303$ K and pH 5.5.

3.1.2. Effect of ionic strength

Increasing the concentration of the salt has the effect of reducing the activity coefficient of ions in solution and so can cause a large change in the activity of the various ions. This change in solution activity can result in a shift in the partition of ions between the surface and the solution phase [24,25]. Fig. 3 shows the influence of ionic strength on Cr(III) uptake from aqueous solutions. As Fig. 3 indicates, there is an opposite effect of increasing ionic strength to the sorption of chromium onto kaolinite. The ionic strength was changed by four orders of magnitude from 0.1 to 0 M. We have found that increased concentration of electrolyte depresses the sorption of Cr(III). The ionic strength enters into electrical double layer calculations and affects the coulombic interactions between the charged surface and the sorbing ions through the number of counter ions in the diffuse double layer and the extent of co-ion exclusion. This in turn affects the possible charge development on the surface. When a positive ion sorbs into a region of negative electrostatic potential, then it will be subject to an attractive coulombic force. This attractive force will be reduced if the negative electrostatic potential is decreased by increasing the ionic strength. Thus at constant solution activity of the sorbing cation, the sorption will be lower at high ionic strength provided that the ions making up the salt concentration are truly indifferent [24,25]. Moreover, the counter-ion shielding effect at high ionic strength decreases both the repulsion from the surface and the free energy of the cation in solution. The double-layer theory predicts that increasing ionic strength will decrease the diffuse layer potential and reduce the attraction between the surface and the specifically adsorbing ion. The double layer model accounts for the effect of ionic strength on ion adsorption through the explicit dependence of Gouy–Chapman–Stern–Grahame (GCSG) diffuse layer charge on the ionic strength, which for a 1:1 electrolyte is given by [26]:

$$\frac{1}{\kappa} = \frac{3}{ZC^{1/2}} \quad (10)$$

where $1/\kappa$ is the thickness of the diffuse layer (\AA), Z denotes the valency and C represents the ion concentration (mol L^{-1})

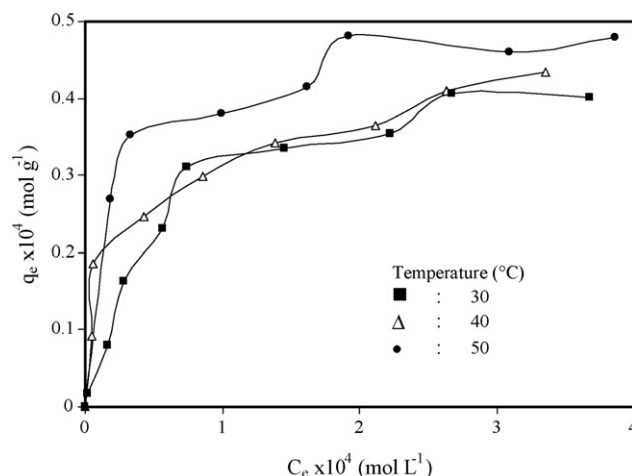


Fig. 4. Effect of temperature for adsorption of chromium on kaolinite at pH 5.5 and ionic strength 0.001 mol L^{-1} .

[27]. This formula indicates that for the same valency the concentration of salt contributes significantly to the thickness of the electrical double layer (EDL) and consequently causes a reduction in the adsorption capacity. Thus the variation of the ionic strength of the medium results in a change in the thickness of the double layer.

3.1.3. Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable information about the enthalpy change during adsorption [9]. The adsorption of chromium on kaolinite was studied as a function of temperature in the range 303–323 K. The results are presented in Fig. 4. There is an increase in the amount of adsorption with a rise in temperature which may be due to higher adsorption caused by an increase in the thermal energy of the adsorbate. This indicates that the adsorption process is endothermic in nature when temperature was increased from 303 to 323 K (Fig. 4). The effect of temperature is fairly common and increasing temperature results in an increase in the rate of approach to equilibrium. In addition, the temperature coefficient for the reverse reaction is lower than for the forward reaction and consequently the equilibrium capacity increases with increased temperature.

3.2. Isotherm analyses

The adsorption isotherms of the systems as presented by the respective parameters were examined with regard to their representative shapes. The equilibrium based adsorption models have been used to describe adsorption on surfaces. In this study, the adsorption results were analysed in terms of Freundlich and Langmuir isotherms.

3.2.1. Langmuir isotherm

The Langmuir model assumes that each site accepts only one molecule, that sorbed molecules are organised as a monolayer, that all sites are energetically equivalent and that there is no interaction between sorbed molecules [28]. The Langmuir equation

is given by Eq. (11):

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e \quad (11)$$

where q_e is the equilibrium copper concentration on adsorbent (mol g^{-1}), q_m the maximum amount of adsorption (mol g^{-1}), K the affinity constant (L mol^{-1}) and C_e is the solution concentration at equilibrium (mol L^{-1}). From a plot of C_e/q_e versus C_e , q_m and K can be determined from its slope and intercept.

3.2.2. Freundlich isotherm

The adsorption effects of chromium ions on kaolinite surface were interpreted with the Freundlich adsorption model, which depends on a heterogeneous surface with a continuous distribution of adsorption sites. The Freundlich adsorption model can be expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (12)$$

where K_F and n are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively; q_e is the amount of chromium adsorbed per unit weight of adsorbent; C_e the equilibrium concentration (mol L^{-1}) [2]. By the logarithmic linearization of Eq. (12), the two parameters of the Freundlich equation, K_F and $1/n$ could be estimated from the intercept and the slope of the straight line, respectively:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (13)$$

Adsorption isotherms were obtained in terms of Eqs. (11) and (13) by using experimental adsorption results in these equations. Table 2 has shown the results of Langmuir and Freundlich isotherm analyses calculated for adsorption chromium on kaolinite from aqueous solutions at different pH, ionic strength and temperatures. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 2, the Langmuir equation represents the adsorption process very well; the R^2 values were all higher than 0.99, indicating a very good mathematical fit. Fig. 5a–c have shown the plots of Langmuir isotherm for the date of Figs. 1, 3 and 4. The Freundlich correlation co-efficients are considerably lower than the corresponding Langmuir co-efficients. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on kaolinite surface; since the Langmuir equation assumes that the surface is homogenous [28].

A comparison between the adsorption capacities of kaolinite and other adsorbents under similar conditions is presented in Table 3. When comparing our results for kaolinite with the results of others, it can be concluded that the kaolinite adsorbed metal ions as effectively as the other adsorbents listed. A lower kaolinite production cost compared to other adsorbents such as activated carbon is another advantage of kaolinite for use as an adsorbent.

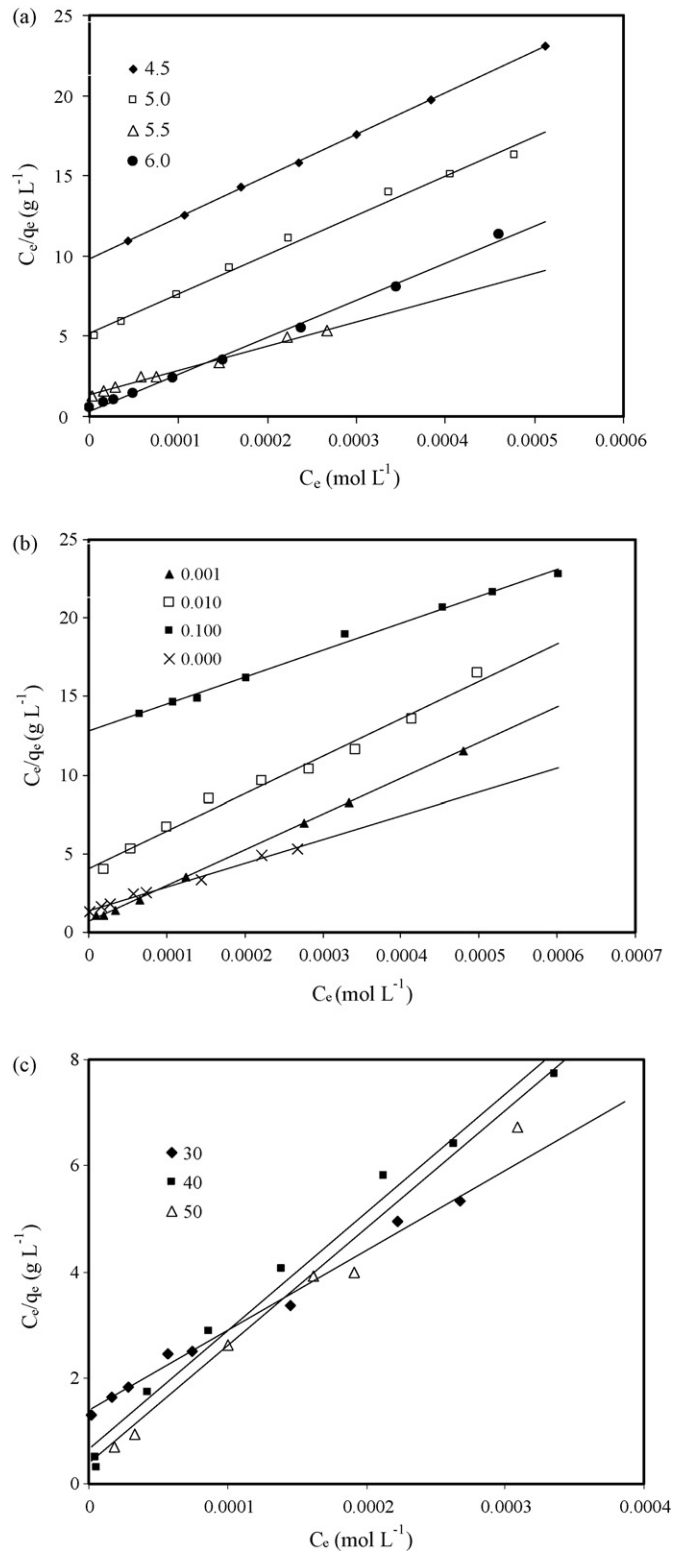


Fig. 5. Langmuir adsorption models for interactions of chromium on kaolinite under different conditions of (a) pH, (b) ionic strength and (c) temperature.

3.3. Enthalpy of adsorption

The isosteric enthalpy of adsorption, ΔH° , from the adsorption data at various temperatures as a function of coverage

Table 2
Isotherm constants for chromium adsorption on kaolinite

Temperature (°C)	pH	Ionic strength (mol L ⁻¹)	Langmuir isotherm			Freundlich isotherm		
			q _m (×10 ⁵ mol g ⁻¹)	K (×10 ⁻⁴ L mol ⁻¹)	R ²	K _F (×10 ³)	n	R ²
30	4.5	–	3.86	0.26	0.9997	4.96	1.42	0.9883
30	5.0	–	4.09	0.47	0.9915	8.36	1.38	0.9818
30	5.5	–	6.62	1.10	0.9905	19.71	1.43	0.9735
30	6.0	–	4.34	6.64	0.9954	53.83	1.23	0.9258
30	5.5	1 × 10 ⁻³	4.40	3.43	0.9993	0.67	2.92	0.8313
30	5.5	1 × 10 ⁻²	4.51	0.75	0.9902	1.48	2.07	0.9811
30	5.5	1 × 10 ⁻¹	5.83	0.13	0.9939	7.82	1.31	0.9960
40	5.5	1 × 10 ⁻³	4.47	3.51	0.9843	0.44	3.45	0.8854
50	5.5	1 × 10 ⁻³	4.98	5.03	0.9950	0.19	5.72	0.9008

Table 3
Summary of adsorption capacity of various adsorbents

Adsorbents	q _m (×10 ⁵ mol g ⁻¹)	References
Activated carbons	6.77–25.60	[4] ^a
Chryseomonas luteola TEM05	5.77	[29] ^a
Peat	43.65	[30] ^a
Saw dust	76.34	[31] ^a
Coconut husk fibres	55.76	[32] ^a
Coconut shell based-activated carbon	38.46	[33]
Sugar beet pulp	33.08	[31] ^a
Palm pressed-fibres	28.85	[32]
Maize cob	26.54	[31] ^a
Sugar cane bagasse	25.77	[31] ^a
Biogas residual slurry	11.29	[34] ^a
Fe(III)/Cr(III) hydroxide	2.75	[35] ^a
Kaolinite	3.86–6.62	In this study

^a Calculated values from mg g⁻¹.

fraction ($\theta = q_e/q_m$) can be estimated from the following equation [9]:

$$\frac{\Delta H^\circ}{R_g} = \left[\frac{\partial(\ln C_e)}{\partial(1/T)} \right]_{\theta=0.5} \quad (14)$$

where R_g is the gas constant. Fig. 6 shows the plot of $-\ln C_e$ against $1/T$. The values of ΔH° was calculated at a specific

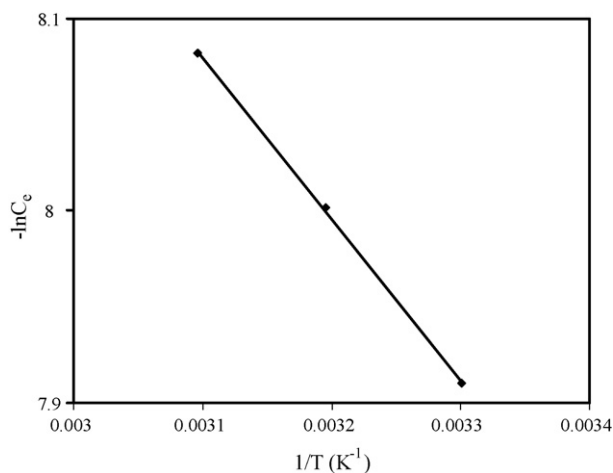


Fig. 6. The relation between $-\ln C_e$ and $1/T$ for adsorption of chromium on kaolinite at pH 4.5, initial concentration of cation 7.69×10^{-4} mol L⁻¹ and ionic strength null.

coverage fraction of 0.5 as 7.0 kJ mol⁻¹. Transfer of ions from aqueous solution to solid surface usually involves physical (predominantly coulombic) and chemical forces. The results show that the interaction between surface and adsorbate molecules is a physical interaction. Since adsorption is an endothermic process, it would be expected that an increase in solution temperature would result in an increase in adsorption capacity [9].

3.4. Single-stage batch adsorption

The schematic diagram for a single-stage adsorption process is shown in Fig. 7. The solution to be treated contains V L solvent, and the chromium concentration is reduced from C_0 to C_e (mol L⁻¹) in the adsorption process. The adsorbent is added to the extent of W g adsorbate-free kaolinite, and the chromium concentration increases from q_0 to q_e (mol g⁻¹). If fresh adsorbent is used, $q_0 = 0$. The mass balance equates the chromium removed from the liquid to that picked up by the solid:

$$V(C_0 - C_e) = W(q_e - q_0) = Wq_e \quad (15)$$

For the adsorption of chromium on kaolinite the Langmuir isotherm has given the best fit to experimental data. Consequently, equation can be best substituted for q_e in the rearranged form of Eq. (11) giving adsorbent/solution ratios for this particular system:

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{((q_m K C_e)/(1 + K C_e))} \quad (16)$$

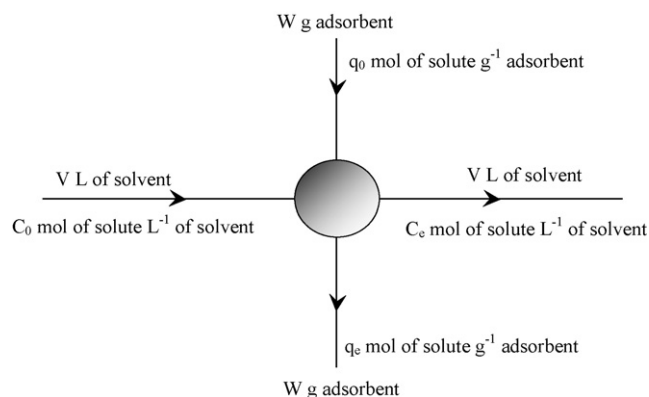


Fig. 7. A single-stage batch adsorber.

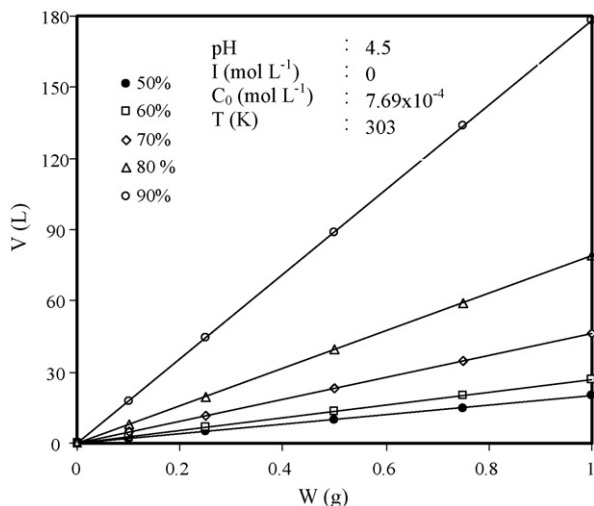


Fig. 8. Volume of effluent (V) treated against adsorbent mass (W) for different percentage chromium removal.

Fig. 8 shows a series of plots derived from Eq. (16) for the adsorption of chromium ions on kaolinite. An initial chromium concentration of $7.69 \times 10^{-4} \text{ mol L}^{-1}$ at 30°C and at pH 4.5 is assumed and figure shows the amount of effluent, which can be treated to reduce chromium ions content by 50, 60, 70, 80 and 90% using various masses of adsorbent [5].

4. Conclusions

Analysing the results obtained in this work, the following conclusions about the removal of trivalent chromium by kaolinite can be made:

- Kaolinite can be effectively used for the removal of Cr(III) from wastewaters.
- Adsorption of chromium(III) is pH dependent. The removal efficiency of adsorbent increases with increase in pH.
- The number of protons released per Cr^{3+} ion adsorbed onto kaolinite was about 1.9 at pHs about 5.4–6.0 and 0.9 at pHs about 6.5.
- The adsorbed amount of chromium ions decreased with increase in ionic strength.
- The adsorbed amount of chromium ions increased with increase in temperature.
- Adsorption enthalpy reveals that the adsorption of Cr(III) by kaolinite is endothermic in nature.
- The adsorption process follows the Langmuir adsorption model.

These findings suggest that this material has significant potential for use as an adsorbent in the removal of Cr(III) from industrial wastewaters.

References

[1] S.J. Park, W.Y. Jung, Adsorption behaviors of chromium(III) and (VI) on electroless Cu-plated activated carbon fibers, *J. Colloid Interf. Sci.* 243 (2001) 316–320.

- [2] C.S. Uyguner, M. Bekbolet, Evaluation of humic acid, chromium(VI) and TiO_2 ternary system in relation to adsorptive interactions, *Appl. Catal. B: Environ.* 49 (2004) 267–275.
- [3] M.M. Araujo, J.A. Teixeira, Trivalent chromium sorption on alginate beads, *Int. Biodeter. Biodegr.* 40 (1) (1997) 63–74.
- [4] D. Aggarwal, M. Goyal, R.C. Bansal, Adsorption of chromium by activated carbon from aqueous solution, *Carbon* 37 (1999) 1989–1997.
- [5] M. Doğan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, *Water Air Soil Pollut.* 120 (2000) 229–248, 2000.
- [6] Y. Lie, H. Xue, Determination of Cr(III) and Cr(VI) species in natural waters by catalytic cathodic stripping voltammetry, *Anal. Chim. Acta* 448 (2001) 121–134.
- [7] R. Weerasooriya, H.J. Tobschall, Mechanistic modeling of chromate adsorption onto goethite, *Colloids Surf. A: Physicochem. Eng. Aspects* 162 (2000) 167–175.
- [8] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes, *J. Hazard. Mater.* B95 (2002) 275–290.
- [9] M. Alkan, M. Doğan, Adsorption of copper(II) onto perlite, *J. Colloid Interf. Sci.* 243 (2001) 280–291.
- [10] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake, *J. Hazard. Mater.* B94 (2002) 49–61.
- [11] K. Chojnacka, A. Chojnacki, H. Gorecka, Biosorption of Cr^{3+} , Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process, *Chemosphere* 59 (2005) 75–84.
- [12] K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay, *J. Hazard. Mater.* B134 (2006) 130–139.
- [13] J. Ikhsan, B.B. Johnson, J.D. Wells, A comparative study of the adsorption of transition metals on kaolinite, *J. Colloid Interf. Sci.* 217 (1999) 403–410.
- [14] R.D. Holtz, W.D. Kovacs, *An Introduction to Geotechnical Engineering*, Prentice-Hall Inc., New Jersey, 733 pp.
- [15] J.K. Mitchell, *Fundamentals of Soil Behavior*, 2nd ed., John Wiley & Sons Inc., America, 1993.
- [16] Y. Yükselen, A. Kaya, Zeta potential of kaolinite in the presence of alkali, alkaline earth and hydrolyzable metal ions, *Water Air Soil Pollut.* 145 (2003) 155–168.
- [17] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, *Appl. Clay Sci.* 20 (2002) 295–300.
- [18] B.C. Raymahashay, A comparative study of clay minerals for pollution control, *J. Geol. Soc. India* 30 (1987) 408–413.
- [19] M. Alkan, Ö. Demirbaş, M. Doğan, Electrokinetic properties of kaolinite in mono- and multivalent electrolyte solutions, *Micropor. Mesopor. Mater.* 83 (2005) 51–59.
- [20] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed., ELBS with Longman.
- [21] M. Alkan, M. Doğan, Surface titrations of perlite suspensions, *J. Colloid Interf. Sci.* 207 (1998) 90–96.
- [22] J.P. Ibanez, Y. Umetsu, Uptake of trivalent chromium from aqueous solutions using protonated dry alginate beads, *Hydrometallurgy* 72 (2004) 327–334.
- [23] D.G. Kinniburgh, in: M.A. Anderson, A.J. Rubin (Eds.), *Adsorption of Inorganic Solid–Liquid Interfaces*, Ann Arbor, MI, 1981, pp. 91–160.
- [24] K. Csoban, M. Parkanyi-Berka, P. Joo, Ph. Behra, Sorption experiments of Cr(III) onto silica, *Colloids Surf. A: Physicochem. Eng. Aspects* 141 (1998) 347–364.
- [25] K.F. Hayes, PhD Thesis, Stanford University, Palo Alto, CA, 1987.
- [26] K. Csoban, P. Joo, Sorption of Cr(III) on silica and aluminium oxide: experiments and modelling, *Colloids Surf. A: Physicochem. Eng. Aspects* 151 (1999) 97–112.
- [27] S. Usui, *Electrical phenomena at interfaces fundamentals, measurements, and applications: electrical double layer*, in: A. Kitahara, A. Watanabe (Eds.), *Surfactant Science Series*, vol. 15, Dekker, New York, 1984, pp. 15–46.
- [28] Y. Sağ, Y. Aktay, Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin, *Process Biochem.* 36 (2000) 157–173.

- [29] G. Ozdemir, S.H. Baysal, Chromium and aluminum biosorption on *Chryseomonas luteola* TEM05, *Environ. Biotechnol.* 64 (2004) 599–603.
- [30] D.C. Sharma, C.F. Forster, Column studies into the adsorption of chromium(VI) using sphagnum moss peat, *Bioresource Technol.* 52 (1995) 261–267.
- [31] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, *Bioresources Technol.* 47 (1994) 257–264.
- [32] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium(VI) from solution by coconut husk and palm pressed fibres, *Environ. Technol.* 14 (1993) 277–282.
- [33] G.J. Alaerts, V. Jitjaturant, P. Kelderman, Use of coconut shell based activated carbon for chromium(VI) removal, *Water Sci. Technol.* 21 (1989) 1701–1704.
- [34] C. Namasivayam, R.T. Yamuna, Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry, *Chemosphere* 30 (3) (1995) 561–578.
- [35] C. Namasivayam, K. Ranganathan, Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater, *Environ. Pollut.* 82 (1993) 255–261.