ELSEVIER

Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay

Ahmet Sarı [a], Mustafa Tuzen [a,*], Mustafa Soylak [b]

[a] *Department of Chemistry, Gaziosmanpasa University, 60250 Tokat, Turkey*
[b] *Department of Chemistry, Erciyes University, 38039 Kayseri, Turkey*

Abstract

This paper presents the adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay. Batch experiments were carried out as a function of the adsorbent dosage, solution pH, shaking time, and temperature. The equilibrium data of fitted well with the linear Langmuir and Freundlich models. Dubinin–Radushkevick (D–R) isotherm model was applied to describe the nature of the adsorption of the metals, and found that it occurred physically. Thermodynamic parameters, the change in Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. These parameters indicated that the adsorption of Pb(II) and Cr(III) on Celtek clay was feasible, spontaneous and exothermic process in nature. Based on the results, it was concluded that Celtek clay had a significant potential for removing Pb(II) and Cr(III) from wastewater using adsorption method.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Lead; Chromium; Celtek clay; Adsorption isotherm; Thermodynamic parameter

1. Introduction

Toxic heavy metals such as cadmium, lead, chromium, arsenic, and selenium are constantly released into the environment. Toxic metals are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in environment and in food chains [1–5]. They can mean danger for ecosystems and human health. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries [5]. Wastewaters from a chemical industry polluted by heavy metal ions represent a hazard for all living organisms especially for human [6,7].

Adsorption is the one of the important procedure for the removal of the traces heavy metals from the environment. The main properties of the adsorbents for heavy metal removal are strong affinity and high loading capacity. Natural adsorbents have generally these properties. Various substances, such as activated carbon, ion exchange resins, natural and synthetic zeolites and clay minerals have been used as adsorbents for the removal of heavy metals from water and wastewater [6–25].

Clay is a natural, earthy, fine-grained material composed largely of a group of crystalline minerals. Clays have been used for thousands of years and they still keep their position among the most important industrial material [26]. Clays have been also used for chemical studies for various purposes including adsorption of various organic, inorganic substances, radioactive specimen and heavy metals [8,9,12,14–18,20,21,23–25].

Celtek clay was chosen as adsorbent material. The clay was collected from Celtek town of Amasya-Turkey. This material has been commonly used as industrial raw material for the construction of ceramic and brick in the middle Anotalia-Turkey. According to our literature survey, Celtek clay has not been used as adsorbent for the removal of heavy metals from water and wastewater.

In this work, the influence of adsorbent dosage, solution pH, shaking time, and temperature on the adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay were investigated. Well-known isotherm models were applied to the equilibrium data. Thermodynamic functions were also calculated and, the nature of the sorption process was described.

2. Experimental procedures

2.1. Instrumentation

A Perkin-Elmer Analyst 700 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A

---

* Corresponding author.
E-mail address: mtuzen@gop.edu.tr (M. Tuzen).

10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase.

2.2. Reagent and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionised water (Milli-Q Millipore $18.2\,M\Omega\,cm^{-1}$ conductivity) was used for all dilutions. The element standard solutions used for calibration were produced by diluting a stock solution of $1000\,mg\,l^{-1}$ of the given element supplied by Sigma and Aldrich.

Sodium phosphate buffer ($0.1\,mol\,l^{-1}$) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers ($0.1\,mol\,l^{-1}$) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. For pH 7, sodium borate ($0.1\,mol\,l^{-1}$) buffer solution was used. Ammonium chloride buffer solutions ($0.1\,mol\,l^{-1}$) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–12.

2.3. Characterization of Celtek clay

Celtek clay was obtained from Celtek town of Amasya in Turkey. It was first dried and sieved form 200-mesh, then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried in electric oven at 378 K for 24 h and then placed in a desiccator before adsorption experiments. The specific surface analysis was found to be $69\,m^2/g$ by using a surface analyzer (Quantachromosorb) and Brunauer–Emmett–Teller (BET) method. The chemical and mineral composition of dry Celtek clay was determined by X-ray powder diffractometry (XRD; RIGAKU D-MAX 2200 model). It was composed of 59.46% SiO_2, 14.92% Al_2O_3, 2.45% K_2O, 1.98% MgO, 5.18% Fe_2O_3, 4.75% CaO, 0.10% SO_3, 0.98% Na_2O, 0.73% TiO_2, and it had a mineral composition of 16.64% kuvars, 8.14% calcite, 11.53% anortite, 42.58% illite and 21.11% chlorite. The ignition loss of the clay at 1273 K was also found to be 8.73% (w/w). Celtek clay was also characterized by FT-IR spectrophotometer (JASCO-430 model) at room temperature. The broad bands was observed at 3417, 3621 and $3696\,cm^{-1}$ was due to the O–H stretching vibration of the silanol (Si–OH) groups and HO–H vibration of the water molecules adsorbed on the silica surface. The bands observed at 1029, 796 and $694\,cm^{-1}$ were because of the Si–O–Si groups of the tetrahedral sheet and the deforming and bending modes of the Si–O bond, respectively.

2.4. Adsorption procedure

Adsorption experiments were carried out using batch method. A sample volume of 50 ml, containing various concentrations of Pb(II) and Cr(III), was transferred into a beaker; 10 ml of buffer solution was added using a mechanical shaker. After a fast shaking, 100 mg of Celtek clay was added, and the mixture was shaken again for 30 min. The solutions were filtered and the concentrations of metal ions were determined by AAS.

3. Results and discussion

3.1. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The influences of Celtek clay dose on the adsorption of Pb(II) and Cr(III) is depicted in Fig. 1. The adsorption of the metals increased with increasing dosage of the clay and, the adsorption was almost constant at higher dosages than 0.1 g. This was because of the availability of more and more adsorbate surfaces for the solutes to adsorb.

3.2. Effect of pH

The pH of the aqueous solution is an important controlling parameter that strongly affects the adsorption of metals on the surface of the clay [6]. The influence of pH on the adsorption of Pb(II) and Cr(III) were investigated at pH values 2–12, and the results were shown in Fig. 2. A significant increase in the adsorption of Pb(II) and Cr(III) on Celtek clay was not observed at pH values higher than 6. Therefore, the pH 6 was selected for all further studies.

3.3. Effect of shaking time

The influence of shaking time for the adsorption of Pb(II) and Cr(III) on Celtek clay were investigated at the temperature
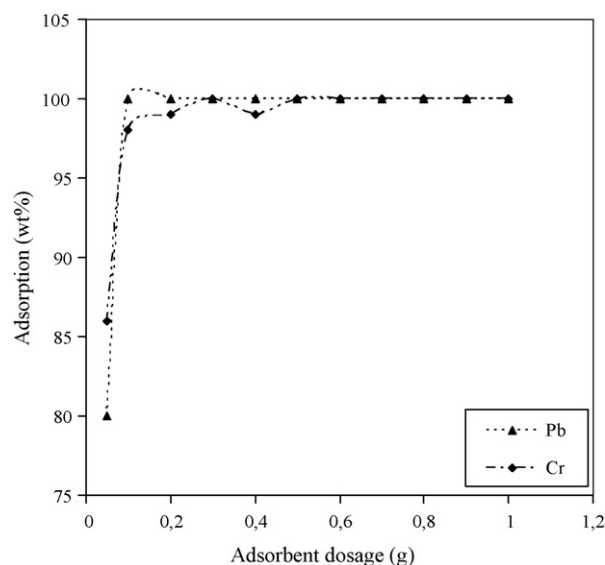

Fig. 1. Effect of dosage of Celtek clay on adsorption of Pb(II) and Cr(III) on Celtek clay (metal concentration: $4\,mg\,l^{-1}$; shaking time: 30 min; pH 6.0; V: 10 ml; T: 293 K).
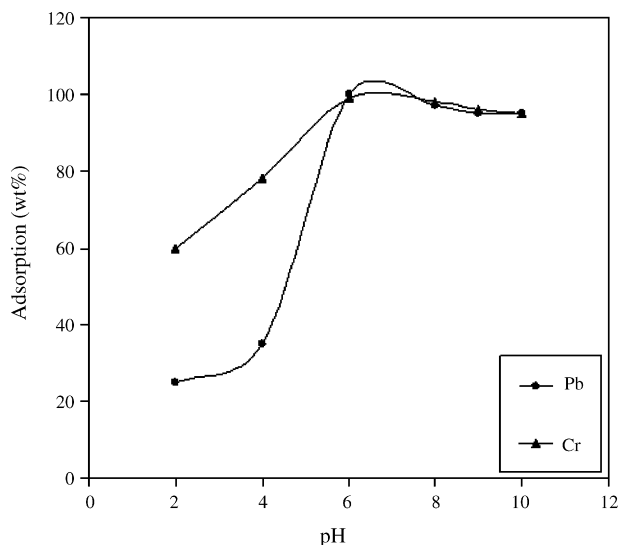
Fig. 2. The effect of pH on adsorption of Pb(II) and Cr(III) on Celtek clay (metal concentration: 4 mg l^{-1}; adsorbent dosage: 0.1 g; shaking time: 30 min; V: 10 ml; T: 293 K).

range of 293–323 K, and the results were depicted in Fig. 3. The adsorption percentages of the analytes were raised with the increasing shaking time and decreasing temperature. On the basis of the results, a 30 min of shaking time was found suitable for maximum adsorption and used in all subsequent measurements at 293 K.

3.4. Adsorption isotherms

Langmuir and Freundlich isotherm models were applied to establish the relationship between the amount of Pb(II) and Cr(III) adsorbed by Celtek clay and their equilibrium concentration in aqueous solution. The experimental data conformed to the linear form of Langmuir model [27] expressed
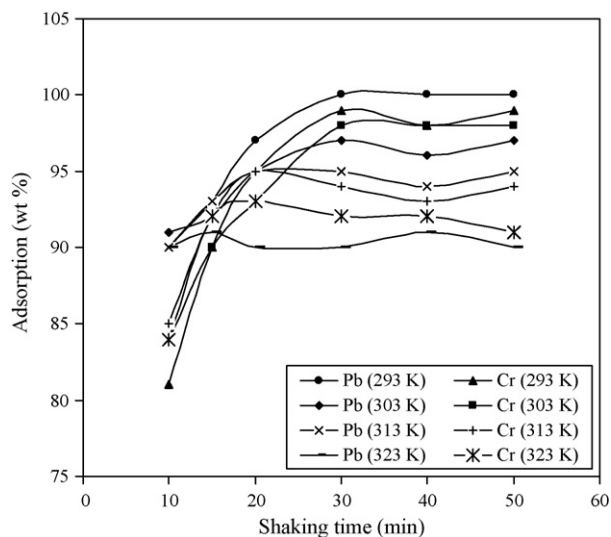

Fig. 3. Variation in adsorption of Pb(II) and Cr(III) on Celtek clay as a function of shaking time at different temperatures (metal concentration: 4 mg l^{-1}; adsorbent dosage: 0.1 g; pH 6.0; V: 10 ml).
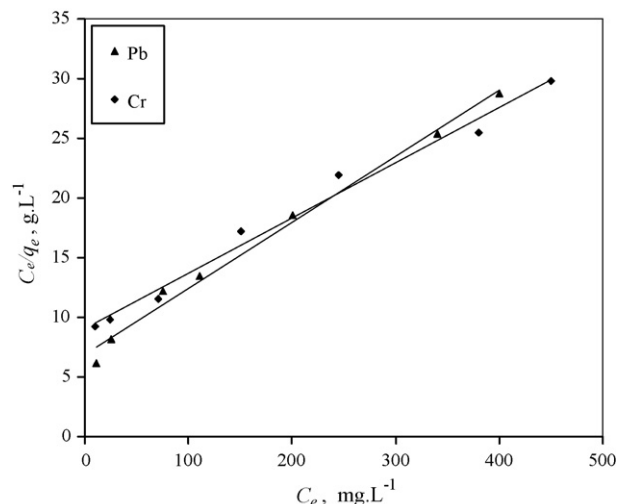

Fig. 4. Linear plots of Langmuir isotherm of Pb(II) and Cr(III) adsorption on Celtek clay (adsorbent dosage: 0.1 g; shaking time: 30 min; pH 6.0; V: 10 ml; T: 293 K).

as the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{1}$$

where C_e is equilibrium concentration of the metal (mg l^{-1}) and q_e is the amount of the metal adsorbed (mg) by per unit of Celtek clay (g). q_m and K_L are Langmuir constant related to adsorption capacity (mg g^{-1}) and the energy of adsorption (l g^{-1}), respectively. q_m and K_L constants were evaluated from slope and intercept of the linear plots of C_e/q_e versus C_e, respectively (Fig. 4).

The sorption equilibrium data was also applied to the Freundlich model in logarithmic form [28] given as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2}$$

where K_F (mg g^{-1}) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. K_F and $1/n$ were determined from the intercept and slope of linear plot of $\log q_e$ versus $\log C_e$, respectively (Fig. 5).

The adsorption pattern of the metals on Celtek clay was well fitted with the Langmuir and Freundlich model because of the r^2 values were in the range of 0.96–0.99 (Figs. 5 and 6). Langmuir model was more applicable than Freundlich model since the r^2 values evaluated from Langmuir model (0.9910 for Pb(II) and 0.9852 for Cr(III)) were higher than that determined from Freundlich model (0.9881 for Pb(II) and 0.9654 for Cr(III)). Langmuir adsorption maxima, q_m, was quite high with the values of 18.08 and 21.55 mg g^{-1} for Pb(II) and Cr(III), respectively. The Langmuir equilibrium constant, K_L, had values of 0.381 g^{-1} for Pb(II) and 0.421 g^{-1} for Cr(III). Freundlich adsorption capacity, K_F, was found to be 0.58 and 0.54 mg g^{-1} for Pb(II)and Cr(III), respectively. Moreover, the Freundlich coefficient ($1/n$) was smaller than 1 and indicating that the adsorption of Pb(II) and Cr(III) on Celtek clay under studied conditions was favorable.
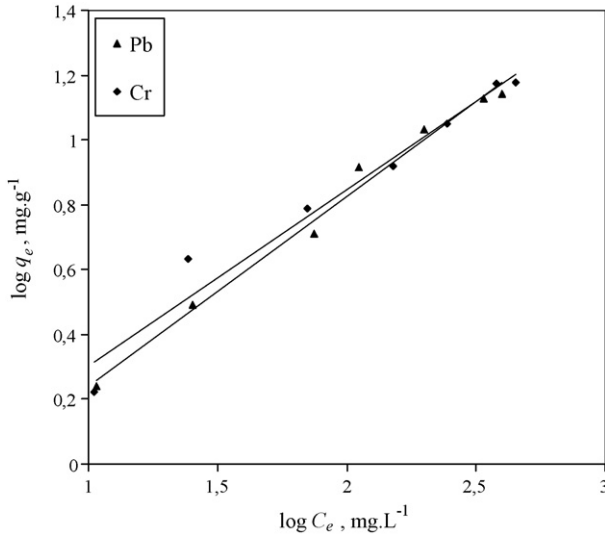
Fig. 5. Linear plots of Freundlich isotherms of Pb(II) and Cr(III) adsorption on Celtek clay (adsorbent dosage: 0.1 g; shaking time: 30 min; pH 6.0; V: 10 ml; T: 293 K).

The sorption data was modeled by D–R isotherm to determinate the adsorption type (physical or chemical). The linear form of this model [10,16,22] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{3}$$

where q_e is the amount of the metal adsorbed onto per unit dosage of the Celtek clay (mol l^{-1}), q_m the monolayer capacity (mol g^{-1}), is the equilibrium concentration (mol dm^{-3}), and β is the activity coefficient related to mean sorption energy (mol^2 J^{-2}). ε is the Polanyi potential described as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{4}$$
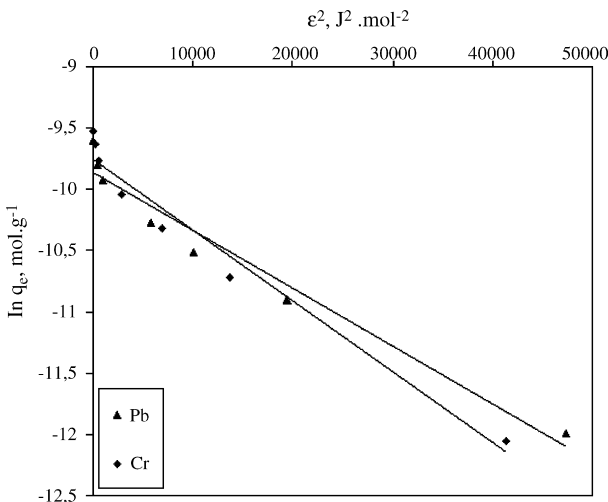

Fig. 6. D–R isotherms of Pb(II) and Cr(III) adsorption on Celtek clay (adsorbent dosage: 0.1 g; shaking time: 30 min; pH 6.0; V: 10 ml; T: 293 K).

The mean sorption energy, E (kJ mol^{-1}), can be calculated by Eq. (5) [10,16,22]:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

As seen in Fig. 6, the slopes of the D–R plots give β constant and, q_m value is calculated from the intercept of the plot. The monolayer sorption capacity (q_m) was evaluated as 5.27×10^{-5} and 5.83×0^{-5} mol g^{-1} for the adsorption of Pb(II) and Cr(III), respectively. The mean sorption energy (E) was found to be 0.10 and 0.09 kJ mol^{-1} for the adsorption of Pb(II) and Cr(III) on Celtek clay, respectively. The E value ranges from 1.0 to 8.0 kJ mol^{-1} for physical adsorption and from 9.0 to 16.0 kJ mol^{-1} for chemical adsorption [10,16]. Therefore, the E values calculated for the adsorption of Pb(II) and Cr(III) was essentially physical in nature.

3.5. Effect of temperature and thermodynamic parameters

In order to investigate the effect of temperature on the adsorption of Pb(II) and Cr(III) on Celtek clay, the distribution coefficient, K_d (l g^{-1}), was calculated at the temperature of 293, 303, 313 and 323 K by using Eq. (6) [10,12,18]:

$$K_d = \frac{q_e}{C_e} \tag{6}$$

The K_d values calculated for the adsorption Pb(II) and Cr(III) on Celtek clay are given in Table 1. As seen from the results, the K_d value decreased with increasing temperature (from 303 to 323 K) and revealing the adsorption of metals on the clay to be exothermic.

Thermodynamic parameters, the enthalpy change (ΔH°) and the entropy change (ΔS°), were calculated from the slope and intercept of the plot of $\ln K_d$ against 1/T, respectively [10,12,14–16,18,22], as shown in Fig. 7:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

The other thermodynamic parameter, Gibbs free energy change (ΔG°) was calculated by

$$\Delta G^\circ = -RT \ln K_d \tag{8}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

The enthalpy change, ΔH° had a value of -35.89 J mol^{-1} for the adsorption of Pb(II) and -32.88 J mol^{-1} for the adsorption of Cr(III). The negative ΔH° exhibited that the adsorption of the

Table 1
Distribution coefficient (K_d) values calculated for the adsorption of Pb(II) and Cr(III) on Celtek clay at different temperatures

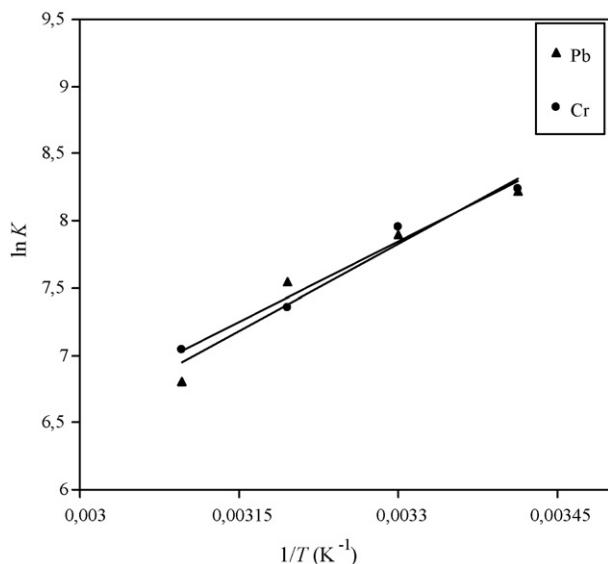| Metal	Distribution coefficient, K_d (l g^{-1})			
	293 K	303 K	313 K	323 K
Pb(II)	3700	2700	1900	900
Cr(III)	3800	2850	1567	1150

Fig. 7. Thermodynamic distribution coefficient (K_d) calculated for the adsorption of Pb(II) and Cr(III) on Celtek clay as a function of temperature (adsorbent dosage: 0.1 g; shaking time: 30 min; pH 6.0; V: 10 ml).

metal ions on Celtek clay was exothermic. The low $\Delta H°$ values mean that there are weak interactions between the metal ions and the functional group (Si–O$^-$) on the surface of clay mineral. Change in the entropy change ($\Delta S°$) was found to be -53.36 and 43.30 J mol^{-1} K^{-1} for the adsorption of Pb(II) and Cr(III), respectively. This result implied that Pb(II) and Cr(III) in bulk phase (aqueous solution) were in a much more chaotic distribution compared to the relatively ordered state of solid phase (surface of adsorbent). Moreover, Gibbs free energy change ($\Delta G°$) was between -20.01, -19.90, -19.64, and -18.27 kJ mol^{-1} for the adsorption of Pb(II) and -20.07, -20.04, -19.15, and -18.93 kJ mol^{-1} for the adsorption of Cr(III) at the temperatures of 293, 303, 313 and 323 K, respectively. The negative $\Delta G°$ values indicated that the adsorption of Pb(II) and Cr(III) on Celtek clay was feasible and spontaneous thermodynamically. In addition, the process proceeded physically because $\Delta G°$ values had lower value than -20.0 kJ mol^{-1} [29]. This result was in well agreement with that obtained from the D–R isotherm.

4. Conclusions

The experimental results indicated that Celtek clay can be successfully used for the adsorption of Pb(II) and Cr(III) from aqueous solutions. Experimental parameters such as dosage of adsorbent, solution pH, shaking time, and temperature must be optimally selected to obtain the highest possible removal of Pb(II) and Cr(III) from aqueous solutions using Celtek clay. The equilibrium data well followed the linear Langmuir and Freundlich models. The value of mean sorption energy, E obtained from the D–R isotherm indicated that the adsorption of the metals on Celtek clay was physical in nature. The negative $\Delta G°$ values showed that the adsorption of Pb(II) and Cr(III) on Celtek clay was feasible and spontaneous. The negative $\Delta H°$ value depicted that the adsorption of Pb(II) and Cr(III) on the clay was an exothermic process. The decrease in the K_d value with

increasing temperature also supported this conception. The negative $\Delta S°$ values revealed that the orderliness of the adsorbed system was higher than the solution phase before adsorption.

On the basis of all results, it can be concluded that Celtek clay can effectively be used for the removal of metal cations from wastewater using adsorption method. This clay mineral presents a major advantage of giving low cost recovery processes making them suitable for use in water purification. Moreover, its regeneration does not present any problem and, when needed, the recovering of the fixed element could be reached even by leaching the loaded material.

References

[1] M.E. Conti, F. Botre, Honeybees and their products as potential bioindicators of heavy metals contamination, Environ. Monit. Assess. 69 (2001) 267–282.

[2] J.T. Nyangababo, L. Henry, E. Omutange, Heavy metal contamination in plants, sediments, and air precipitation of katonga, simiyu, and nyando wetlands of Lake Victoria basin, East Africa, Bull. Environ. Contam. Toxicol. 75 (2005) 189–196.

[3] S. Hora, G. Simu, R. Rad, A. Popa, M. Milos, Utilizarea unor suporturi polimere care contin coloranti imobilizati pentru separarea ionilor de Cu(II) si Zn(II) din solutii apoase, Rev. Chim. 55 (2004) 948–951.

[4] J. Yao, K. Jankowski, Y. Tuo, Z.F. Yao, Y. Xiao, S.H. Xiao, Z.Z. Tan, Online preconcentration of trace nickel from electrolytic manganese using ninicolumn packed activated carbon for electrothermal atomic absorption spectrometry, J. Wuhan Univ. Technol. Mater. Sci. Edit. 19 (2004) 17–20.

[5] Y. Bulut, Z. Baysal, Removal of Pb(II) from wastewater using wheat bran, J. Environ. Manage. 78 (2006) 107–113.

[6] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, J. Hazard. Mater. B 129 (2006) 123–129.

[7] Y. Bayrak, Y. Yesiloglu, U. Gecgel, Adsorption behavior of Cr(VI) on activated hazelnut shell ash and activated bentonite, Microporous Mesoporous Mater. 91 (2006) 107–110.

[8] N.L. Dias, W.L. Polito, Y. Gushikem, Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay, Talanta 42 (1995) 1031–1036.

[9] M. Tuzen, E. Melek, M. Soylak, Celtek clay as sorbent for separation–preconcentration of metal ions from environmental samples, J. Hazard. Mater. B 136 (2006) 597–603.

[10] J. Romero-Gonzalez, J.R. Peralta-Videa, E. Rodrıguez, S.L. Ramirez, J.L. Gardea-Torresdey, Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto *Agave lechuguilla* biomass, J. Chem. Thermodyn. 37 (2005) 343–347.

[11] Y.S. Ho, G. McKay, The sorption of the lead(II) ions on peat, Water Res. 33 (1999) 578–584.

[12] S.S. Gupta, Bhattacharyya, Interaction of metal ions with clays. I. A case study with Pb(II), Appl. Clay Sci. 30 (2005) 199–208.

[13] V.K. Gupta, P. Singh, N. Rahman, Adsorption behavior of Hg(II) and Cd(II) from aqueous solution on Duolite C-433: a synthetic resin, J. Colloid Interf. Sci. 275 (2004) 398–402.

[14] A.A. Khan, R.P. Singh, Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H$^+$, Na$^+$ and Ca^{2+} forms, Colloids Surf. 24 (1987) 33–42.

[15] R. Nassem, S.S. Tahir, Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent, Water Res. 35 (2001) 3982–3986.

[16] R. Donat, A. Akdoğan, E. Erdem, H. Çetişli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solution, J. Colloid Interf. Sci. 286 (2005) 43–52.

[17] A. Kaya, A.H. Ören, Adsorption of zinc from aqueous solutions to bentonite, J. Hazard. Mater. B 125 (2005) 183–189.

[18] G. Bereket, A.Z. Aroğuz, M.Z. Özel, Removal of Pb(II), Cd(II), Cu(II), and Z(II) from aqueous solutions by adsorption on bentonite, J. Colloid Interf. Sci. 187 (1997) 338–343.

[19] A. Demirbaş, E. Pehlivan, F. Gode, T. Altun, G. Arslan, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II), from aqueous solution on Amberlite IR-120 synthetic resin, J. Colloid Interf. Sci. 282 (2005) 20–25.

[20] F. Barbier, G. Duc, M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface, Colloids Surf. A 166 (2000) 153–159.

[21] A. Demirbaş, Adsorption of Cr(III) and Cr(IV) ions from aqueous solutions on to modified lignin, Energy Sources 27 (2005) 1449–1455.

[22] S.S. Tahir, R. Nassem, Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution, J. Chem. Thermodyn. 35 (2003) 2003–2009.

[23] M.J. Angove, B.B. Johnson, J.D. Wells, Adsorption of cadmium(II) on kaolinite, Colloids Surf. A 126 (1997) 137–147.

[24] A. Mellah, S. Chegrouche, The removal of zinc from aqueous solutions by natural bentonite, Water Res. 31 (3) (1997) 621–629.

[25] R.W. Puls, H.L. Bohn, Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions, Soil Sci. Soc. Am. J. 52 (1988) 1289–1292.

[26] O. Altin, O.H. Ozbelge, T. Dogu, Effect of pH, flow rate and concentration on the sorption of Pb and Cd on montmorillonite. I. Experimental, Chem. Tech. Biotechnol. 74 (1999) 1131–1138.

[27] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[28] H. Freundlich, Über die adsorption in lösungen, Zeitschrift für Physikalische Chemie (Leipzig) 57 (1906) 385–470.

[29] Y. Yu, Y.Y. Zhuang, Z.H. Wang, Adsorption of water-soluble dye onto functionalized resin, J. Colloid Interf. Sci. 242 (2001) 288–293.