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TiO_2-kaolinite nanocomposite prepared from the Jordanian Kaolin clay: Adsorption and thermodynamics of Pb(II) and Cd(II) ions in aqueous solution

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ABSTRACT

Metal oxides nanoparticles/clay nanocomposites attractd much attention as an adsorbent for the removal of metal ions. TiO_2/kaolinite nanocomposite was prepared from the raw Jordanian kaolin clay and evaluated for the removal of Pb(II) and Cd(II) ions from aqueous solutions through adsorption process. The removal percent (%R) of metal ions was determined as a function of contact time, solution pH, adsorbent dosage and temperature. The maximum adsorption capacity, q_{max} for Pb(II) and Cd(II) ions as evaluated by Langmuir isotherm model were 333.33 mg/g and 250 mg/g, respectively. The prepared TiO_2/kaolinite nanocomposite from the Jordanian kaolin clay displayed the main advantage for complete removal of Pb(II) and Cd(II) ions from aqueous solutions by a batch adsorption treatment. In view of promising adsorption efficiency for Pb(II) and Cd(II) ions, the TiO_2/kaolinite nanocomposites could possibly be used for the adsorption metal ions form industrial wastewater.

Capsule Summary: A novel and eco-friendly natural adsorbent (TiO_2/kaolinite nanocomposite) was used for the removal of toxic Pb(II) and Cd(II) ions and the prepared adsorbent from the Jordanian kaolin clay showed promising efficiency for the removal of Pb(II) and Cd(II) ions from aqueous solutions.

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INTRODUCTION

Water is one of the most important natural resources in Jordan. In the meantime, water contamination, with heavy toxic metals has become an environmental issue. Different methods and techniques have been developed to remove these heavy toxic metals such as chemical precipitation, ion exchange, electrochemical, membrane separation, electrocoagulation and ion flotation (Mavrow et al., 2003; Verbych et al., 2004; González-Muñoz et al., 2006; Sudilovskiy et al., 2007; Boudrahem et al., 2011; Hossain et al., 2012; Tran et al., 2017; Taseidifar et al., 2017). Green methods using different parts of the plants were also reported in literature as adsorbents for removal of toxic heavy metal ions from water, aqueous solutions and industrial wastewater such as grape stalk waste (Martinez et al., 2006), modified grape stem (Schwantes et al., 2018), *barbadensis* Miller waste leaves powder (Gupta, 2019), *Eriobotrya japonica* leaves (Al-Dujaili et al., 2012), *Ficus carcia* leaves (Farhan et al., 2013), loquat bark (Awwad et al., 2010), *Sophora japonica* pods powder (Amer et al., 2015), *Moringa oleifera* pods (Oluwaseun et al., 2011), *Terminalia catappa* L. fruit shell (Hervira et al., 2015), *Acacia galpinii* seeds and seed pods (Dube and Chingoma, 2016).

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 using natural and modified nanomaterial adsorbents for water, aqueous solutions and industrial wastewater such as Alumina-coated carbon nanotubes (Gupta et al., 2011), nanocarbon materials, nanometal particles, and polymer-supported nanoparticles (Wang et al., 2012), titanate/TiO_2 added lignin (Fu et al., 2019), nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite (Sheet et al., 2014), zero valent silver nanoparticles (Al-Qahtani et al., 2019), carbon-based nanomaterials, zero-valent metal, metal-oxide based nanomaterials, and nanocomposites (Yang et al., 2019), polymer-modified magnetic nanoparticles (Ge et al., 2012), flowerlike α-Fe_2O_3 nanostructures (Gao et al., 2012), three-dimensional magnetic graphene oxide foam/Fe_3O_4 nanocomposite (Lei et al., 2014), nanocomposite Fe_3O_4@SiO_2-mPD/SP (Tan et al., 2014), coating Fe_3O_4 magnetic nanoparticles with humic acid (Liu et al., 2008), γ-Fe_2O_3 nanotubes (Roy and Bhattacharya, 2012 and 2013), surface modified magnetic nanoparticles (Ojemaye et al., 2017), gum Arabic modified magnetic nano-adsorbent (Banerjee et al., 2007), a composite from magnetic nanoparticles (Fe_3O_4) capped with cetyltrimethylammonium bromide (Elfeky et al., 2017, Wang et al., 2012; Jin et al., 2012), sulfur-modified magnetic nanoparticles (Jafarinejad et al., 2018), nanostructured kaolinite (Alasadi et al., 2019; Amer and Awwad, 2017), hematite nanoparticles (Grover et al., 2012), Fe_3O_4@ montmorillonite composite (Hande et al., 2016), Sawdust-kaolinite composite (Ogbu etal., 2019), porous calcium alginate/graphene oxide composite aerogel (Pan et al., 2018), polyrhodanine-encapsulated magnetic nanoparticles (Song et al., 2011), polyvinyl alcohol-modified kaolinite clay (Unuabonah et al., 2008), chitosan-coated agrillaceow limestone (Zhang et al., 2019), Amino-decorated Zr-based magnetic metal-organic frameworks composites (Zr-MFCs) (Huang et al., 2018), nanocomposites of nanosilica-immobilized-nanopolyaniline and crosslinked nanopolyaniline (Mahmoud et al., 2016), hydroxyapatite/cellulose composite (Cho and Jeong, 2008), kaolinite/smectite natural composite (El-Naggaret al.2019), Fe_3O_4/cyclodextrin polymer nanocomposites (Badruddoza et al., 2013) and magnetic cellulose-based beads with embedded chemically modified magnetite nanoparticles and activated Carbon (Luo et al., 2016). Hence, nanocomposites proved to be highly efficient for the removal of metal ions form wastewater (Bhatia and Nath, 2020; D'Cruz et al., 2020; Kefeni and Mamba, 2020; Mukwevho et al., 2020; Yue et al., 2020).

In this study, we report a new, rapid and cost-effective route for the adsorption of Pb(II) and Cd(II) ions from aqueous solution onto TiO_2/kaolinite nanocomposite prepared from the natural Jordanian kaolin clay. Chemical treatment of natural Jordanian kaolin clay at ambient temperature produced nanocomposite composed mainly from 1.8 wt.% titanium oxide and 98.0 wt.% kaolinite. Adsorption variables such as pH, contact time, adsorbent dose and concentration are reported. Surface characterization of the composite by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transmission infrared (FTIR) and scanning electron microscope (SEM) were discussed. One of the advantageous of this preparation route of TiO_2/kaolinite nanocomposite from the raw Jordanian kaolin clay is the production of a by-product of a red pigment composed mainly from nano-iron oxide (hematite).

MATERIAL AND METHODS

Chemical, reagents and materials

Lead nitrate $Pb(NO_3)_2$ and cadmium nitrate $Cd(NO_3)_2$ were analytical grade obtained from Sigma-Aldrich, Germany and used without further purifications. Hydrochloric acid (37%) and sodium hydroxide (NaOH) were obtained Merck, Germany. Kaolin clay sample was obtained from Batin El Ghoul deposits, south Jordan. Distilled and de-ionized water were used in all experimental work.

Preparation of TiO_2/kaolinite nanocomposite

TiO_2/kaolinite nanocomposite was prepared as follows: The raw Jordanian kaolin clay samples were mechanically crushed ground and sieved to 350 meshes (particle size < 5µm). 500g of the fine powder was treated with hydrochloric acid (20%) under mechanical stirring for 3h at ambient temperature (27°C) and then left overnight at room temperature. After that, a a red-yellow solution (upper layer) removed by decantation. Afterwards the kaolin particles treated with 10% sodium hydroxide under mechanical stirring for 30min. By decantation, filtration and washing with de-ionized water, a white powder was obtained and dried in an oven at 80°C for 4h. The obtained TiO_2/kaolinite nanocomposites powder was subjected to chemical analysis, XRF, XRD and SEM.

Adsorption experiments

Adsorption of Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite was performed in glass flasks of 250 ml containing 0.5 g of adsorbent mass and 20 ml of metal ions solutions with an initial concentrations ranging between 5 to 80 mg/L. The mixture was shaken (~200 rpm) until the equilibrium was reached using a water shaker bath. Then, the solid phase was separated from the liquid phase by centrifugation (2000 rpm for 10 min) and the concentrations of metal remaining were determined by atomic absorption, The amount of adsorbed Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite was calculated using relations shown in Eqs. 1-2.

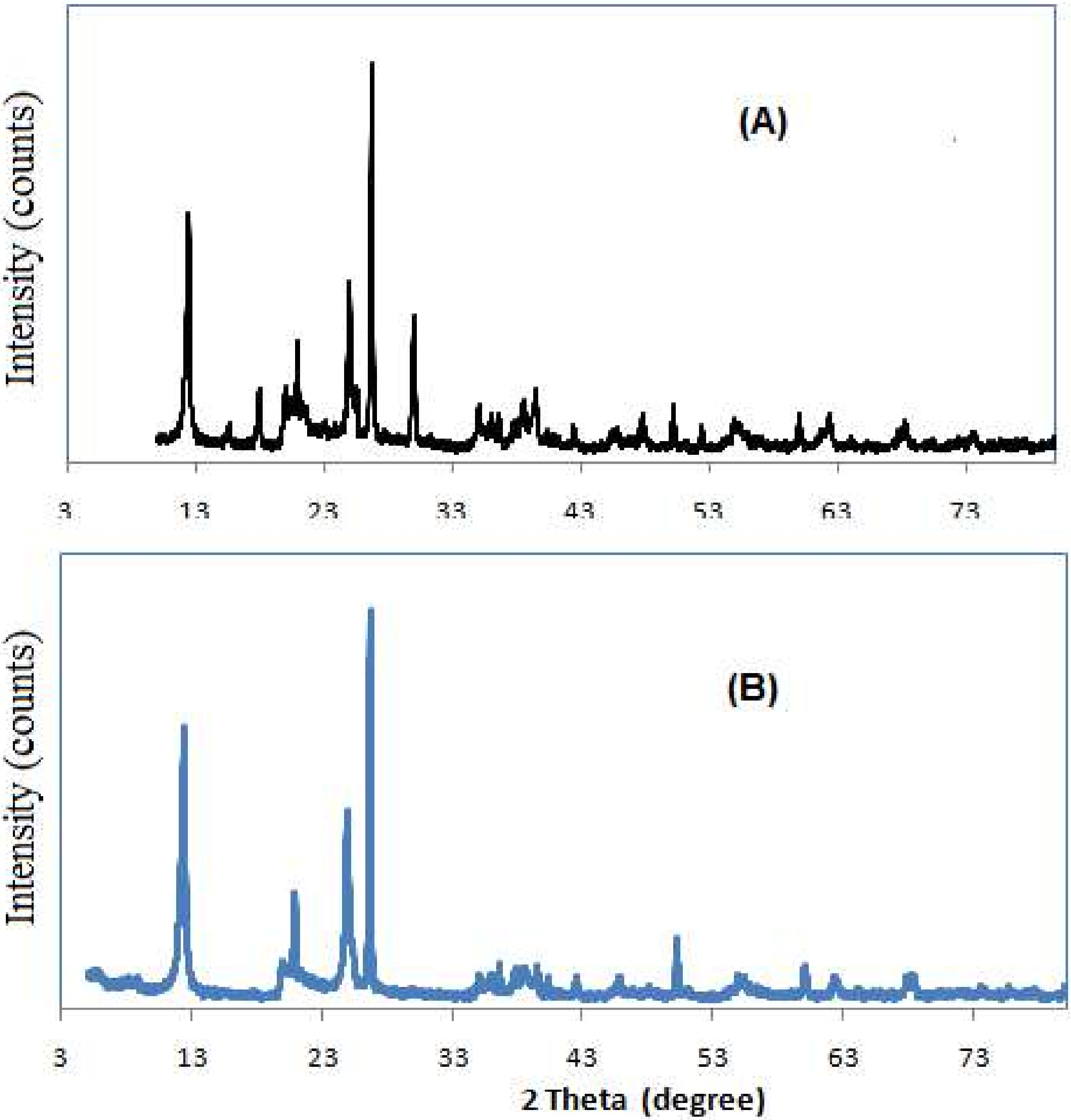

Fig. 1: XRD of raw kaolin clay (A) and the prepared TiO2/kaolinite nanocomposite (B)

$$Removal\ (\%) = \frac{C_o - C_e}{C_o}\ x\ 100 \qquad (1)$$

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

Where, C_o (mg/L) is the initial concentration of metal ions and C_e (mg/L) is the equilibrium concentration in aqueous solution. M is the concentration of TiO_2/kaolinite nanocomposite, V (L) is the volume of solution. q_e is the amount of adsorbed metal per gram of adsorbent (mg/g) and R% represent the removal percent of metal ions.

Morphology studies

Lead (II) and cadmium (II) ions concentrations were determined by AAS600 atomic spectrophotometer (Schimadzu, Japan), pH measurements were done by WTW pH meter. Fourier transforms infrared spectrophotometer (IR Prestige-21, Schimadzu). TiO_2/kaolinite nanocomposite prepared were characterized by X-ray diffractometer, (XRD-6000, Shimadzu) equipped with Cu K α radiation source (λ =0.154056 nm) using Ni as filter at a setting of 30 kV/30mA. All XRD and XRF data were collected under the experimental conditions in the angular range $3^{o} \leq 2\theta \leq 80^{o}$. Scanning electron microscopy (SEM) images were taken using a field emission scanning electron microscopy (Hitachi S4700, 15 kV).

RESULTS AND DISCUSSION

XRD analysis

The chemical composition of raw Jordanian kaolin clay and the prepared TiO_2/kaolinite nanocomposite by XRF analysis has been determined as: 63.17% SiO_2, 23.46% Al_2O_3, 2.66% Fe_2O_3, 1.56% TiO_2, 0.84% CaO, 0.19% MgO, 0.22% Na_2O, 0.27% K_2O and 7.43% loss of ignition. The prepared TiO_2/kaolinite nanocomposite analysis as: 76.61% SiO_2, 19.82% Al_2O_3 and 1.8% TiO_2. XRF analysis showed that the ratio of SiO_2/Al_2O_3 equals 2.69 for raw kaolin clay and 3.87 for the prepared TiO_2/kaolinite nanocomposite. Results of the X-ray diffraction analysis of raw kaolin clay and the prepared TiO_2/kaolinite nanocomposite is shown in Fig. 1. XRF and XRD measurements have shown that the raw kaolin clay composed mainly from kaolinite and metal oxides. HCl and NaOH activities eliminate most metal oxides associated with kaolinite such as calcium, magnesium, potassium, sodium and iron oxides. On the other hand, the prepared TiO_2/kaolinite nanocomposite is composed mainly of aluminum silicates and titanium oxide TiO_2. This method indicated that the removal of the associated metal materials from the raw kaolin clay by hydrochloric and sodium hydroxide introduced a change into the chemical structure of kaolin clay and increases the surface area and adsorption capacity. XRD analysis of the raw Jordan kaolin clay (A) and the prepared TiO_2/kaolinite nanocomposite are illustrated Fig. 1.

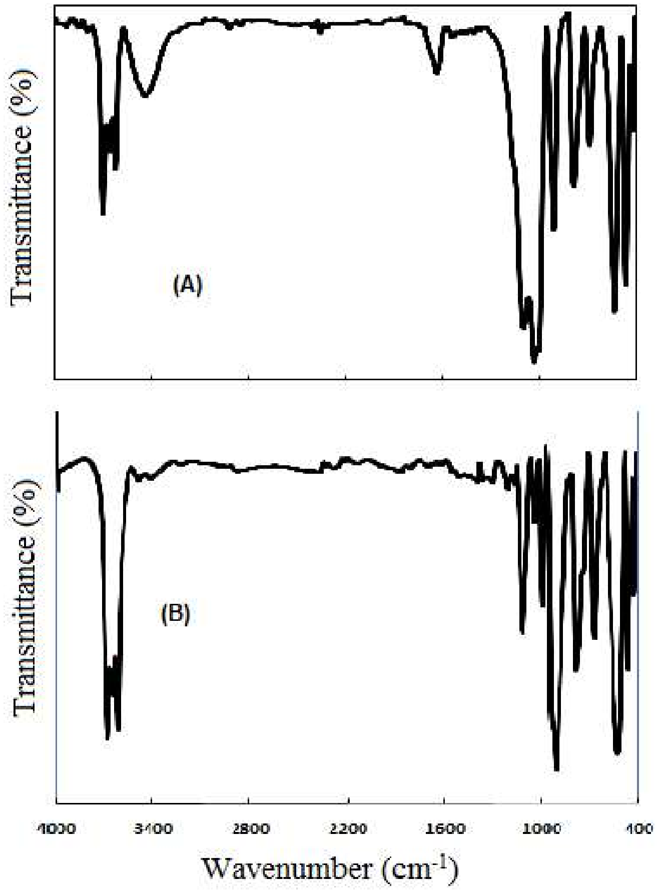

Fig. 2: FT-IR of raw kaolin clay (A) and the prepared TiO_2/kaolinite nanocomposite (B)

FT-IR analysis

FT-IR analysis (Fig. 2) showed the hydroxyl stretching vibration bands at 3695 and 3622 cm^{-1}, which corresponds to the inner surface –OH stretching vibration of kaolinite. Band at 3486cm^{-1} belongs to the stretching vibration of the outer-surface hydroxyl groups, indicating the presence of kaolinite in raw kaolin clay. The disappearance of bands at 3486 cm^{-1} and 1627 cm^{-1} indicated the acid treatment was effected on these positions. Absorption band at 1627 cm^{-1} assigned for the -OH bending vibration and C=O stretching vibration. The bands at 1110 cm^{-1} and 1026 cm^{-1} moved to 1119 cm^{-1} and 995 cm^{-1} moved in the kaolin clay treated by HCl and sodium hydroxide, corresponding to Si-O bending and stretching vibrations. Absorption band at 914 cm^{-1} corresponds to the Al-O bending vibration. Bands at 540 and 470 cm^{-1} represent to Al-O-Si skeletal vibration. The characteristic hydroxyl (-OH) bands of kaolinite at 3695 cm^{-1} and 3622 cm^{-1} still exists. The intensity of band at 3486cm^{-1} disappears and new band appears at 1119cm^{-1}. These results indicated that the hydrogen bonding between the layers of raw kaolin and formation of new hydrogen bonding between the inner–surface hydroxyl groups. The obtained results indicated that the removed associated metal oxides from the raw kaolin clay changed the structure to kaolinite.

Scanning electron microscopy (SEM) analysis

Scanning electron microscopy (SEM) of raw kaolin clay and the prepared TiO_2/kaolinite nanocomposite are illustrated in Fig. 3. SEM of TiO_2/kaolinite nanocomposite showed that the platelets shape and the average size 18 nm.

Effect of contact time

Adsorption of Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite described as a function of contact time, Fig. 4. The adsorbent loading was kept at a constant value of 0.5g and a contact time of 80min. Adsorption capacity equilibrium was achieved between 30-60 min.

Table 1: Langmuir and Freundlich parameters

Metal ion	Langmuir constants		
	q_{max} (mg/g)	K_L(L/mg)	R^2
Pb(II)	333.33	0.003	0.9999
Cd(II)	250.14	0.004	0.9999
	Freundlich constants		
	K_F	n	R^2
Pb(II)	2.26	1;493	0.9868
Cd(II)	2.97	1.901	0.9759

Table 2: Thermodynamic parameters of Pb(II) and Cd(II ions onto TiO_2/ kaolinite nanocomposite

Metal ion	T/K	K_D	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol)
Pb(II)	293	5.5	-4.2	11.5	53.5
	303	6.42	-4.7		
	313	7.44	-5.2		
Cd(II)	293	3.4	-3.7	23.5	90.4
	303	4.64	-4.3		
	313	6.3	-4.9		

Effect of pH

The pH has been identified as one of the most important parameter that is effective on metal adsorption. The effect of pH on the adsorption of Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite was studied at pH 1.0–8.0, Fig.5. The maximum adsorption was observed at pH 5.5-6.0 for PbII) and Cd(II) ions. Therefore, all the remaining adsorption experiments were carried out at this pH value. At highly acidic pH (pH < 3.0), the overall surface charge on the active sites became positive and metal cations and protons compete for binding sites onto TiO2/kaolinite nanocomposite, which results in lower uptake of metal. The adsorbent surface was more negatively charged as the pH solution increased from 5.0 to 6.0.

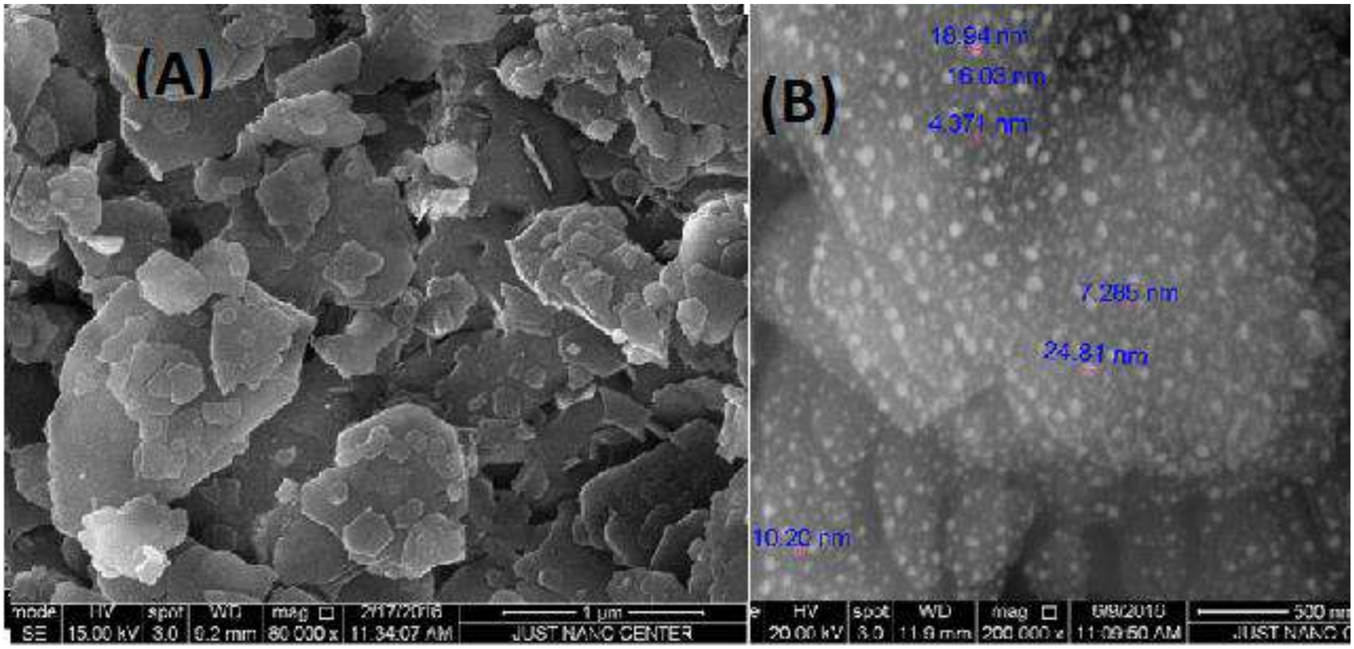

Fig. 3: SEM of raw kaolin clay (A), TiO_2/kaolinite nanocomposite (B)

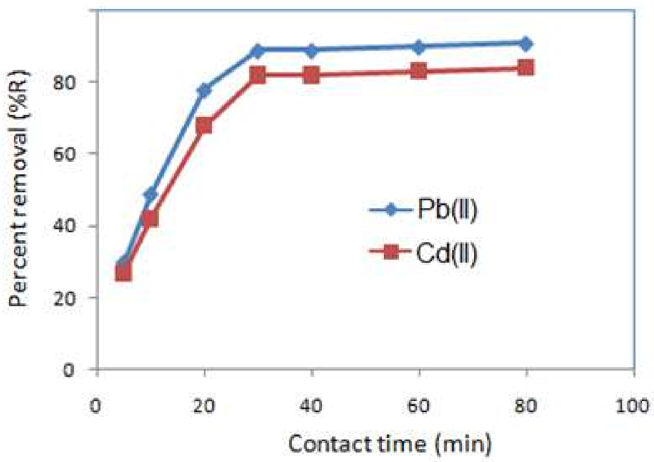

Fig. 4: Effect of contact time (min) on percent removal of metal ions

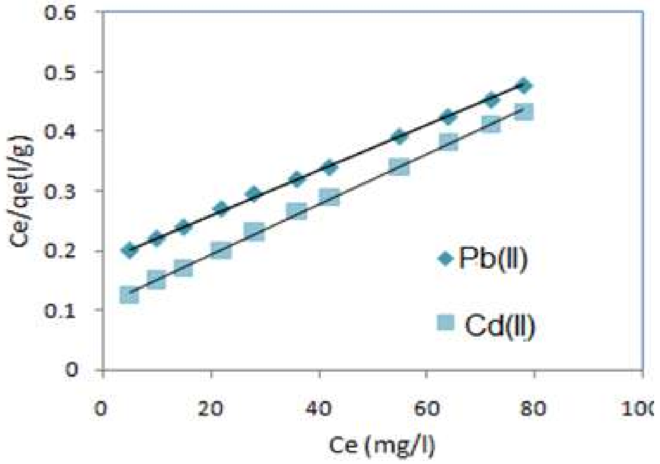

Fig. 6: Plot of Langmuir model for adsorption Pb(II) and Cd(II) onto TiO_2/kaolinite nanocomposit

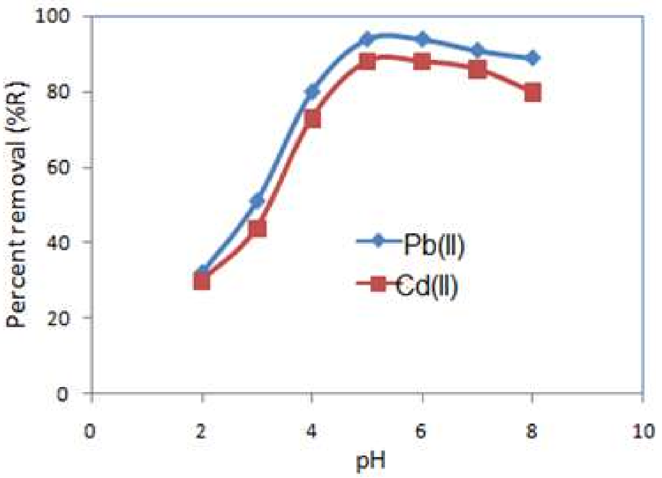

Fig. 5: Effect of pH on the percent removal of metal ions

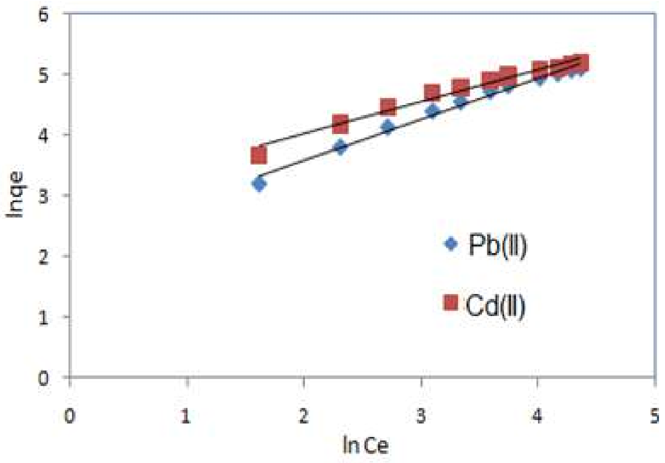

Fig. 7: Plot of Freundlich model for adsorption Pb(II) and Cd(II) onto TiO_2/kaolinite nanocomposit

Effect of adsorbent dose

The adsorption efficiency for Pb(II) and Cd(II ions as a function of adsorbent dosage was investigated. The percentage of the metal adsorption increases with the adsorbentt loading up to 0.5 g/0.1L. This result can be explained by the fact that the adsorpent 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 94.0% for Pb(II) and 88% for Cd(II) was attained at adsorbent dosage, 0.5 g/0.1L. Therefore, the optimum adsorbent dosage was taken as 0.5 g/0.1L for further experiments. As the adsorbent dose increased, more active sites to bind metal ions, thus it results an increase in the adsorption efficiency until saturation.

Adsorption isotherms

The linear form of the Langmuir isotherm model is described in 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. 6. Values of q_{max}, K_L and regression coefficient R^2 are listed in Table 1. These values for magnetite/kaolinite nanocomposite adsorbent indicated that Langmuir model describes the adsorption phenomena favarouble. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed in Eq. 4.

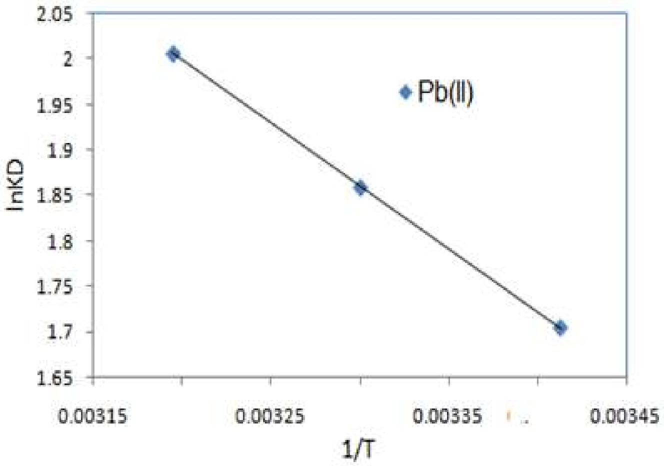

Fig. 8: Plot of lnK_D versus 1/T for adsorption of Pb(II) ions onto TiO_2/kaolinite nanocomposite

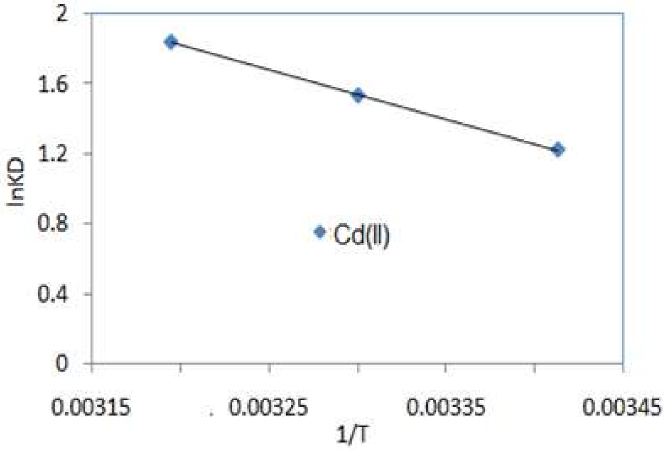

Fig. 9: Plot of ln K_D versus 1/T for adsorption of Cd(II) ions onto TiO_2/kaolinite nanocomposite

$$R_L = \frac{1}{1+K_L C_e} \qquad (4)$$

Where, K_L is the Langmuir constant and C_e is the initial concentration of lead (II) and cadmium (II) ions. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L= 0), favorable ($0<R_L<1$), linear (R_L=1) or unfavorable ($R_L>1$). The R_L was found to be 0.64-0.88 for concentration of 10–40 mg/L of Pb(II) and Cd(II). They are in the range of 0-1 which indicates the favourable adsorption.

The Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This 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 is an empirical equation and can be employed to describe heterogeneous systems and is expressed in Eq. 5 (Freundlich, 1906).

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (5)$$

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 from the plot of lnq_e versus lnC_e, Fig. 7 on the basis of the linear of Freundlich equation. 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 to be 1.49 for Pb(II) and 1.90 for Cd(II) ions, Table 1. Since n lie between 1 and 10, this indicate the physical adsorption lead (II) and cadmium (II) ions onto TiO_2/kaolinite nanocomposite. 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 study

Thermodynamic parameters; enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) for Pb(II) and Cd(II) ions adsorption onto TiO_2/kaolinite nanocomposite were determined as shown in Eq. 6-8.

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

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

$$K_D = \frac{C_a}{C_e} \qquad (8)$$

Where, K_D is the equilibrium distribution constant, C_a is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of lnK_D vs. 1/T. The calculated values of thermodynamic paramours ΔG°, ΔH°, and ΔS° for the adsorption of Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite are listed in Table 2. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the adsorption process. It was also noted that the change in free energy, ΔG^o increase as the temperature increased, indicating more driving force and hence resulting in higher adsorption process. This could be possibly because of activation of more sites on the surface of nanocomposite 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. In the physical adsorption the free energy change (ΔG°) 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) and Cd(II) ions adsorption onto TiO_2/kaolinite nanocomposite. nanocomposite was in the range of (-3.7 to -5.2) kJ/mol and so the adsorption was predominantly physical adsorption. A positive value of ΔS^o as 53.5-90.4 J/mol K showed increased randomness at solid solution interface during the adsorption of Pb(II) and Cd(II) ions onto TiO_2/kaolinite nanocomposite.

Efficiency of TiO_2/kaolinite nanocomposites

A comparative of the maximum adsorption capacity, q_{max} of TiO_2/kaolinite nanocomposite with those of some other adsorbents reported in literature, for removal of Pb(II) and Cd(II) ions from aqueous solutions is given in Table 3. Differences in q_{max} are due to: Nature and properties of each adsorbent; particle size of adsorbents; surface area; and the main functional groups in the structure of the adsorbent. A comparison with other adsorbents indicated a high Pb(II) and Cd(II) ions adsorption capacity of TiO_2/kaolinite nanocomposite prepared by simple, economic and low-cost natural kaolin clay, Table 3. In view of promising efficiency of TiO_2/kaolinite nanocomposites for the adsorption of Pb(II) and Cd(II) ions and in comparison to reported studies (Chen et al., 2020; Chowdhury et al., 2020; Ghorbani et al., 2020; Kamari and Shahbazi, 2020; Saeedi-Jurkuyeh et al., 2020; Shahzad et al., 2020; Sheydaei et al., 2020), the nanocomposites have potential to remove metal ions from wastewater.

CONCLUSIONS

The experimental investigation concluded that TiO_2/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 TiO_2/kaolinite nanocomposite. Langmuir model showed the best fit for the experimental data. The maximum adsorption capacity (qmax) of Pb(II) and Cd(II) ions onto TiO_2/kaolinie nanocomposite at pH 6.0 and 30°C is 333.33mg/g for Pb(II) ions and 250mg/g for Cd(II) ions. Compared to various adsorbents reported in the literature, the TiO_2/kaolinite nanocomposite showed good promise for its use in water and wastewater treatments.

Table 3: Maximum adsorption capacity q_{max} (mg/g) for Pb(II) and Cd(II) ions and the published values in literature

Adsorbents	Pb(II)	Cd(II)	References
Natural kaolin clay	2.35	0.88	Jiang et al. (2010)
Kaolinite	11.5	6.8	Gupta and Bhattacharyya (2008)
Montmorillinite	31.1	30.7	Gupta and Bhattacharyya (2008)
Kaolinite/Smectite natural	0.78		El-Naggar et al. (2019)
Ball clay		27.17	Rao & Kashifuddin (2016)
Montmorillinite		6.98	de Pablo et al. (2011)
Nanoplatelets kaolinite	175.44		Al-a'qarbeh et al. (2020)
Tripolyphosphate impregnated kaolinite clay	88.5	53.48	Unuabonah et al. (2007)
Grafting kaolinite with dietthanolamiine	45.87	31.45	Koteja and Matusik (2015)
Grafting kaolinite with triethanolamine	30.21	23.26	Koteja and Matusik (2015)
polyphosphate-modified kaolinite clay	40	13.23	Amer et al. (2010)
Acid-modified monmorillinite	1.62	0.62	Akpomie and Dawadu (2016)
A novel nano-clay	56.18	41.67	Unuabonah et al. (2008)
NanoIllite/smectite clay	2.56		Yin et al. (2018)
Kaolinite	87.26	35.92	Adebowale et al. (2005)
Phosphate-modified kaolin	93.28	61.44	Adebowale et al. (2005)
Sulfate -modified kaolin	89.08	42.57	Adebowale et al. (2005)
Kaolinite clay	25.32	22.38	Ogbu et al. (2019)
Sawdust-clay modified	37.98	36.36	Ogbu et al. (2019)
TiO_2/kaolinite nanocomposite	333.33	250	This work

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