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Adsorptive removal of Pb(II) and Cd(II) ions from aqueous solution onto modified Hiswa iron-kaolin clay: Equilibrium and thermodynamic aspects

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In view of promising adsorption efficiency of clay based materials, a modified iron-kaolin clay was used as an adsorbent of Pb(II) and Cd(II) ions from aqueous solutions. The effects of various experimental parameters, such as initial metal ions concentration, contact time, temperature and pH were investigated. The Langmuir and Freundlich adsorption isotherm models were applied to the experimental equilibrium data at different temperatures. The maximum adsorption capacities of Pb(II) and Cd(II) ions were 76.92 and 75.19 (mg/g), respectively. Thermodynamic parameters such as the change of Gibbs free energy, enthalpy and entropy of adsorption were also calculated and it was found that the lead and cadmium ions uptake by modified kaolin clay is endothermic and spontaneous in nature.

Capsule Summary: A modified iron-kaolin clay was used as an adsorbent of Pb(II) and Cd(II) ions removal as a function of various process variables and modified clay furnished promising adsorption capacity for Pb(II) and Cd(II) ions.

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INTRODUCTION

Water contamination, with heavy toxic metals has become an environmental issue. Different methods and techniques have been developed to remove these heavy toxic metals from water include chemical precipitation, conventional coagulation, reverse osmosis, ion-exchange and adsorption. Nowadays, nanomaterials have provided a promising technique for removal of toxic heavy metal ions from water, aqueous solutions and industrial wastewater, due to its low cost-effective, high efficiency, and simple to operate. Different natural minerals and the composites are studied such as montmorillonite (Barbier et al., 2000), zeollitic tuff (Budianta et al., 2020), bentonite (Mohajeri et al., 2018), expanded perlite (Torab-Mostaedi et al., 2010), natural zeolite (Panayotova, M., Velikov, B., 2002), natural diatomite (ElSayed, 2018), natural clay (Bedelean et al., 2009), activated alumina (Naiya et al., 2009), activated phosphate rock (Elouaer et al., 2008), ball clay (Rao and Kashifuddin, 2016), hydroxyapatite porous materials (Ramdani et al., 2020), manganoxide minerals (Sónmezay et al., 2012), natural phosphate (Yaacoubia et al., 2014), natural calcite (Yavuz et al., 2007), Sepiolite (Padilla et al., 2011), polyvinyl alcohol-modified kaolinite clay (Unuabonah et al., 2008), hydroxyapatite/chitosan composites (Park et al., 2015), polyphosphate-modified kaolinite clay (Amer et al., 2010), alkaline modification of kaolin (David et al., 2020), Nano kaolinite (Alasadi et al., 2019) unmodified and modified kaolinite clay (Al-Essa and Khalili, 2018; Abukhadra et al., 2019), magnetic core–zeolitic shell nanocomposites (Padervand and Gholami, 2013), natural mixture of kaolinite-albite-montmorillonite-illite clay (Eba et al., 2011), kaolinite and montmorillonite surfaces (Gupta and Bhattacharyya, 2008), Al(13)-pillared acid-activated montmorillonite (Yan et al., 2008). hydroxyapatite/alginate/gelatin nanocomposites (Sangeetha et al., 2018), Iron nanocomposite and modified by Fe-S nanoparticles (Shahryari et al., 2019), thiol-lignocellulose sodium bentonite (TLSB) nanocomposites (Zhang et al., 2020), lignocellulose-g-acrylic acid/montmorillonite nanocomposite (Du et al., 2016), EPS-montmorillonite composites (Yan et al., 2019), nanocomposites Fe_3O_4@SiO_2–EDTA (Gong and Tang, 2020) and magnetite- kaolinite nanocomposite (Lasheen et al., 2016).

In this research work, Hiswa natural kaolin clay, south Jordan was modified with hydrochloric acid and ammonium hydroxide to magnetite/kaolinite composite for adsorption of Pb(II) and Cd(II) ions from aqueous solution.

MATERIAL AND METHODS

Materials

Natural kaolin clay samples were collected from Hiswa deposits located south Jordan. Kaolin clay rocks were rolled crushed by a jaw crusher to obtain grains of kaolin with dimensions between 0.08 and 2.5 mm and then sieved to obtain 0.5–2 mm sized fraction. This fraction was washed with distilled water to remove soluble elements and dried at 105°C. Dried kaolin clay was treated with concentrated hydrochloric acid (37%) with agitation from time to time and left overnight. Later, an aqueous solution of NH_4OH is added drop wise to precipitate iron chloride as magnetite - kaolin clay. This method was repeated twice before the sample was washed thoroughly with de-ionized water and dried in an oven at 105 °C for 4 h. Once the Fe_3O_4/kaolinite composite was examined by X-ray fluorescence (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR) techniques.

Preparation of Pb(II) and Cd(II) solutions

Stock solutions of 1000 mg/l PbIII) and Cd(II) ions were prepared by appropriate dilutions of the stock solution immediately prior to their use. Standard acid of 0.1 M HNO_3 and a base solution of 0.1M NaOH were used for pH adjustment. All of the reagents were of analytical grade and used without further purifications.

Adsorption isotherms

Adsorption equilibrium was obtained by shaking 0.5-1.0 g of dry adsorbent Fe_3O_4/kaolinite composite in a series of 100 mL flasks containing 20 mL of initial concentration of Pb(II) and Cd(II) ions ranging from 5 to 120 mg/L for 120 min. The initial pH value of metal ions solution was adjusted from 1 to 7.0 with either 0.01 M HNO_3 or 0.01 M NaOH at temperatures (293.15, 303.15, and 313.15) K. Flasks were agitated on a shaker at a 350 rpm constant shaking rate for 120 min to ensure equilibrium was reached and filtered. The supernatant was analyzed for lead and cadmium by a sequential plasma emission spectrometer (ICPS-7510, Shimadizu). Each experiment was run in triplicate, and mean values are reported. The Pb(II) and Cd(II) percent removal (%) and adsorption capacity was calculated using Eq. 1-2, respectively.

$$\text{Percent removal (\%R)} = \frac{C_o - C_e}{C_o} \, x \, 100 \quad (1)$$

$$qe = \frac{C_o - C_e}{M} \, x \, V \quad (2)$$

Where, C_o is the initial concentration, C_e is the equilibrium concentration of metal ions, q_e is the adsorption at equilibrium (mg/g), M is the mass of adsorbent and V is the volume of solution.

RESULTS AND DISCUSSION

X-ray fluorescence analysis (XRF) analysis

X-ray fluorescence analysis of natural Hiswa kaolin clay and modified kaolin clay are listed in Table 1. XRF analysis showed that the kaolin clay and modified, both have a high percent of iron oxide.

Effect of pH value

The effect of pH solutions on the adsorption percent removal of metals onto the Fe_3O_4/kaolinite composite is shown in Fig. 1. The removal percent (%R) of Pb(II) and Cd(II) ions increases with increasing pH from 1.0 to 5.5 and then decreases to reach pH 7.0. The maximum percent removal was observed around pH 5.5 at all temperatures, which decreased beyond this pH value.

Effect of contact time and temperature

Effect of contact time and temperature on the adsorption of Pb(II) and Cd(II) ions onto Fe_3O_4/kaolinite nanocomposite is shown in Fig. 2. The percent removal of Pb(II) and Cd(II) ions increases with contact time until equilibrium is attained between the amount of metal ions onto nanocomposite increases with contact time from (0–60) min and then becomes almost constant up to the end of the experiment. It can be concluded that the binding of metal ions with modified kaolin clay is high at initial stages and becomes almost constant after an optimum contact time of 120 min.

Table 1: XRF analysis of natural kaolin clay and the modified kaolin clay

Metal oxide	Raw kaolin clay (Hiswa Clay)	Modified kaolin clay
SiO_2	51.24	74.24
Al_2O_3	26.45	16.19
Fe_2O_3	8.14	9.43
TiO_2	0.89	ND
Na_2O	0.06	ND
CaO	0.08	ND
MgO	0.14	ND
K_2O	1.08	ND
P_2O_5	0.05	ND
SO_3	0.64	ND
LOI	9.92	ND
Total	98.69	99. 86

Table 2: Langmuir and Freundlich constants for the adsorption of Pb(II) and Cd(II) ions

Isotherms		Pb(II)	Cd(II)
Langmuir			
	q_{max}	76.92	75.19
	K_L	0.038	0.026
	R^2	0.9999	0.9999
Freundlich			
	K_F	2.867	3.399
	n	1.274	1.181
	R^2	0.9956	0.9975

Table 3: Thermodynamic parameters for metal ions onto adsorbent

Metal ions	T/K	$\ln K_d$	ΔG^o (KJ/Mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol K)
Pb(II)	293	1.8406	4.48	11.86	55.94
	303	2.0015	5.04		
	313	2.1518	5.59		
Cd(II)	293	1.6074	3.91	12.22	55.26
	303	1.7544	4.42		
	313	1.9286	5.02		

Effect of adsorbent dose

Effect of adsorbent dose of nanocomposites on removal of Pb(II) and Cd(II) ions increased very rapidly with an increase in dosage of Fe_3O_4/kaolinite nanocomposites from (0.1–0.9) g/L and a marginal increase was observed on further increase in the adsorbent dose. Adsorbent dose of 0.5 g/L, gave maximum removal percent of 99.2 % were observed at 303.15 K. The increase in of Pb(II) and Cd(II) ions removal may be attributed to the fact that, with an increase in the adsorbent dose, more adsorbent surface and adsorption sites were available for the metal ions to be adsorbed.

Adsorption isotherms

Langmuir isotherm

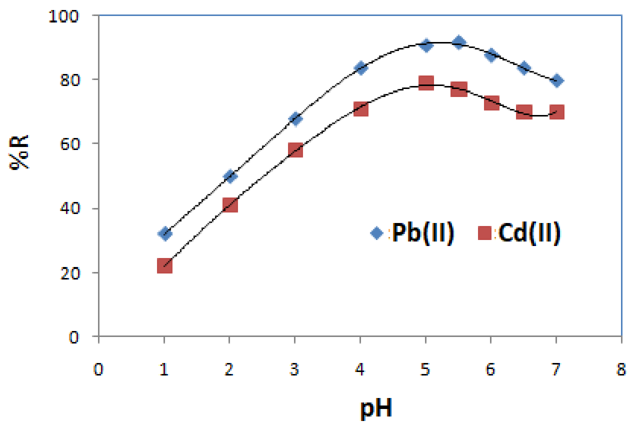

Fig. 1: Effect of pH on the percent removal of Pb(II) and Cd(II) ions from aqueous solution

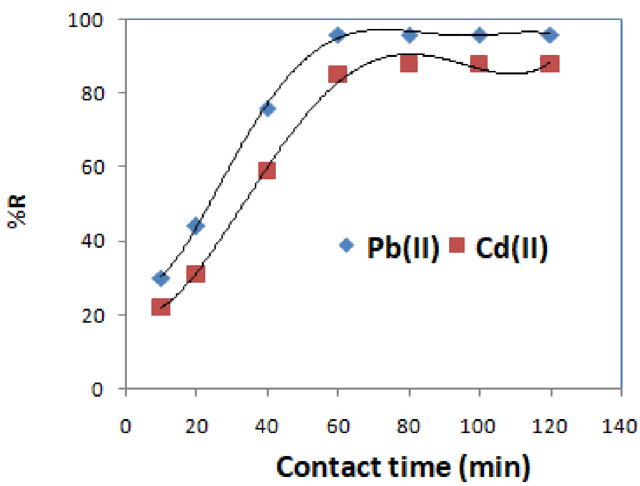

Fig. 2: Effect of contact time on percent removal of Pb(II) and Cd(II) ions

Langmuir isotherm assumes monolayer adsorption onto a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described (Eq. 3) (Langmuir, 1918).

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

Where K_L is the Langmuir constant related to the energy of adsorption and q_{max} is the maximum adsorption capacity (mg/g). Values of Langmuir parameters, q_{max} and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Fig. 3. Values of q_{max}, K_L and regression coefficients R^2 are in Table 1. These values for magnetite/kaolinite nanocomposite adsorbent indicated that Langmuir model describes the adsorption phenomena as favorable.

Freundlich isotherm model

This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form (Eq. 4) (Freundlich and Hellen, 1939).

$$lnq_e = lnK_F + \frac{1}{n}\ln C_e \qquad (4)$$

Where, K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined by plotting $\ln q_e$ versus $\ln C_e$, Fig. 4. if n =1, then adsorption is linear; if n < 1, then adsorption is achemical process, if n > 1, then adsorption is a physical process (Table 2).

Thermodynamic study

Enthalpy change (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o) for the adsorption of Pb(II) and Cd(II) ions onto Fe_2O_3/kaolinite nanocomposite were calculated from the following Eqs. 5-7 (Amer et al., 2010; Rao et al., 2016; David et al., 2020).

$$K_d = \frac{C_a}{C_e} \qquad (5)$$

$$\Delta G^o = -RT \ln K_d \qquad (6)$$

$$lnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (7)$$

Where, K_d is the distribution coefficient for the adsorption of metal ions onto adsorbent. T is the temperature and R^2 is the gas constant (8.314 J/mol K). Plotting ln K_d vs 1/T, the calculated data of thermodynamic parameters were for the adsorption of Pb(II) and Cd(II) ions onto Fe_3O_4/kaolinite composite are listed in Table 3.

CONCLUSIONS

The findings revealed that Fe_3O_4/kaolinite nanocomposite could be used as potential adsorbent for removal of Pb(II) and Cd(II) ions from aqueous solutions. The batch adsorption parameters: pH of solution, adsorbent dose, contact time, initial metal concentration and temperature were found to be effective on the adsorption process. Thermodynamic parameters ΔG^o, ΔH^o and ΔS^o showed the endothermic and spontaneous nature of the adsorption of Pb(II) and Cd(II) ions onto Fe_3O_4/kaolinite nanocomposite. Langmuir model showed the best fit for the experimental data. The maximum adsorption capacity (q_{max}) of Pb(II) and Cd(II) ions onto

Fe_3O_4/kaolinie nanocomposite at pH 5.5 and 30°C are 76.92 for Pb(II) ions and 75.19 mg/g for Cd(II) ions. Compared to various adsorbents reported in the literature, the Fe_3O_4/kaolinite nanocomposite showed good promise for its use in water and wastewater treatments.

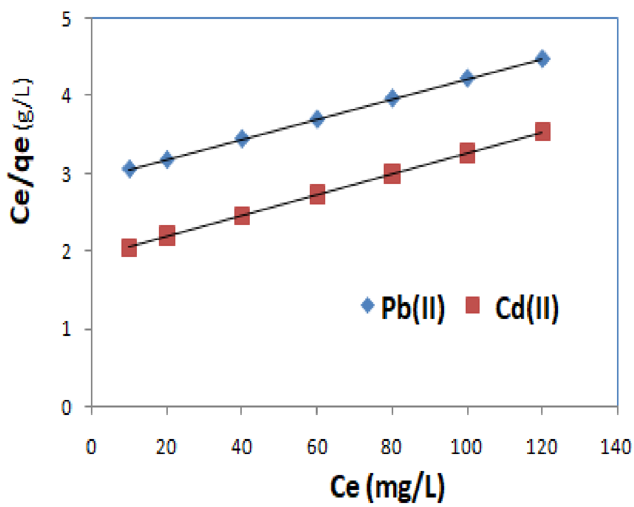

Fig. 3: C_e/q_e versus C_e for adsorption of Pb(II) and Cd(II) ions onto Fe_2O_3/kaolinite nanocomposites

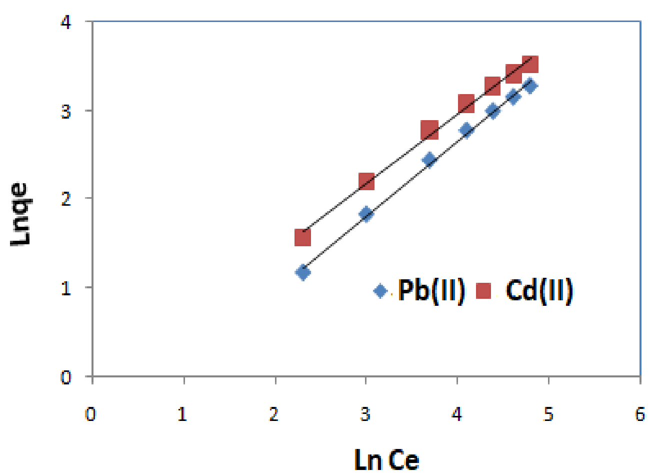

Fig. 4: lnCe versus lnqe for adsorption of Pb(II) and Cd(II) ions onto Fe_2O_3/Kaolinite nanocomposites

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