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Nano platelets kaolinite for the adsorption of toxic metal ions in the environment

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Contamination of water reservoirs with different toxic metal ions from industrial activities has emerged as one of major issues in recent years. The adsorption of Pb(II) ions from aqueous solution onto Nano platelets kaolinite has been investigated. The adsorption studies were determined as a function of pH, contact time, initial metal ion concentration, adsorbent dosage and temperature. Nano platelets kaolinite prepared from raw Jordanian kaolin clay showed size in the range of 12-80 nm. Maximum adsorption capacity as determined by Langmuir isotherm model is 175.44 mg/g for Pb(II). Thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o were revealed that the adsorption process is spontaneous and endothermic process. The results showed that Nano platelets kaolinite can be efficiently used as a low-cost alternative and eco-friendly adsorbent for the removal of toxic heavy metals from wastewater.

Capsule Summary: A novel natural adsorbent nano platelets kaolinite was used for the removal of toxic Pb(II) ions from aqueous solution. Nano platelets kaolinite adsorbent showed promising efficiency, which could possibly be used for the adsorption of heavy metals ions from industrial effluents.

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INTRODUCTION

Industrial wastewater is considered as the major source of toxic heavy metals i.e., lead, zinc, nickel, copper, chromium and cadmium. These metals must be removed from wastewater prior to discharge in the environment. Lead(II) ions have been released to the environment through phosphate fertilizers, electrical wiring, manufacturing batteries, air conditioning tubing, plumbing, electroplating, and pigments (Huang et al., 2019; Khan et al., 2017; Kong et al., 2019; Liu et al., 2019; Tomei and Mosca Angelucci, 2019). Removal of Pb(II) ions from aqueous and wastewater was developed using un modified and modified kaolin clay such as tripolyphosphate-impregnated kaolinite clay (Unuabonah et al., 2007), HCl treatedkaolin (Drweesh et al., 2016), illitic clay (Ozdes et al., 2011), 3-amino propyl trimethoxy silane-modified kaolinite (Fatimah, 2018), modified and unmodified kaolinite clay (Jiang et al., 2009,2010; Sari and Tuzen, 2014; Sdiri et al., 2016; Khan and Singh, 2010; Omar and Al-Itawi, 2007; Shahmohammadi et al., 2011; Etoh et al., 2015; Malima et al., 2018), nanoscale zero-valent iron (Zhang et al., 2010), raw clay and broken–brick waste (El-Shahat and Shehata, 2013), polyphosphate-modified kaolinite clay (Amer et al., 2010), Polyvinyl alcohol-modified kaolinite clay (Unuabonah et al., 2008), Nano illite/smectite clay (Yin et al.,2018), bentonite clay (Al-Jlil, 2018), kaolinite and

Table 1: Chemical analysis of raw kaolin clay (RK) and nano kaolinite (NK)

Parameters	Raw kaolin clay	Platelets Nano kaolinite
SiO2	63.17	79.88
Al2O3	23.46	16.45
Fe2O3	2.66	ND
TiO2	1.56	0.12
Na20	0.22	ND
CaO	0.84	ND
MgO	0.19	ND
K2O	0.27	ND
P2O5	0.07	ND
SO3	0.19	ND
LOI	7.43	ND

ND = not detected

Table 2: Thermodynamic parameters of nano platelets kaolinite for Pb(II) ions adsorption

Metal ion	T /K	K_D	$-\Delta G^o$ / kJ/mol	ΔH^o/ kJ/mol	ΔS^o/ J/K mol
Pb(II)	293	4.54	1.60	19.23	19.76
	303	5.62	1.89		
	313	6.82	2.17		

metakaloinite (Essomba et al., 2014), and calcined corncob-kaolinite (Chukwuemeka-Okorie et al., 2018).

The present research work aimed to modify raw Jordanian kaolin clay to Nano-platelets kaolinite for use as an efficient adsorbent for Pb (II) ions from aqueous solutions. It was found that platelets nano kaolinite exhibits high adsorption capacity for Pb (II)) ions from aqueous solutions.

MATERIAL AND METHODS

Materials

Kaolin clay samples were collected from the deposits at Batin El Ghoul, south Jordan. Hydrochloric acid (HCl) and lead nitrate ($PbNO_3$) were purchased from E-Merck. De-ionized water was used in all experimental work.

Preparation of platelets nano kaolinite

Raw Jordanian kaolin clay rocks obtained from kaolin deposits at Batin El Ghoul, south Jordan was crushed and ground to obtain fine powder. Raw kaolin clay was treated with 37% hydrochloric acid under stirring for 6h at room temperature (27 ^oC) and then left overnight. A brown-whitish emulsion was obtained. After separation and washing with de-ionized water, platelets nano kaolinite was dried at 80 ^oC for 4h and subjected to characterization by X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM).

Preparation of metal ions solutions

Stock solutions of 1000 mg/L Pb(II) ions were prepared. Working solutions with different concentrations of lead ions were prepared by appropriate dilution of the stock solution prior to their use. 0.1M HNO_3 and 0.1M NaOH were used for pH adjustment.

Characterization techniques

The obtained platelets nano kaolinite samples were analysed by X-ray fluorescence (XRF, Brucker S8 Tiger) to determine their mineralogical composition Scanning electron microscopy (SEM, Quanta FEI 450) The concentrations of metal ions in the solutions before and after equilibrium were determined by AAS6300 atomic absorption spectrometer (Shimadzu). The pH of the solution was measured with a WTW pH meter using a combined glass electrode.

Adsorption isotherms

Adsorption equilibrium was obtained by shaking 1 g of dry platelets nano kaolinite in a series of 250 mL flasks containing 100 mL of initial concentration of metal ions ranging from 5 to 120 mg/L. The initial pH value of metal ion solutions was adjusted from 1 to 8.0 with 0.1M HNO_3 or 0.1M NaOH at three 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 through filter paper (Schleicher and SchÜ ll 589). The supernatant was analyzed for lead ions by a sequential plasma emission spectrometer (ICPS-7510, Shimadizu). Experiment were run in triplicate and data was averaged.

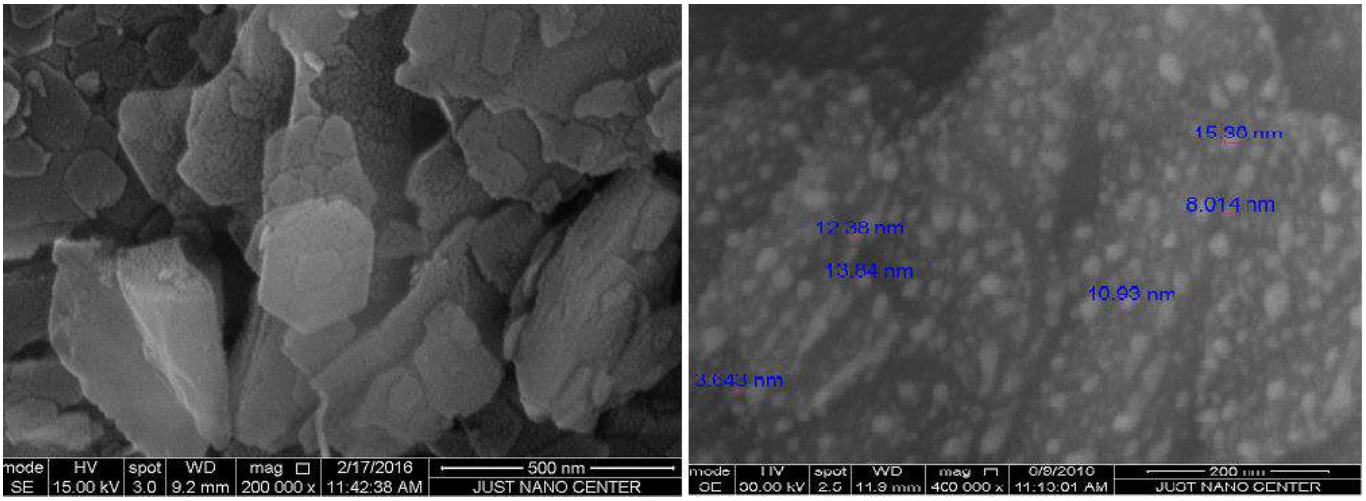

Fig. 1: SEM images of plateletes nano kaolinite

The amount of metal adsorbed (mg/g) at equilibrium (q_e) and percentage recovery were calculated using relations shown in Eqs. 1-2, respectively.

$$R\ (\%) = \frac{C_0 - C_e}{C_0}\ x\ 100 \qquad (1)$$

$$q_e = \frac{C_0 - C_e}{M}\ x\ V \qquad (2)$$

Where, q_e is the metal ions adsorbed (mg/g), C_o and C_e are the initial and equilibrium concentrations of the metal ions (mg/L), M is the weight of adsorbent (g) and V is the volume of the solution (L).

RESULTS AND DISCUSSION

X-ray fluorescence analysis (XRF) analysis

The XRF analysis was carried out to determine the chemical composition of raw kaolin clay, as well as to verify the chemical changes that occurred due to treatment by hydrochloric acid. Table 1 showed the chemical composition of the prepared platelets nano kaolinite with ratio of Si/Al 4.86.

Scanning electron microscopy analysis (SEM)

Scanning electron microscopy (SEM) images of the prepared platelets nano kaolinite are presented in Fig. 1. Platelets nano kaolinite prepared with average diameter 12-80 nm and thickness 8nm with particles platelets shape.

Effect of pH

The effect of pH on the removal of Pb(II) ions on the removal amount of metal ions increased with pH increasing from 1.0 to 8.0, Fig. 2. As the pH values increased, the high pH was favorable for the absorption of metal ions. In conclusion, the removal amount of metal ions was at pH = 6.5, while the acidic environment is not favored for metal ions removal from aqueous solutions.

Adsorptions isotherms

To investigate the effect of different parameters pH, adsorbent dose (g/L), contact time (t, min) and initial metal ion concentration (C_o, mg/L) on the adsorption performance. From our results, we conducted all adsorption process at pH = 5-7, adsorbent dose 0.5 g/0.1L, contact time at 60 min and initial metal concentration 5-120 mg/L.

Adsorption of metal ions onto nano platelets kaolinite was modeled by Langmuir isotherms. The linear form of the Langmuir isotherm model (Langmuir, 1918) is shown in Eq. 3.

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

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 coefficient R^2: 175.44 mg/g, 0.0065 and 0.9999, respectively. These values for Nano platelets kaolinite adsorbent indicated that Langmuir model describes the adsorption phenomena as favorable.

Freundlich isotherm model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation, also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm employed to describe heterogeneous systems and is expressed in linear form in Eq. 4 (Freundlich and Hellen, 1939).

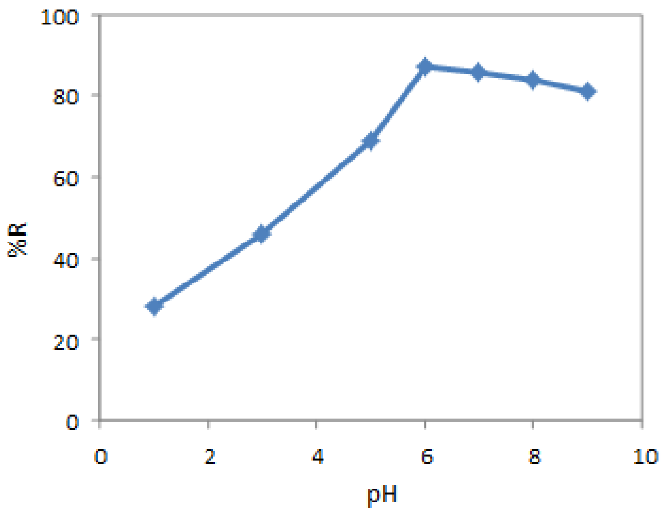

Fig. 2: Effect of pH solution on the percent removal Pb(II) ions by platelets nano kaolinite; (= 303 K; C_o= 40 mg/L; pH= 6.5).

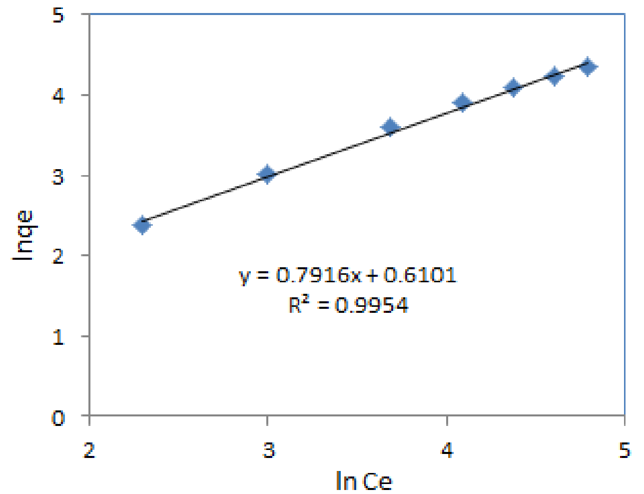

Fig. 4: Freundlich isotherm for Pb(II) ions onto platelets nano kaolinite

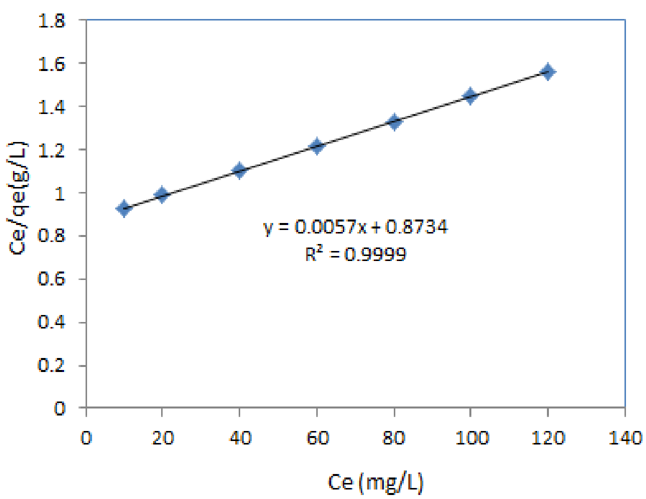

Fig. 3: Langmuir isotherm for Pb(II) ions onto platelets nano kaolinite

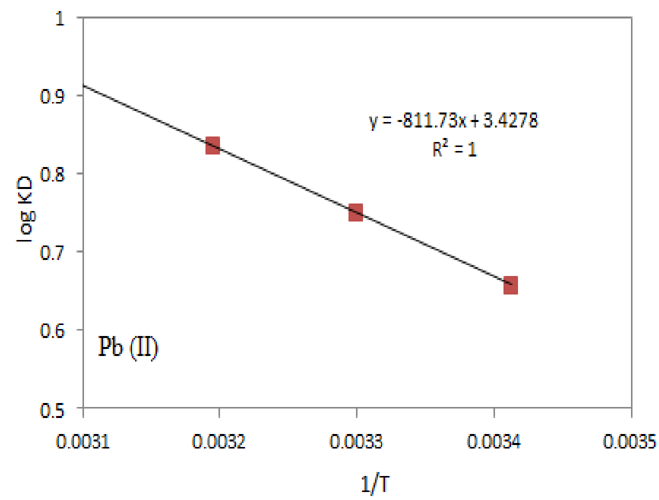

Fig. 5: Log K_D vs 1/T for the adsorption of Pb(II) ions by nano platelets kaolinite

$$lnq_e = lnk_F + \frac{1}{n} lnC_e \quad (4)$$

Where, K_F is 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 from the plot of lnq_e versus lnC_e, Fig. 4. 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 n value in Freundlich equation was found at 30 ^oC to be 1.26 for Pb(II) ions. Since n lie between 1 and 10, this indicates the physical adsorption of Pb(II) ions onto Nano platelets kaolinite. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

Thermodynamic parameters

Thermodynamics adsorption of Pb(II) ions onto Nano platelets kaolinite were calculated as shown in Eq. 5.

$$\Delta G^o = -RTlnK_D \quad (5)$$

Where, R is the universal gas constant (8.314 J/mol K); T (K) is the temperature and K_D is the distribution coefficient. According to thermodynamics, the Gibb's free energy change is also related to the enthalpy change (ΔH^o) and entropy change (ΔS^o) at constant temperature by the Gibbs–Helmholtz relation shown in Eqs. 6-7.

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (6)$$

$$\ln K_D = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (7)$$

The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated from the slope and intercept of the plot of ln K_D vs. 1/T, Fig. 5. The obtained data are reported in Table 2. A negative value of the free energy (ΔG^o) indicated the spontaneous nature of the adsorption process. It was also noted that the change in free energy, increases with rise in temperature. This could be possibly because of activation of more sites on the surface of N-PK with increase in temperature or that the energy of adsorption sites has an exponential distribution and a higher temperature enables the energy barrier of adsorption to be overcome. For physical adsorption, the free energy change (ΔG^o) ranges from (-20 to 0) kJ/mol and for chemical adsorption it ranges between (-80 and -400) kJ/mol. The ΔG^o for Pb (II) adsorption onto N-PK was in the range of (-1.6 to -2.17) kJ/mol and so the adsorption was predominantly physical. A positive value of ΔS^o as 19. 76 J/mol K showed increased randomness at solid solution interface during the adsorption of Pb(II) ions onto nano platelets kaolinite.

Comparison of platelets nano kaolinite with other kaolin adsorbents

A comparative of the maximum adsorption capacity, q_{max} of Nano platelets kaolinite with those of some other adsorbents reported in literature is given in Table 3. Differences in q_{max} are due to the nature and properties of each adsorbent such as surface area and the main functional groups in the structure of the adsorbent. A comparison with other adsorbents indicated a high metal ion adsorption capacity of nano platelets kaolinite. Present study results are in line with previous studies (Abukhadra et al., 2019; Amer and Awwad, 2018; Chen et al., 2019; Fatimah, 2018; He et al., 2019; Kuang et al., 2019; Liu et al., 2019; Ma et al., 2019; Nabbou et al., 2019; Ruyter-Hooley et al., 2017; Zhu et al., 2018) that kaolinite could be a potential adsorbent for the pollutants of environmental concern.

Table 3: Maximum adsorption capacity of Pb(II) ions on different adsorbents and present study

Adsorbents	q_{max} (mg/g)	References
Tripolyphosphate impregnated kaolinite clay	126.58	Unuabonah et al. (2007)
Polyphosphate modified kaolinite clay	40	Amer et al. (2010)
TTP-Kaolinite clay	126.58	Unuabonah et al. (2007)
Kaolinite	10.416	Ghogomu et al. (2013)
Metakaolinite	10.101	Ghogomu et al. (2013)
Nano Illite/Smectite Clay	0.256	Yin et al. (2018)
Polyvinyl alcohol-modified Kaolinite Clay	56.18	Unuabonah et al. (2008)
Natural Mixture of Kaolinite-Albite-Montmorillonite-Illite Clay	24.12	Eba et al. (2011)
Modified kaolin	20	Jiang et al. (2009)
Nano platelets kaolinite	175.44	This work

CONCLUSIONS

The experimental investigation concluded that N-PK could be used as potential adsorbent for removal of Pb(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) ions onto Nano platelets kaolinite. Langmuir model showed the best fit for the experimental data. The maximum adsorption capacity of Pb(II) ions at pH 7 and 30 °C is 175.44 mg/g. Compared with various raw kaolin and modified kaolin adsorbents reported in the literature, the nano platelets kaolinite showed good promise for its use in wastewater treatment.

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