



Removal of Zn(II), Cd(II) and Cu(II) Ions from Aqueous Solution by Nano-Structured Kaolinite

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The adsorption of Zn(II), Cu(II) and Cd(II) ions from aqueous solution onto nano-structured kaolinite (NSK) has been investigated. In this study, the effects of adsorbent dose, solution pH, initial metal concentration, contact time and temperature were determined. Thermodynamic parameters, the negative values of ΔG° revealed that the adsorption process was spontaneous and endothermic. The Langmuir and Freundlich isotherm models were employed to fit the isothermal adsorption. The monolayer adsorption capacity of Zn(II), Cu(II) and Cd(II) ions was 52.63, 45.87 and 41.32 mg/g, respectively. The results of this study showed that nano-structured kaolinite can be efficiently used as a low-cost alternative for the removal of Zn(II), Cu(II) and Cd(II) ions from aqueous solutions.

Keywords: Zn(II) ions, Cu(II) ions, Cd(II) ions, Adsorption, Nano-structured kaolinite, Thermodynamic.

INTRODUCTION

Heavy metals are commonly used in various industrial processes such as mining, metal cleaning, plating baths, pulp, painting, paper board mills, electroplating, fertilizer industries and pharmaceuticals which are the potential sources of zinc(II), Cu(II) and Cd(II) ions in industrial effluents. According to WHO the maximum acceptable concentration of heavy metals in drinking water is 5 mg/L [1]. Removal of Zn(II), Cu(II) and Cd(II) ions from the environment is very important to prevent its deleterious impact on ecosystem and on public health. Different methods of treating effluent containing Zn(II), Cu(II) and Cd(II) ions have been developed over years which include electrocoagulation, modified activated carbon, cation exchange, electrochemical treatment, membrane separation, reverse osmosis and sonochemical route [2-6]. However, some of these techniques have some disadvantages such as complicated treatment process, toxic by-products, energy consumption and high cost. Adsorption is one of the effective and economic methods and most useful for the removal of toxic heavy metals from aqueous solution. Kaolinite is a 1:1 clay mineral including a tight interlayer structure with the ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ have found use in heavy metals removal from aqueous solution and wastewater. Removal of Zn(II), Cu(II) and Cd(II) ions from aqueous solution was investigated by natural kaolinite clay [7-13], kaolinite supported by polyphosphate [14], kaolinite-supported zero-valent iron nanoparticles [15], kaolinite impregnated by *E. coli* biofilm supported on kaolin [16],

polyphosphate-modified kaolinite [17], amino-functionalized magnetite/kaolin clay [18] and Na-form of kaolin [19].

In the present work, a nano-structured kaolinite (NSK) is developed from Jordanian natural kaolinite clay for removal Zn(II), Cu(II) and Cd(II) ions from aqueous solution.

EXPERIMENTAL

Preparation of nanostructured kaolinite clay: The raw kaolinite clay (RKC) samples were collected from the deposits of Batn El-Ghoul area in southern Jordan. Kaolinite clay was rolled crushed by a jaw crusher to obtain grains of kaolinite clay with dimensions between (0.08 and 2.5 mm) and then ground in small grains using a vibrating disc mill (model RS 200, Retsch-Germany) and sieved through 100 μm , 325 M to obtain 44 μm -sized fractions. Dried powder kaolinite clay was treated with hydrochloric acid (20 %) under continuous stirring for 12 h and then left 24 h at room temperature. An aqueous coloured acid solution which formed was separated from kaolinite by decantation and washing with distilled water. Afterwards, the obtained kaolinite was treated with hydrogen peroxide (30 %) under stirring for 2 h at room temperature. The final powder was washed and dried at a temperature of 80 °C and then examined by X-ray fluorescence, X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy.

Characterization techniques: The X-ray diffraction patterns of raw and nano-structured kaolinite clay were

reordered by Shimadzu XRD-6000 with $\text{CuK}\alpha$ radiation $\lambda = 1.5405 \text{ \AA}$ over a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 80^\circ$). Chemical analysis has been performed by X-ray fluorescence of Shimadzu, Japan. Scanning electron microscopy analysis was done using Quanta FEI 450 SEM machine. Fourier transform infrared spectroscopy (FT-IR, IR Prestige 21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the nano-structured kaolinite clay. The specific surface areas of raw and nano-structured kaolinite clay were estimated by a surface analyzer (Quanta chromosorb) and BET method. The concentrations of metal ions in the solutions before and after equilibrium were determined by a Shimadzu AAS6300 atomic absorption spectrometer. The pH of the solution was measured with a WTW pH meter using a combined glass electrode.

Batch adsorption study: Stock solutions of Zn(II), Cd(II) and Cu(II) solutions (1000 mg/L) were prepared by dissolving appropriate amounts of zinc sulfate, cadmium nitrate and copper chloride in 1000 mL of deionized water. Different concentrations ranging from 10-100 mg/L were prepared from the stock solutions by serial dilution. In each experimental study, an accurately weighed quantity of nano-structured kaolinite was added to 100 mL of aqueous solution taken in a 250 mL conical flask and the reaction mixture was agitated at 120 rpm in a rotary shaker. The analysis of sample was done after filtering by Whitman 42 filter paper. Each determination was repeated three times and the results obtained were their average value. The data obtained in these batch studies were used to calculate the percentage removal (R %) and equilibrium quantity (q_e) of Zn(II), Cu(II) and Cd(II) ions by using the following mass balance relationships:

$$R (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{M} \times V \quad (2)$$

where C_o and C_e are the initial and final equilibrium concentration (mg/g), V is the volume of solution (L) and M is the weight of the adsorbent (g).

RESULTS AND DISCUSSION

X-ray fluorescence (XRF) and diffraction spectroscopy (XRD) analysis: The mineralogical composition of the dried natural raw kaolinite and nano-structured kaolinite is presented in Table-1.

X-ray diffraction analysis of the prepared nano-structured kaolinite is illustrated in Fig. 1. X-ray diffraction showed that the kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5]$, is the main mineral found with other trace minerals such as dickite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ and quartz (SiO_2). The diffraction intensities were compared with the kaolinite clay standard (JCPDS-No. 80-2186). Particle size of the nanostructured kaolinite was calculated using Debye-

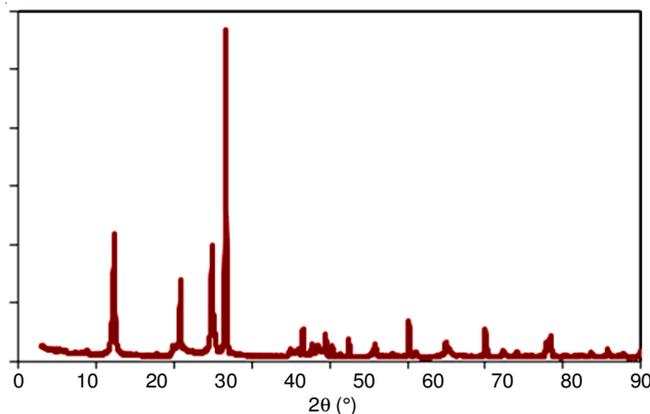


Fig. 1. XRD pattern of prepared nano-structured kaolinite (NSK)

Scherrer formula [20,21]. The average particle size was found to be 40 nm.

The specific surface area of the natural and nano-structured kaolinite clay was found to be $10.2 \text{ m}^2/\text{g}$ and $24.6 \text{ m}^2/\text{g}$, respectively by using a surface analyzer and BET method.

FT-IR spectra of nano-structured kaolinite: Fig. 2 showed the broad bands observed at 3691 , 3618 and 3417 cm^{-1} are due to the O-H stretching vibration of silanol (Si-OH) groups and HO-H vibration of water molecules adsorbed on the silica surface. The spectral bands at 1624 cm^{-1} reflect the bending H-OH bond of water molecules retained in the silica matrix. The bands observed at 910 , 794 , 690 , 528 and 462 cm^{-1} represent the Si-O-Si groups of tetrahedral sheet and deforming and bending modes of Si-O bond, respectively.

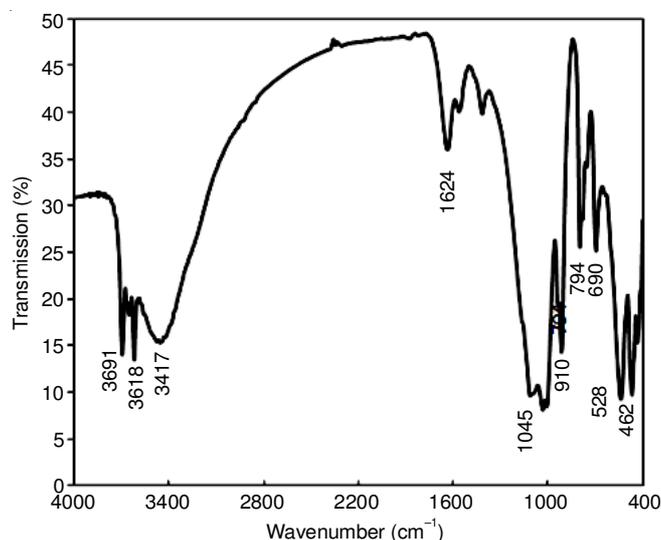


Fig. 2. FT-IR spectrum of prepared nano-structured kaolinite clay (NSK)

Scanning electron microscopy (SEM) analysis: Nano-structured kaolinite was mainly composed of Nano platelets with the average size in the range of 20 nm. Fig. 3 showed a quite dense morphology comprised of randomly oriented

TABLE-1
X-RAY FLUORESENE (XRF) ANALYSIS OF NATURAL KAOLINITE (NK) AND NANO-STRUCTURED KAOLINITE (NSK)

Metal	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI
Raw kaolinite	64.89	24.11	1.18	0.62	0.32	0.94	0.12	0.12	8.12
Nano-structured kaolinite	71.45	22.68	0.11	0.32	—	—	—	—	—

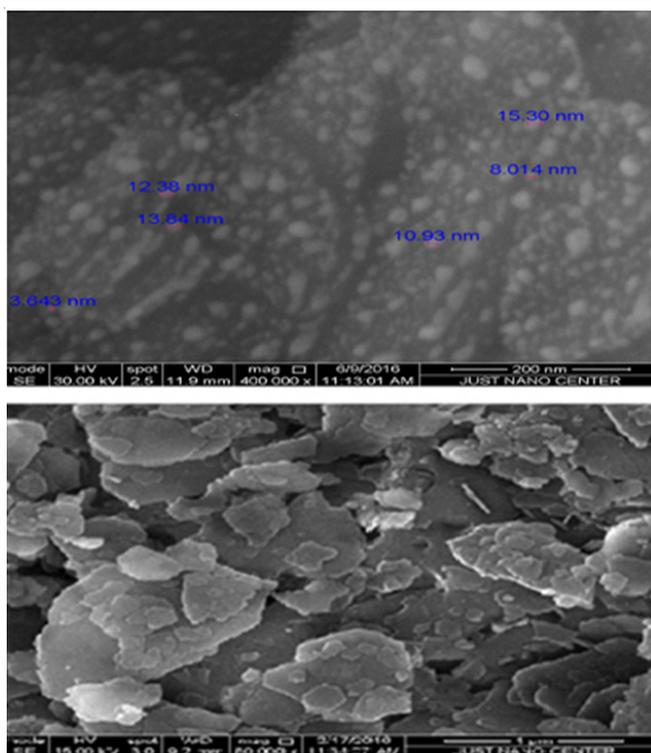


Fig. 3. Scanning electron microscopy images of nano-structured kaolinite

overlapping, thin plates of nano-structured kaolinite where the individual plates appear to have a lateral dimension of less than one micron. A good estimate of the platelets thickness is in the range of 10 to 30 nm. However, it is possible that the thicker platelets may consist of several thinner platelets aggregated to form nano-platelets networks, which agrees well with the XRD results.

Effect of pH: The pH of solution was varied from 1.0 to 8.0. Uptake of Zn(II), Cu(II) and Cd(II) ions depended on pH, the optimum Zn(II), Cu(II) and Cd(II) removal efficiency occurred at pH 5.5-7.0 and then decreased at higher pH. Fig. 4 presents the adsorption of Zn(II), Cu(II) and Cd(II) onto nano-structured kaolinite with an increase of pH from 2 to 8. Generally, the adsorption of Zn(II), Cu(II) and Cd(II) was increased with the pH of solutions increasing, for example, 98.8 % Zn(II) at pH of 6, 94 % Cu(II) at pH of 7 and 98 % Cd(II) at pH of 6.5 can be removed. This may be attributed to the surface of the nano-structured kaolinite containing a large

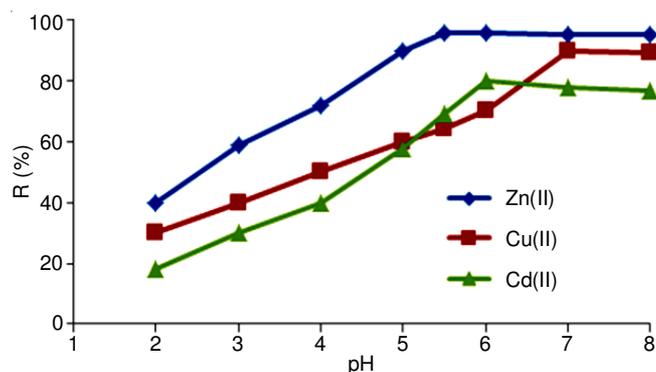


Fig. 4. Effect of pH on the adsorption of Zn(II), Cu(II) and Cd(II) onto nano-structured kaolinite

number of active sites. Consequently, it may become positively charged at low pH, leading to increase the competition between H^+ and the metal ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction. However, for the adsorption of Zn(II), the amount adsorbed was increased up to pH 5.5 after which it was near constant. Similar results were observed using nano-structured kaolinite for the adsorption of Cu(II) and Cd(II). In this study, the pH at 7 for the removal of Zn(II), Cd(II) and Cu(II) was determined.

Effect of nano-structured kaolinite dosage: The adsorption efficiency of Zn(II), Cu(II) and Cd(II) ions as a function of adsorbent dosage was investigated. The percentage of the Zn(II), Cu(II) and Cd(II) ions adsorption steeply increases with the adsorbent loading up to 0.5 g/0.1/L. This result can be explained by the fact that the adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose. The maximum adsorption was attained at adsorbent dosage, 0.5 g/0.1/L. Therefore, the optimum adsorbent dosage was taken as 0.5 g/0.1/L for further experiments. This can be explained as when the adsorbent ratio is small, the active sites for binding zinc and copper ions on the surface of nano-structured kaolinite is less, so the adsorption efficiency is low. As the adsorbent dose increased, more active sites to bind metal ions, thus it results an increase in the adsorption efficiency until saturation.

Effect of contact time on the removal of metal ions: The rate of adsorption is important for designing batch adsorption experiments. Therefore, The effect of contact time on the adsorption of Zn(II), Cu(II) and Cd(II) was investigated at different time intervals in the range of 10-120 min. The adsorbent loading was kept at a constant value 0.5 g/0.1 L and a contact time of 120 min was employed. Adsorption equilibrium of the metal ions studied was achieved between 10 and 40 min. Fig. 5 showed the removal of Zn(II), Cu(II) and Cd(II) ions became constant at 30 min. In this study, 96 % of Zn(II), 80 % of Cu(II) and 69 % of Cd(II) were adsorbed

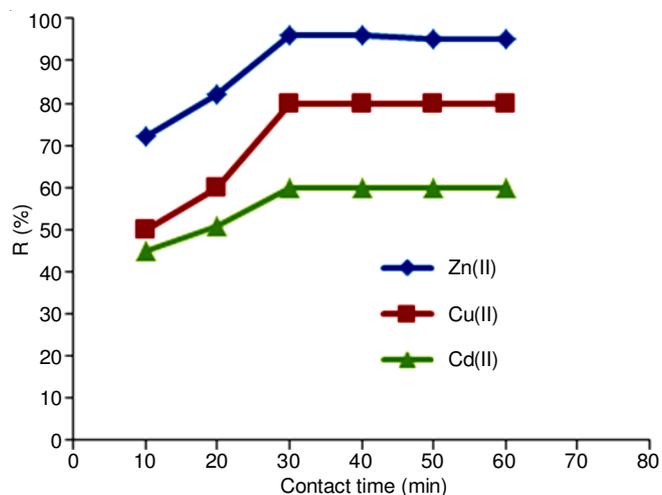


Fig. 5. Effect of contact time on amount of adsorption of Zn(II), Cu(II) and Cd(II) onto nano-structured kaolinite at temperature of solution 30 °C

on the nano-structured kaolinite when the equilibrium was reached at 30 min. On the basis of these results, it can be observed that nano-structured kaolinite can be used to remove these metal ions, however, the removal capacity for different metal ions on the kaolinite clay was in order of Zn(II) > Cu(II) > Cd(II). It indicated that Nano-structured kaolinite showed stronger preference for Zn(II) than for Cu(II) and Cd(II). Thus, the contact time of 30 min was optimized and selected for the rest of the study.

Effect of temperature on removal of Zn(II), Cu(II) and Cd(II) ions removal: Temperature dependence of Zn(II), Cu(II) and Cd(II) adsorption onto nano-structured kaolinite was carried out at 293, 303, 313 K. The percent removal of Zn(II), Cu(II) and Cd(II) ions from aqueous solution increases with an increase in temperature, indicating the adsorption is endothermic process.

Adsorption isotherms: Adsorption isotherms describe the fraction of sorbate molecules that partitioned between solution and solid phase at equilibrium. Adsorption of Zn(II), Cu(II) and Cd(II) ions onto nano-structured kaolinite were modeled by Langmuir and Freundlich isotherms [22,23].

The Langmuir model assumes uniform energies of adsorption on the surface. The linear form of Langmuir isotherm equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (3)$$

The Langmuir constant q_{\max} (mg/g) is a measure of the monolayer adsorption capacity (q_e) of nano-structured kaolinite. Langmuir constant K_L denotes the adsorption energy. By plotting of C_e/q_e versus C_e (Fig. 6), the Langmuir parameters were calculated from the slope and intercept of the isotherm and are listed in Table-2. The high value of the regression correlation coefficient ($R^2 = 0.9999$) is obtained which indicates a good agreement between the experimental values and isotherm parameters.

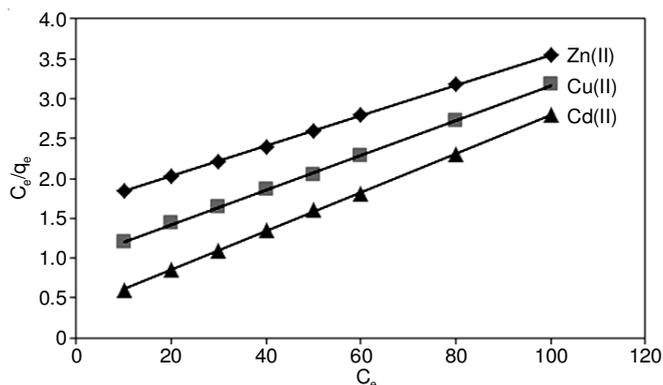


Fig. 6. Langmuir isotherm for Zn(II), Cu(II) and Cd(II) ions onto nano-structured kaolinite

Metal	q_{\max} (mg/g)	K_L (L/g)	R^2	n (g/L)	K_F (mg/g)	R^2
Zn(II)	52.63	0.03	0.9999	1.49	1.15	0.95618
Cu(II)	45.87	0.02	0.9994	1.26	0.44	0.95790
Cd(II)	41.32	0.01	0.9996	1.31	0.26	0.95640

Equilibrium parameter or separation factor (R_L) is defined by the following equation:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (4)$$

where C_0 is the initial Zn(II) and Cu(II) ions concentration and K_L is the Langmuir constant. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The R_L for Zn(II), Cu(II) and Cd(II) ions adsorption by nano-structured kaolinite was found to be 0.25-0.77 for concentration of 10-100 mg/L of metal ions. They are in the range of 0-1 which indicates the favourable adsorption.

The Freundlich isotherm model has the following form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$ (Fig. 7). The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The Freundlich parameters were calculated from the slope and intercept of the isotherm and are listed in Table-2.

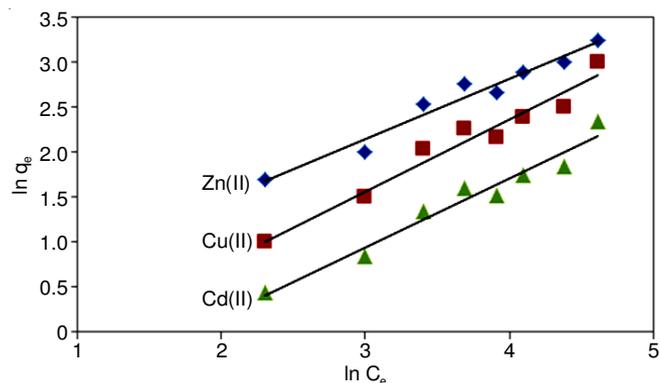


Fig. 7. Freundlich isotherm for Zn(II), Cu(II) and Cd(II) ions onto nano-structured kaolinite

Thermodynamic parameters: The values of enthalpy change (ΔH°), the free energy change (ΔG°) and entropy change (ΔS°) for the adsorption of Zn(II), Cu(II) and Cd(II) onto nano-structured kaolinite were calculated from the following equations [12,24]:

$$K_d = \frac{C_a}{C_e} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

where C_a and C_e are mg of adsorbate adsorbed per liter and the equilibrium concentration of solution in mg/L. K_d is the distribution coefficient for the adsorption. T (K) is the temperature and R is the gas constant (8.314 J/mol K). From slope and intercept of plot $\ln K_d$ vs. $1/T$, the calculated values of thermodynamic parameters K_d , ΔG° , ΔH° and ΔS° for the

adsorption of zinc(II), Cu(II) and Cd(II) ions onto nano-structured kaolinite are listed in Table-3. The negative values of the change in standard Gibbs free energy (ΔG°) at all temperatures studied reflect the feasibility of the adsorption process and the positive values of the standard enthalpy (ΔH°) indicated the endothermic adsorption process. The positive values of the standard entropy (ΔS°) suggests increased randomness of solid-solution interface during the adsorption of Zn(II), Cu(II) and Cd(II) ions onto nano-structured kaolinite (NSK).

TABLE-3
THERMODYNAMIC PARAMETERS OF METAL IONS
ONTO NANO-STRUCTURED KAOLINITE

Metal ion	T (K)	K_d	$-\Delta G^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
Zn(II)	293	5.13	3.98	11.21	51.85
	303	6.02	4.52		
	313	6.88	5.02		
Cu(II)	293	4.22	3.51	12.62	55.15
	303	5.21	4.16		
	313	5.87	4.61		
Cd(II)	293	3.49	3.05	14.12	58.61
	303	4.26	3.65		
	313	5.05	4.22		

Desorption studies: Desorption studies explore the possibility of recycling the nano-structured kaolinite and recovery of Zn(II), Cu(II) and Cd(II) resource. Desorption studies were conducted by mixing 0.5 g of nano-structured kaolinite with 25 mL of 40 mg/L metal ions concentration. Desorption studies were carried out using 0.1 M HNO₃ solution as stripping agent. From our sorption experiments, metal loaded on nano-structured kaolinite c was transferred to Erlenmeyer flasks and shaken with 50 mL of 0.1 M HNO₃ acid for 4 h. Then the sorbents were taken out from the solution and washed with deionized water and the filtrate analyzed for desorbed metal ions. Adsorption-desorption processes were repeated three times using the same sorbents. The total loss amount of metal released from sorbents varied between 1 to 3 %.

Conclusion

The potential of nano-structured kaolinite for the removal of Zn(II), Cu(II) and Cd(II) ions from aqueous solutions was dependent on the adsorption process, such as pH, initial metal ions concentration, adsorbent dose, contact time and temperature. The data obtained from thermodynamic studies were used to calculate the thermodynamic quantities, such as ΔG° , ΔH° and ΔS° of adsorption. The results indicated that Zn(II), Cu(II) and Cd(II) adsorption onto nano-structured kaolinite was found to be spontaneous and endothermic. The equilibrium data have been analyzed using Langmuir isotherm. The characteristic parameters for isotherm and related correlation coefficient, R² were determined. The Langmuir adsorption isotherm was demonstrated to provide the best correlation for the adsorption of metal ions onto nano-structured kaolinite. It can be concluded that since the nano-structured kaolinite is available, low-cost adsorbent and has a considerable high adsorption capacity, it may be treated as an alternative adsorbent for the treatment of electroplating wastewater containing Zn(II), Cd(II) and Cu(II) ions.

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