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Adsorptive removal of Cd(II) and Pb(II) ions from aqueous solutions by using Turkish illitic clay

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ABSTRACT

The ability of Turkish illitic clay (TIC) in removal of Cd(II) and Pb(II) ions from aqueous solutions has been examined in a batch adsorption process with respect to several experimental conditions including initial solution pH, contact time, initial metal ions concentration, temperature, ionic strength, and TIC concentration, etc. The characterization of TIC was performed by using FTIR, XRD and XRF techniques. The maximum uptake of Cd(II) (11.25 mg g^{-1}) and Pb(II) (238.98 mg g^{-1}) was observed when used 1.0 g L^{-1} of TIC suspension, 50 mg L^{-1} of initial Cd(II) and 250 mg L^{-1} of initial Pb(II) concentration at initial pH 4.0 and contact time of 240 min at room temperature. The experimental data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin Radushkevich (D-R) isotherm models. The monolayer adsorption capacity of TIC was found to be 13.09 mg g^{-1} and 53.76 mg g^{-1} for Cd(II) and Pb(II) ions, respectively. The kinetics of the adsorption was tested using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models. The results showed that the adsorption of Cd(II) and Pb(II) ions onto TIC proceeds according to the pseudo-second-order model. Thermodynamic parameters including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes indicated that the present adsorption process was feasible, spontaneous and endothermic in the temperature range of 5–40 °C.

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1. Introduction

Heavy metals such as cadmium, lead, chromium, mercury, and copper are released into the environment as a result of several industrial activities including microelectronics, electroplating, metal finishing, battery manufacture, tannery, metallurgical, and fertilizer industries and taken into the body via inhalation, ingestion, and skin adsorption (Potgieter et al., 2006). They are non-biodegradable and, hence, are accumulated by living organisms causing a large number of diseases and disorders such as damage to mental or central nervous function, lower energy level and damage to blood composition, lungs, kidneys, livers and, other vital organs (Amarasinghe and Williams, 2007). Hence, the development of efficient techniques for the removal of Cd(II) and Pb(II) ions and also other heavy metals from waters and wastewaters is an important task in terms of protection of public health and environment.

A number of technologies such as adsorption, chemical oxidation, precipitation, solvent extraction, ion exchange, membrane processes, and reverse osmosis have been developed for the removal of metal ions from aqueous solutions (Eloussaief and Benzina, 2010). Among them, adsorption technique is found to be the most effective treatment process with selection of a proper adsorbent (Aydın et al., 2008; Eloussaief and Benzina, 2010). The significant advantages of the adsorption technique are; high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimization of chemical or biological sludge, and regeneration of adsorbent (Ahalya et al., 2003). A wide range of adsorbents including activated carbon (Dias et al., 2007) waste mud (Ozdes et al., 2009) montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina (Katsumata et al., 2003) lime mud and boiler ash generated from a pulp and paper factory (Sthiannopkao and Sreesai, 2009), and bacteria (Stanley and Ogden, 2003) have been tested for their heavy metal adsorption capacity. Activated carbon is recognized as an effective adsorbent due to its large surface area and high adsorption capacity. On the other hand its high cost and the difficulties in recovering activated carbon particles from treated water, limit its use as an adsorbent (Unuabonah et al., 2008).

Clay minerals have great potential as efficient adsorbents due to their low cost, large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity (Bhattacharyya and Gupta, 2008; Eloussaief and Benzina, 2010). There are several types of clay minerals such as smectites (montmorillonite and saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, and sepiolite, which are classified based

on the differences in their layered structures. Clay minerals exhibit high adsorption capacity for positively charged materials because of the presence of interlayer exchangeable cations on their structure and net negative charges on their surfaces (Sposito et al., 1999).

The main objective of the present study was to evaluate the applicability of TIC in removal of Pb(II) and Cd(II) ions from aqueous solutions by batch adsorption process. According to our literature survey, no adsorption studies have been performed with TIC for removal of Pb(II) and Cd(II) ions from aqueous solutions. The TIC was used without any pretreatment. The utilization of it without previous activation treatment is one of the significant features of this study with respect to decrease in the cost of the adsorption process. The effects of various analytical conditions such as initial pH of the solution, contact time, initial adsorbate and adsorbent concentration, etc. were evaluated in detail on the removal performance of TIC.

2. Material and method

2.1. Characterization of investigated illitic clay

The TIC was supplied from Dazkırı (Afyon/Turkey). The samples were sieved to obtain a particle size of 200 mesh and dried in an oven at 105 °C for 24 h and maintained in a desiccator until used (Sari et al., 2007).

The mineralogical composition of the TIC was determined from the X-Ray Diffraction (XRD) patterns of the sample taken on a Rigaku D−Max III automated diffractometer using Ni filtered Cu Kα radiation.

The chemical composition of the TIC was determined by Thermo ARL-9800 model X-Ray Fluorescence (XRF) Spectrometer and wet analysis.

In order to determine the surface functional groups, the Fourier Transform Infrared (FTIR) spectrum of the TIC was obtained by using PerkinElmer 1600 FTIR spectrophotometer.

The specific surface area of TIC was determined from the N_2 gas adsorption isotherm at 77 K using a Quantachrome Corporation, Autosorb-1-C/MS model specific surface area analyzer.

The cation exchange capacity (CEC) of TIC was calculated by using the copper bisethylenediamine copper (II) ($[Cu(en)_2]^{2+}$) complex method (Bergaya and Vayer, 1997). For this; 50 mL of 1 M copper(II) chloride ($CuCl_2$) solution was mixed with 102 mL of 1 M ethylenediamine ($C_2H_8N_2$) solution. The slight excess of the amine ensures complete formation of the complex. The solution was diluted with deionized water to 1 L to give a 0.05 M solution of the complex. 0.5 g of TIC was mixed with 5 mL of the complex solution in a 100 mL flask, diluted with deionized water to 25 mL and the mixture was shaken for 30 min in a thermostatic water bath and then centrifuged. The concentration of the complex remaining in the supernatant was determined by iodometric method. For this, 5 mL of the supernatant was mixed with 5 mL of 0.1 M HCl solution to destroy the $[Cu(en)_2]^{2+}$ complex and about 1 g of KI salt was added to this solution. The mixture was titrated with 0.02 M $Na_2S_2O_3$ solution with starch as indicator. The CEC was calculated from the following formula:

$$CEC \ (meg/100 \ g) \ = \ \frac{MSV(x - y)}{1000m} \tag{1}$$

where M is the molar mass of Cu-complex, S is the concentration of thio solution, V is the volume (mL) of complex taken for iodometric titration, m is the mass of adsorbent (g) taken, x is the volume (mL) of $Na_2S_2O_3$ solution required for blank titration (without adding the adsorbent) and y is the volume (mL) of $Na_2S_2O_3$ solution required for the titration (with the clay adsorbent).

All other characterization parameters such as pH and moisture content of TIC were determined using standard methods (APHA, 1985).

2.2. Adsorption experiments

All chemicals were of analytical reagent grade and purchased from Merck (Darmstadt, Germany). All glassware and sample bottles were cleaned by soaking overnight in 10% (w/v) HNO_3 and then rinsing with deionized water several times. A stock solution of 5000 mg L^{-1} Pb(II) and Cd(II) ions were prepared separately by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in deionized water. The required concentrations of metal ion solutions were prepared by appropriate dilutions of the stock solutions. The pH of the solutions was adjusted to 4.0 by using either dilute HNO_3 or NaOH solutions. The adsorption tests of metal ions onto TIC were studied in a batch adsorption process by mixing 100 mg of TIC sample (10 g L^{-1}) with 10 mL of Pb(II) solutions and 150 mg of TIC sample (15 g L^{-1}) with 10 mL of Cd(II) solutions in the concentration range of 50−1200 mg L^{-1} (for both metal ions) in polyethylene centrifuge tubes, separately. The mixtures were agitated at a speed of 400 rpm on a mechanical shaker (Edmund Bühler GmbH) for 240 min to reach equilibrium for both metal ions. After equilibrium, the adsorbent was separated from the metal ion solutions by centrifugation at 3000 rpm for 5 min and the filtrates were analyzed for the Pb(II) and Cd(II) levels by a flame atomic absorption spectrometer, FAAS (Unicam AA-929). All experiments were conducted in triplicate and the averages of the results were presented in this study. The metal ion concentrations, retained in the adsorbent phase (q_e, mg g^{-1}), were calculated by using the following equation;

$$q_e \ = \ \frac{(C_o - C_e)V}{m_s} \tag{2}$$

where C_o (mg L^{-1}) is the initial metal ion concentration, C_e (mg L^{-1}) is the equilibrium concentration of metal ions in aqueous solution, V (L) is the volume of solution, m_s (g) is the mass of the TIC and q_e (mg g^{-1}) is the calculated metal ion adsorption amount onto TIC.

2.3. Effect of initial pH

The pH of the aqueous solution has been identified as one of the most important variable in adsorption studies because the protonation of the functional groups on the adsorbent surface and ionization degree of the adsorbates depend on the initial pH of the aqueous solution. Hence the effects of initial pH on the removal of Pb(II) and Cd(II) ions were studied with initial Cd(II) concentration of 50 mg L^{-1}, Pb(II) concentration of 100 mg L^{-1} and TIC concentration of 10 g L^{-1} by varying the pH of the solutions over a range of 1−8 for Cd(II) and 1−5 for Pb(II).

2.4. Effect of TIC concentration

In order to evaluate the effects of TIC concentration on the removal of Cd(II) and Pb(II) ions, a series of experiments were carried out by varying TIC concentrations in the range of 1−30 g L^{-1}. The experiments were conducted for 240 min of contact time by using initial Cd(II) concentration of 50 mg L^{-1}, Pb(II) concentration of 250 mg L^{-1} at pH 4.0.

2.5. Effect of ionic strength

The NaCl, KCl, $NaNO_3$, and Na_2HPO_4 salts, which may present in industrial wastewaters besides heavy metal ions and may interfere with heavy metal ions uptake by an adsorbent, were chosen as

electrolytes to investigate the effect of ionic strength on Pb(II) and Cd(II) adsorption onto TIC. For that purpose different concentrations of salts solutions (in the range of 0.01–0.5) were treated with initial Cd(II) concentration of 50 mg L^{-1} and Pb(II) concentration of 125 mg L^{-1} at pH 4.0. The TIC suspensions were 10 and 15 g L^{-1} for Pb(II) and Cd(II) ions, respectively and the equilibrium time was 240 min.

2.6. Effect of temperature and thermodynamic of adsorption

The effect of temperature on the removal efficiency was investigated in the temperature range of 5–40 °C by using initial Cd(II) concentration of 50 mg L^{-1} and Pb(II) concentration of 250 mg L^{-1} at pH 4.0. The TIC concentrations were 10 and 15 g L^{-1} for Pb(II) and Cd(II) ions, respectively and the equilibrium time was 240 min.

2.7. Effect of contact time and adsorption kinetics

The time-dependent behavior of Cd(II) and Pb(II) adsorption onto TIC was evaluated for different equilibrium time intervals from 1 to 600 min at room temperature by using initial Cd(II) concentration of 50 mg L^{-1} and Pb(II) concentration of 250 mg L^{-1} at pH 4.0. The TIC suspensions were 10 and 15 g L^{-1} for Pb(II) and Cd(II) ions, respectively.

2.8. Effect of initial adsorbate concentration and estimation of adsorption parameters

The effects of initial metal ions concentration on the adsorption process were evaluated by varying initial metal ions concentration in the range of 50–1200 mg L^{-1}. The initial pH of the metal ions solutions were adjusted to 4.0. The TIC suspensions were 10 and 15 g L^{-1} for Pb(II) and Cd(II) ions, respectively and the equilibrium time was 240 min.

3. Results and discussion

3.1. Characterization of TIC

XRD measurements were shown that the TIC is mainly composed of illite, besides quartz, kaolinite and smectite (montmorillonite). The significant peaks have been identified on the XRD spectrum (Fig. 1). The chemical composition of TIC was given in Table 1. The FTIR spectrum of TIC was depicted in Fig. 2. The
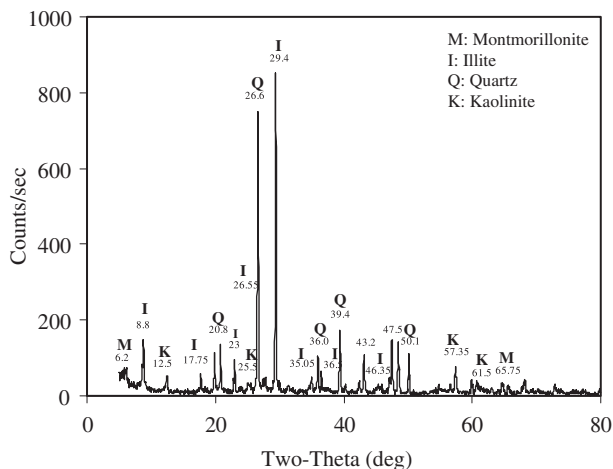
Table 1
Characteristics of TIC.

Chemical composition of TIC (%)	
SiO_2	31.4
Al_2O_3	9.8
Fe_2O_3	4.7
CaO	23.9
MgO	4.1
Na_2O	0.7
K_2O	1.4
Loss of ignition	23.8
Pore structure of TIC	
BET surface area ($m^2 g^{-1}$)	3.10
Langmuir surface area ($m^2 g^{-1}$)	4.64
Micropore area ($m^2 g^{-1}$)	1.58
External surface area ($m^2 g^{-1}$)	1.52
Micropore volume ($cm^3 g^{-1}$)	0.0008
Average pore diameter (nm)	10.81
Other parameters	
pH	9.6
CEC (meq/100 g)	2.0
Moisture content (%)	1.3

absorption band observed at 3624 cm^{-1} for TIC is attributed to hydroxyl group vibrations in Mg–OH–Al, Al–OH–Al, and Fe–OH–Al units in the octahedral layer. The band at 3440 cm^{-1} is due to the O–H stretching vibration of the silanol (Si–OH) groups and HO–H vibration of the water adsorbed silica surface and the broad band near 1000 cm^{-1} is related to the stretch vibrations of the Si–O groups. The FTIR spectrum also contains a broad band at 1430 cm^{-1}, due to the calcite impurity. This band is related to the stretch vibrations of C=O group. The asymmetric and symmetric bending modes of O–Si–O are observed at 530 and 470 cm^{-1}. The BET surface area, Langmuir surface area, micropore area, external surface area, micropore volume and average pore diameter (4 V/A by BET) of TIC and also other characterization parameters including CEC, moisture content and pH values of TIC were given in Table 1.

3.2. Effect of initial pH

At highly acidic pH values (pH 1.0–2.0) the surface of the TIC was associated with H_3O^+ ions and the competition between the metal cations and H_3O^+ ions for the active adsorption sites on the surface of the adsorbent lead to decrease in uptake of metal ions. On the other hand as the pH value was increased, the surface of the TIC became more negatively charged and hence electrostatic repulsion between the metal cations and adsorbent surface sites
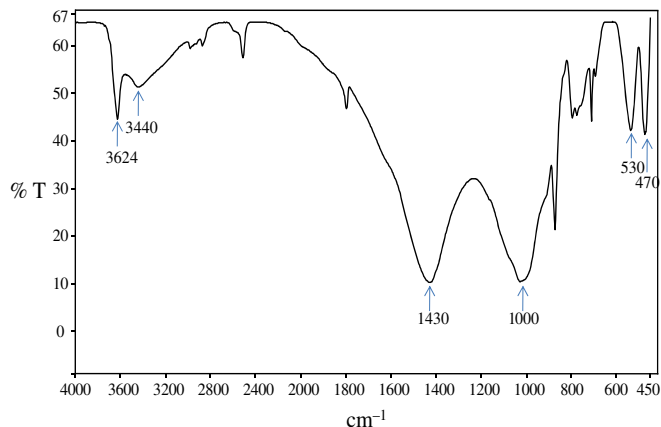

Fig. 1. X-ray diffraction pattern of TIC.

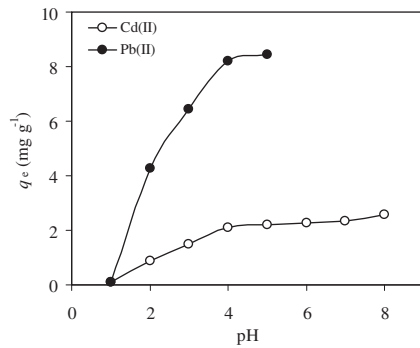
Fig. 2. FTIR spectrum of TIC.

Fig. 3. Effect of initial pH on metal ions uptake by TIC.

and competing effect of H_3O^+ ions decreased which increased the adsorption amount of metal ions onto TIC (Echeverria et al., 2005; Jiang et al., 2010; Unuabonah et al., 2008). Experiments were not conducted beyond pH 6.0 for Pb(II) and pH 9.0 for Cd(II) to avoid the precipitation of metal ions and hence initial pH was specified as 4.0 for both of the metal ions (Fig. 3).

3.3. Effect of TIC concentration

As the TIC concentration was increased, the percentage amount of adsorption increased by virtue of increased more availability of active adsorption sites. On the other hand the amount of adsorbed metal ions per unit mass of the TIC (q_e) decreased with an increase in TIC concentration (Fig. 4(a) and (b)). This can be explained by two
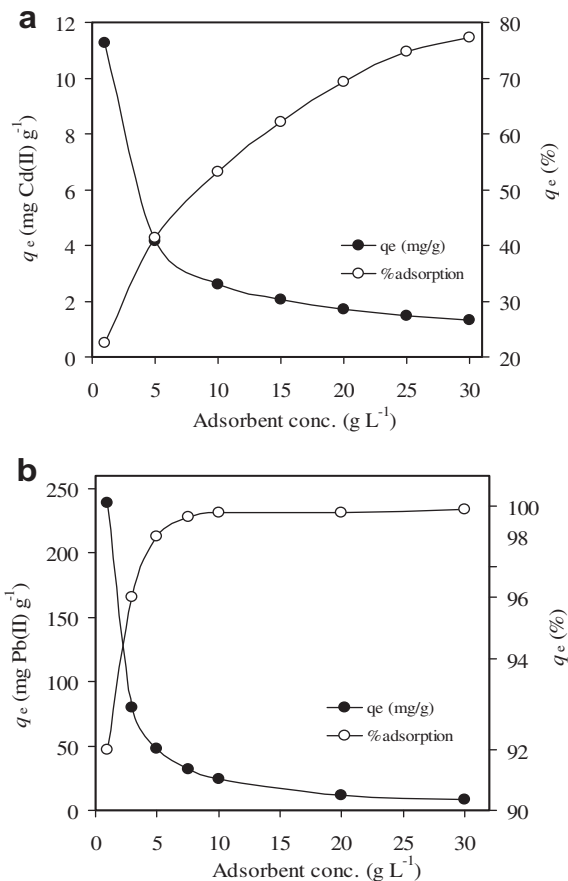
reasons: (i) the total surface area of the adsorbent decreased due to aggregation of the adsorbent particles (ii) the higher amount of adsorbent lead to unsaturated adsorption sites (Bhattacharyya and Gupta, 2006).

3.4. Effect of ionic strength

It was observed that there was a decrease in the adsorption capacities of TIC for Cd(II) (Fig. 5(a)) and Pb(II) (Fig. 5(b)) ions with increasing the concentration of electrolytes. These results can be attributed by these reasons: (i) the competition between cations of the salts and metal ions for the active adsorption sites of TIC so the electrostatic interactions between metal ions and surface functional groups of TIC were impeded in the presence of ionic strength (ii) the active adsorption sites of the TIC may be blocked in the presence of these salts so metal ions were hindered to bind the surface of the adsorbent (Arief et al., 2008; Jiang et al., 2010).

3.5. Effect of temperature and thermodynamic of adsorption

The adsorption efficiency increased from 9.36 mg g^{-1} (37.4% removal) to 24.06 mg g^{-1} (96.2% removal) for Pb(II) ions and increased from 2.10 mg g^{-1} (63.0% removal) to 2.25 mg g^{-1} (67.5%

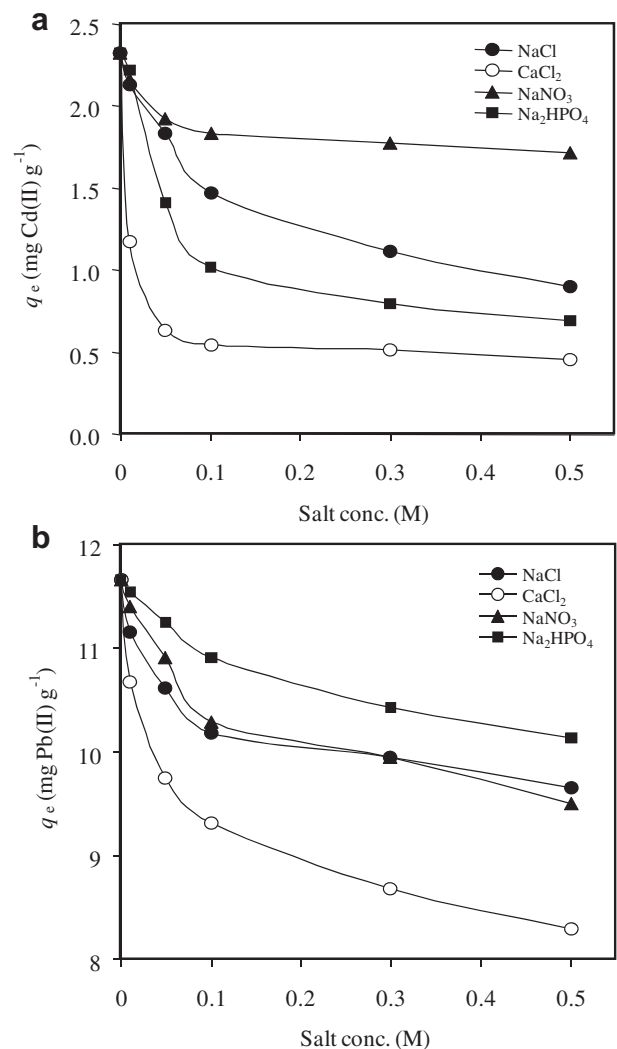**Fig. 4.** Effect of TIC concentration on a) Cd(II) uptake b) Pb(II) uptake.

Fig. 5. Effect of ionic strength on a) Cd(II) uptake b) Pb(II) uptake.

removal) for Cd(II) ions when the temperature was increased from 5 to 40 °C, indicating that the adsorption process for both metal ions was endothermic in nature (Fig. 6). The increase in the adsorption capacity of TIC with temperature may be attributed to either increase in number of available active surface sites on the TIC surface or increase in the mobility of metal cations (Echeverria et al., 2005; Tertre et al., 2006).

The thermodynamic parameters including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy changes (ΔS) can be calculated using the following equations (Smith and Van Ness, 1987);

$$\Delta G = -RT \ln K_d \qquad (3)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and K_d is the distribution coefficient. The K_d value was calculated using following equation;

$$K_d = q_e/C_e \qquad (4)$$

where q_e (mg L^{-1}) and C_e (mg L^{-1}) are the equilibrium concentration of metal ions adsorbed onto TIC and remained in the solution, respectively. The enthalpy (ΔH) and entropy (ΔS) changes of adsorption were estimated from the following equation;

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

This equation can be written as;

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (6)$$

According to Eq. (6) the ΔH and ΔS were calculated from the slope and intercept of the plot between ln K_d versus $1/T$, respectively. The ΔG values were obtained by using Eq. (3) in the temperature range of 5–40 °C. The negative values of ΔG, except 5 °C for Pb(II) ions, suggested the feasibility of the present adsorption process and spontaneous nature of the adsorption of Pb(II) and Cd(II) ions onto TIC (Table 2). On the other hand the magnitude of ΔG increased with increasing the temperature indicated that a better adsorption is actually obtained at higher temperatures. The positive values of ΔH, for both metal ions, indicated that the endothermic nature of adsorption which was also supported by the increase in amount of metal uptake with the rise in temperature. The positive ΔS values suggested an increase in the randomness at the solid/solution interface during the adsorption of Pb(II) and Cd(II) ions onto TIC. Echeverria et al. have evaluated the retention of Pb(II) ions on illite mineral in the temperature ranges of 5–45 °C. In their study, although the ΔG value obtained at 25 °C (−2.46 kJ mol^{-1}) is similar to Pb(II) adsorption onto TIC, the ΔH (12.74 kJ mol^{-1}) and ΔS (50.9 J K^{-1} mol^{-1}) values were lower than the ΔH and ΔS values for the adsorption of Pb(II) ions onto TIC. Also the retention of Pb(II)
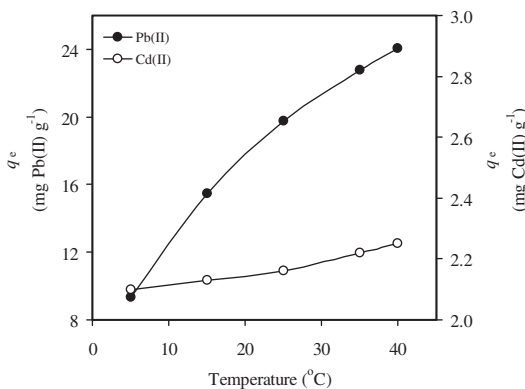
Table 2
Thermodynamic parameters of Cd(II) and Pb(II) adsorption onto TIC at different temperatures.

		Thermodynamic parameters		
	T (°C)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})[a]	ΔH (kJ mol^{-1})[a]
Pb(II)	5	1.19	260.20	73.86
	15	−1.16		
	25	−2.72		
	35	−5.98		
	40	−8.43		
Cd(II)	5	−1.71	24.54	5.15
	15	−1.89		
	25	−2.08		
	35	−2.41		
	40	−2.58		

[a] Measured between 278 and 313 K.

ions on illite slightly favored by increasing the temperature, similar to Pb(II) and Cd(II) adsorption on TIC (Echeverria et al., 2005).

3.6. Effect of contact time and adsorption kinetics

The metal ions uptake was rapid for the first 30 min because at the beginning of the adsorption the active adsorption sites on the adsorbent surface were more available thus metal ions could interact easily with these sites. Afterward it continued at a slower rate and finally reached to the equilibrium by virtue of the saturation of adsorption sites on adsorbent surface. The equilibrium
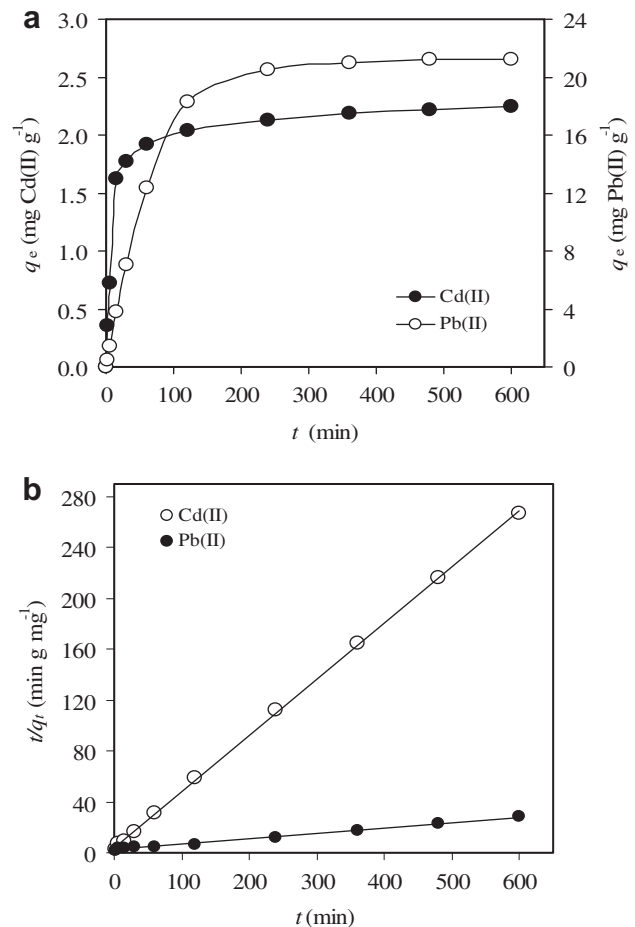
Fig. 7. a) Effect of contact time on metal ions uptake b) Pseudo-second-order kinetic model.

Fig. 6. Effect of temperature on metal ions uptake.

was reached within 240 min for both Cd(II) and Pb(II) ions, and thus, further adsorption experiments were carried out for a contact time of 240 min (Fig. 7(a)).

Some of the commonly used kinetic models including pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models were applied to the experimental data in order to examine the mechanism of the adsorption process.

The pseudo-first-order equation can be written as follows (Lagergren, 1898);

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \tag{7}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of the metal ions adsorbed on the adsorbate at equilibrium and at any time t, respectively; and k_1 (min^{-1}) is the rate constant of the first order adsorption. After integration and applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the integrated form of Eq. (7) becomes;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

The value of k_1 and q_e can be obtained from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ versus t, respectively. The calculated $q_{e\ cal}$ values were not in a good agreement with the experimental values of $q_{e\ exp}$ and the correlation coefficients were found relatively low values (Table 3) for both Cd(II) and Pb(II) ions. These observations suggested that the pseudo-first-order model is not suitable for modeling the adsorption of Cd(II) and Pb(II) ions onto TIC.

The pseudo-second-order model is in the following form (Ho and McKay, 1998);

$$\frac{d_q}{d_t} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order equation; q_e (mg g^{-1}) is the maximum adsorption capacity; q_t (mg g^{-1}) is the amount of adsorption at time t (min). After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the Eq. (9) becomes the following;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \tag{10}$$

For both Cd(II) and Pb(II) ions adsorption, the pseudo-second-order kinetic model constants, k_2 and $q_{e\ cal}$ values were determined from the intercept and slope of the plot of t/q_t versus t (Fig. 7(b)), respectively and presented in Table 3 along with the corresponding correlation coefficients. The calculated $q_{e\ cal}$ values were much close to the experimental values of $q_{e\ exp}$ and correlation coefficients were found relatively high values. Hence it can be concluded that the pseudo-second-order adsorption mechanism is predominant for the adsorption of Cd(II) and Pb(II) ions onto TIC.

The Elovich equation is given as follows (Cheung et al., 2001);

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \tag{11}$$

where α (mg g^{-1} min^{-1}) is the initial sorption rate, β (g mg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption. If Cd(II) and Pb(II) adsorption onto TIC fits the Elovich model, a plot of q_t versus $\ln(t)$ should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha\beta)$. The Elovich model constants, α and β values along with the corresponding correlation coefficient were presented in Table 3. The correlation coefficient values were relatively small indicating that Elovich model is not suitable for modeling the adsorption of Cd(II) and Pb(II) ions onto TIC.

The intraparticle diffusion model equation is expressed as (Weber and Morriss, 1963);

$$q_t = k_{id} t^{1/2} + c \tag{12}$$

where q_t (mg g^{-1}) is the amount of sorption at time t (min) and k_{id} (mg g^{-1} min$^{-1/2}$) is the rate constant of intraparticle diffusion model. The plot of q_t versus $t^{1/2}$ may present multilinearity indicating that any adsorption process takes place in three main steps which are;

(i) film diffusion
(ii) intraparticle or pore diffusion
(iii) sorption onto interior sites.

The last step generally occurs rapidly thus it is considered that the sorption should be controlled by either film diffusion or pore diffusion depending on which step is slower. By evaluating the intraparticle mass transfer curve, it was observed that the Cd(II) and Pb(II) adsorption process was found to be followed by two distinct phases. The first phase is attributed to the diffusion of metal ions through the solution to the external surface of TIC and the second phase indicates the intraparticle diffusion of metal ions into the pores of TIC. The intraparticle rate constants for the first phase ($k_{id,1}$) and second phase ($k_{id,2}$) and c parameters were obtained from the plot of q_t versus $t^{1/2}$ and the results were given in Table 3. By comparing the rate constants, the lower values of $k_{id,2}$ than $k_{id,1}$ indicating that the rate limiting step for Cd(II) and Pb(II) adsorption process is intraparticle diffusion. However the intraparticle diffusion model is not the only rate limiting mechanism since the line did not pass through the origin. As a result, Cd(II) and Pb(II) adsorption onto TIC is considered as a complex process and both intraparticle diffusion and surface sorption contributes to the rate limiting step (Bulut et al., 2008; Maliyekkal et al., 2008).

3.7. Effect of initial adsorbate concentration and estimation of adsorption parameters

The changes in initial metal concentration can alter the metal uptake efficiency of an adsorbent through a combination of several factors such as the availability of specific surface functional groups

Table 3
Parameters of pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models.

Pseudo-first order kinetic model					Pseudo-second order kinetic model		
Metals	$q_{e\ exp}$ (mg g^{-1})	k_1 (min^{-1})	$q_{e\ cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e\ cal}$ (mg g^{-1})	R^2
Pb(II)	21.24	−0.0126	19.48	0.9761	7.03×10^{-4}	23.92	0.9949
Cd(II)	2.25	−0.00780	1.00	0.8685	0.045	2.27	0.9997

Intraparticle diffusion model					Elovich model		
Metals	$k_{id,1}$ (mg g^{-1} min$^{-1/2}$)	R^2	$k_{id,2}$	R^2	C	β (g mg^{-1})	α (mg g^{-1} min^{-1})	R^2
Pb(II)	1.860	0.9883	0.083	0.8937	2.01	3.970	0.430	0.9240
Cd(II)	0.241	0.8547	0.015	0.9808	1.03	0.297	5.71	0.9122

and the ability of these groups to bind metal ions (Arief et al., 2008). The equilibrium concentration increased from 2.4 to 11.5 mg g^{-1} for Cd(II) and 4.8–52.0 mg g^{-1} for Pb(II) ions whereas adsorption percentage decreased from 72.0% to 14.4% for Cd(II) (Fig. 8(a)) and 97.0% to 43.3% for Pb(II) ions (Fig. 8(b)). As increasing the initial metal ion concentration, the driving force of the metal ions toward the active adsorption sites on the adsorbent increases thus the amount of metal ion adsorbed per unit mass of the adsorbent increases. On the other hand, at higher metal ion concentrations, the saturation of the available active adsorption sites on the adsorbent surface leads to prevent further metal ion binding hence the adsorption percentages decrease (Arief et al., 2008; Jiang et al., 2010).

The equilibrium adsorption isotherms are one of the most important data in order to clarify the mechanism of the adsorption process. The relationship between the amount of Cd(II) and Pb(II) ions adsorbed onto the TIC and their equilibrium concentrations in aqueous solution were evaluated in terms of Langmuir, Freundlich, Temkin and Dubinin Radushkevich isotherm models.

The Langmuir isotherm model is valid for monolayer adsorption on a surface containing a finite number of identical sites. The Langmuir isotherm model has the following form (Langmuir, 1918);

$$q_e = \frac{bq_{max}C_e}{1 + bC_e} \tag{13}$$

where q_e (mg g^{-1}) is the amount of the metal ions adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the equilibrium metal ion concentration in aqueous solution, q_{max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the adsorption capacity and free energy or net enthalpy of adsorption, respectively. The Langmuir model in linear form;

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{14}$$

The linear plot of C_e/q_e versus C_e shows that sorption obeys the Langmuir model and the constants q_{max} and b are evaluated from slope and intercept of the linear plot, respectively.

Based on the further analysis of Langmuir equation the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by Weber and Chakkravorti (1974);

$$R_L = \frac{1}{1 + b \cdot Co} \tag{15}$$

where C_o (mg L^{-1}) is the initial amount of adsorbate and b (L mg^{-1}) is the Langmuir constant described above. There are four probabilities for the R_L value: (i) for favorable adsorption $0 < R_L < 1$, (ii) for unfavorable adsorption $R_L > 1$, (iii) for linear adsorption $R_L = 1$ and (iv) for irreversible adsorption $R_L = 0$.

The Freundlich isotherm model can be applied for modeling the adsorption on heterogeneous surfaces. The model has the form (Freundlich, 1906);

$$q_e = K_f C_e^{1/n} \tag{16}$$

where K_f is a constant related to sorption capacity (mg g^{-1}) and $1/n$ is an empirical parameter related to sorption intensity. The value of n varies with the heterogeneity of sorbent and gives an idea for the favorability of sorption process. The value of n should be less than 10 and higher than unity for favorable sorption conditions.

The Freundlich model in linear form;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{17}$$

The Freundlich constants K_f and $1/n$ can be determined from the intercept and slope of linear plot of $\ln q_e$ versus $\ln C_e$, respectively.

The Temkin isotherm model considers that the heat of the adsorption of all the molecules would decrease linearly with coverage due to adsorbate/adsorbate interactions. The Temkin isotherm is given as (Temkin and Pyzhev, 1940);

$$q_e = RT/b(\ln A \cdot C_e) \tag{18}$$

$$B = RT/b \tag{19}$$

where B (J mol^{-1}) is the Temkin constant related to heat of adsorption, A (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy, R (8.314 J mol^{-1} K^{-1}) is the universal gas constant and T (Kelvin) is the absolute solution temperature.

The Temkin model in linear form is;

$$q_e = B(\ln A) + B(\ln C_e) \tag{20}$$

The Temkin constants A and B can be determined from the intercept and slope of linear plot of q_e versus $\ln C_e$, respectively.

The Dubinin Radushkevich (D-R) isotherm model is used to determine the adsorption type; physical or chemical. The model is given as follows (Dubinin and Radushkevich, 1947);

$$q_e = q_m \exp\left(-\beta \varepsilon^2\right) \tag{21}$$

where q_e (mol g^{-1}) is the amount of metal adsorbed onto per unit mass of adsorbent, q_m (mol g^{-1}) is the monolayer adsorption capacity, β (mol^2 kJ^{-2}) is the activity coefficient related to the mean
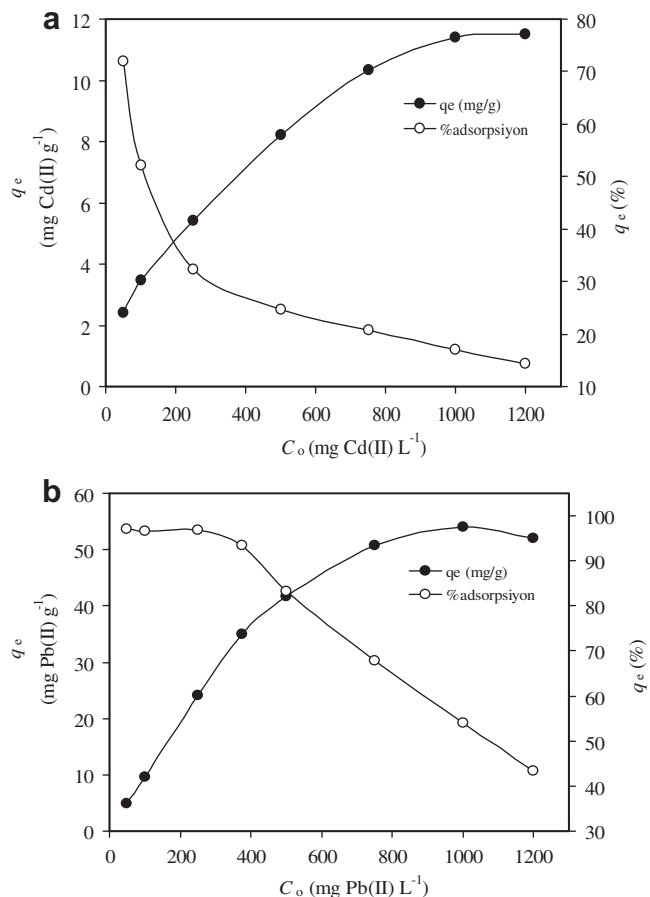

Fig. 8. a) Effect of initial Cd(II) concentration b) Effect of initial Pb(II) concentration.

sorption energy, ε is the Polanyi potential and can be calculated as following equation;

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{22}$$

where C_e (mol L^{-1}) is the equilibrium metal ion concentration in aqueous solution. The mean adsorption energy, E (kJ mol^{-1}), can be calculated using the following equation;

$$E = 1/(-2\beta)^{1/2} \tag{23}$$

The linear form of D-R isotherm model is expressed as;

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{24}$$

The D-R model constants, q_m and β, can be determined from the intercept and slope of linear plot of $\ln q_e$ versus ε^2, respectively.

The equilibrium data obtained from the adsorption of Cd(II) and Pb(II) ions onto TIC were fitted the Langmuir, Freundlich, Temkin and D-R isotherm models (Fig. 9(a) and (b)). All of the isotherm constants and correlation coefficients were calculated from the linear equations of the models and provided in Table 4. According to the Langmuir isotherm model, the maximum monolayer adsorption capacity of TIC for Pb(II) was found to be higher than for Cd(II) ions indicating that the Pb(II) ions were well adsorbed onto TIC surfaces than Cd(II) ions. Between 50 and 1200 mg L^{-1} of initial metal ions concentration, the R_L values ranged from 0.76 to 0.11 for Cd(II) ions and from 0.22 to 0.01 for Pb(II) ions then approached zero with increase in the C_o values of both metal ions, indicated that the Pb(II) and Cd(II) adsorption onto TIC is favorable under studied conditions. Furthermore n values, obtained from Freundlich

Table 4
Langmuir, Freundlich, Temkin and Dubinin Radushkevich (D-R) isotherm parameters for the adsorption of Cd(II) and Pb(II) adsorption onto TIC.

	Metal ions	
	Pb(II)	Cd(II)
Langmuir isotherm model		
q_{max} (mg g^{-1})	53.76	13.09
b (L mg^{-1})	0.069	6.48×10^{-3}
R^2	0.9990	0.9764
Freundlich isotherm model		
K_f (mg g^{-1})	7.13	0.81
n	2.82	2.58
R^2	0.8382	0.9906
Temkin isotherm model		
A (L g^{-1})	1.57	0.12
B	8.22	2.29
b (J mol^{-1})	301.41	1081.91
R^2	0.9645	0.9362
D-R isotherm model		
q_m (mg g^{-1})	134.97	20.97
β (kJ^2 mol^{-2})	0.0034	0.0046
E (kJ mol^{-1})	12.13	10.42
R^2	0.8946	0.9741

isotherm model, were higher than unity which supported the favorability of adsorption process. The mean sorption energy (E), obtained from D-R isotherm model, gives information about mechanisms of adsorption process. If E value lies between 8 and 16 kJ mol^{-1} the adsorption process takes place chemically while $E < 8$ kJ mol^{-1}, the adsorption process proceeds physically (Helfferich, 1962). The values of E were found to be 12.13 and 10.42 for Pb(II) and Cd(II) ions, respectively may suggest that the mechanisms for the adsorption of both Pb(II) and Cd(II) ions onto TIC is chemical in nature. By comparing the correlation coefficient values obtained from Langmuir, Freundlich, Temkin and D-R isotherm models, it can be concluded that the Langmuir isotherm model is more suitable for Pb(II) ions while the experimental data obtained for Cd(II) ions adsorption were fitted well to Freundlich isotherm model. This may be due to both homogeneous and heterogeneous distribution of active sites on the surface of the TIC.

4. Conclusions

The potential usage of Turkish illitic clay mineral in removal of Cd(II) and Pb(II) ions from aqueous solutions in a batch adsorption process was tested in presented study. One of the essential features of this study was to use the clay mineral without any previous activation treatment which decreases the adsorption costs down.

Adsorption characteristics of Cd(II) and Pb(II) ions onto TIC were found to be influenced by initial pH of aqueous solution, contact time, initial metal ions concentration, temperature, TIC concentration, and ionic strength. Perfect metal uptake efficiencies were obtained under operating conditions such that for Pb(II) ions by keeping the experimental conditions as follows; initial pH: 4.0, contact time: 240 min, TIC concentration: 10 g L^{-1} and initial Pb(II) concentration: 250 mg L^{-1}, nearly 100% removal efficiency was obtained. And for Cd(II) ions, the removal efficiency was reached to 78%, while the experimental conditions were as follows; initial pH: 4.0, contact time: 240 min, TIC concentration: 30 g L^{-1} and initial Cd(II) concentration: 50 mg L^{-1}. The Cd(II) and Pb(II) ions removal efficiency of the TIC was tested in the light of equilibrium, kinetics and thermodynamics parameters. The monolayer adsorption capacity of TIC was found to be 53.76 mg g^{-1} and 13.09 mg g^{-1} for Pb(II) and Cd(II) ions, respectively by using Langmuir model equations. The kinetics of both of metal ions onto TIC followed by
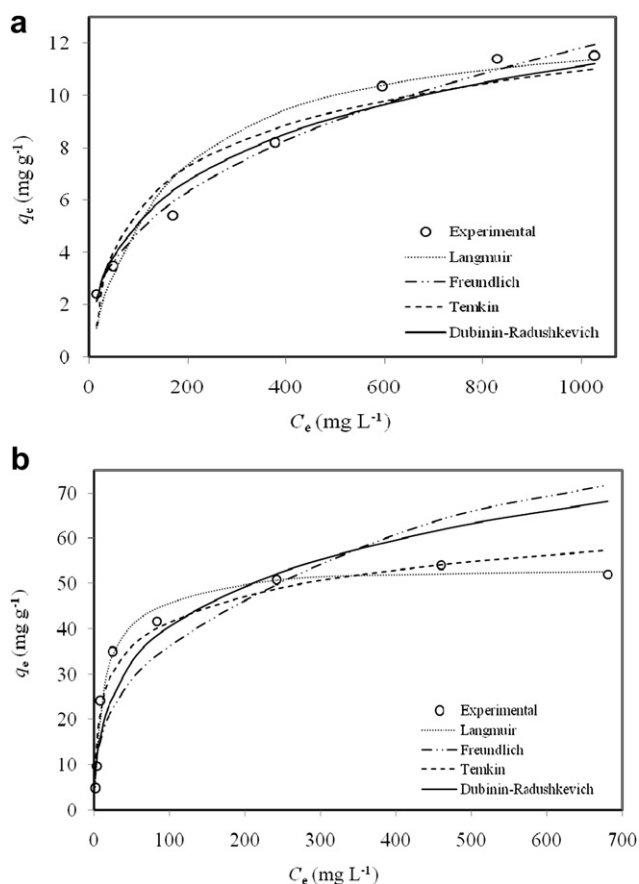

Fig. 9. Comparison of equilibrium isotherms between the experimental data and theoretical data for a) Cd(II) uptake b) Pb(II) uptake.

pseudo-second-order model. The negative ΔG values indicated that the adsorption of Cd(II) and Pb(II) ions onto TIC was feasible and spontaneous. The positive values of ΔH suggested the endothermic nature of adsorption while the positive values of ΔS revealed the increasing randomness at the solid/solution interface during the adsorption process.

In the view of these results, it can be concluded that the TIC can be utilized as a low cost and effective adsorbent in removal of Cd(II) and Pb(II) ions from aqueous solutions.

Conflict of interest

The authors have declared no conflicts of interest.

Acknowledgements

References

Ahalya, N., Ramachandra, T.V., Kanamadi, R.D., 2003. Biosorption of heavy metals. Res. J. Chem. Environ. 7, 71–78.

Amarasinghe, B.M.W.P.K., Williams, R.A., 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem. Eng. J. 32, 299–309.

APHA, 1985. Standard Methods for the Examination of Water and Wastewater, eighteenth ed.. American Public Health Association, Washington, DC.

Arief, V.O., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S., 2008. Recent Progress on Biosorption of heavy metals from Liquids using low cost Biosorbents: characterization, Biosorption parameters and mechanism studies. Clean 36 (12), 937–962.

Aydın, H., Bulut, Y., Yerlikaya, C., 2008. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. J. Environ. Manage. 87, 37–45.

Bergaya, F., Vayer, M., 1997. CEC of clays: measurement by adsorption of a copper ethylenediamine complex. Appl. Clay Sci. 12, 275–280.

Bhattacharyya, K.G., Gupta, S.S., 2006. Pb(II) uptake by kaolinite and montmorillonite in aqueous medium: influence of acid activation of the clays. Colloid Surf. A 277, 191–200.

Bhattacharyya, K.G., Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv. Colloid Interface Sci. 140, 114–131.

Bulut, E., Özacar, M., Şengil, İ.A., 2008. Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design. Micropor. Mesopor. Mat 115, 234–246.

Cheung, C.W., Porter, J.F., McKay, G., 2001. Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. Water Res. 35, 605–612.

Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J., Sanchez-Polo, M., 2007. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review. J. Environ. Manage. 85, 833–846.

Dubinin, M.M., Radushkevich, L.V., 1947. Equation of the characteristics curve of activated charcoal. Chem. Zent 1, 875.

Echeverria, J.C., Zarranz, I., Estella, J., Garrido, J.J., 2005. Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of lead on illite. Appl. Clay Sci. 30, 103–115.

Eloussaief, M., Benzina, M., 2010. Efficiency of natural and acid-activated clays in the removal of Pb(II) from aqueous solutions. J. Hazard. Mater. 178, 753–757.

Freundlich, H.M.F., 1906. Über die adsorption in lösungen. Z. Phys. Chem. 57, 385–470.

Helfferich, F., 1962. Ion Exchange. McGraw-Hill, New York.

Ho, Y.S., McKay, G., 1998. Kinetic models for the sorption of dye from aqueous solution by wood. J. Environ. Sci. Health Part B. Process Saf. Environ. Prot. 76, 183–191.

Jiang, M., Jin, X., Lu, X., Chen, Z., 2010. Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay. Desalination 252, 33–39.

Katsumata, H., Kaneco, S., Inomata, K., Itoha, K., Funasaka, K., Masuyama, K., Suzuki, T., Ohta, K., 2003. Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials. J. Environ. Manage. 69, 187–191.

Lagergren, S., 1898. About the theory of so-called adsorption of soluble substance. Kung Sven. Veten. Hand 24, 1–39.

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

Maliyekkal, S.M., Shukla, S., Philip, L., Nambi, I.M., 2008. Enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules. Chem. Eng. J. 140, 183–192.

Ozdes, D., Gundogdu, A., Kemer, B., Duran, C., Senturk, H.B., Soylak, M., 2009. Removal of Pb(II) ions from aqueous solution by a waste mud from copper mine industry: equilibrium, kinetic and thermodynamic study. J. Hazard. Mater. 166, 1480–1487.

Potgieter, J.H., Potgieter-Vermaak, S.S., Kalibantonga, P.D., 2006. Heavy metals removal from solution by palygorskite clay. Miner. Eng. 19, 463–470.

Sari, A., Tuzen, M., Citak, D., Soylak, M., 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay. J. Hazard. Mater. 149, 283–291.

Smith, J.M., Van Ness, H.C., 1987. Introduction to Chemical Engineering Thermodynamics, fourth ed. McGraw-Hill, Singapore.

Sposito, G., Skipper, N.T., Sutton, R., Park, S., Soper, A.K., Greathouse, J.A., 1999. Surface geochemistry of the clay minerals. Proc. Natl. Acad. Sci. 96, 3358–3364.

Stanley, L.C., Ogden, K.L., 2003. Biosorption of copper (II) from chemical mechanical planarization wastewaters. J. Environ. Manage. 69, 289–297.

Sthiannopkao, S., Sreesai, S., 2009. Utilization of pulp and paper industrial wastes to remove heavy metals from metal finishing wastewater. J. Environ. Manage. 90, 3283–3289.

Temkin, M.J., Pyzhev, V., 1940. Recent modifications to Langmuir isotherms, Acta Physiochim. USSR 12, 217–222.

Tertre, E., Berger, G., Simoni, E., Castet, S., Giffaut, E., Loubet, M., Catalette, H., 2006. Europium retention onto clay minerals from 25 to 150 °C: experimental measurements, spectroscopic features and sorption modeling. Geochim. Cosmochim. Acta 70, 4563–4578.

Unuabonah, E.I., Adebowale, K.O., Olu-Owolabi, B.I., Yang, L.Z., Kong, L.X., 2008. Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: equilibrium and thermodynamic studies. Hydrometallurgy 93, 1–9.

Weber Jr., W.J., Morriss, J.C., 1963. Kinetics of adsorption on carbon from solution. J. Sanitary Eng. Div. Am. Soc. Civ. Eng. 89, 31–60.

Weber, T.W., Chakkravorti, R.K., 1974. Pore and solid diffusion models for fixed bed adsorbers. AIChE J. 20, 228–238.