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Removal of lead ions from aqueous solutions using intercalated tartrate-Mg–Al layered double hydroxides

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ABSTRACT

The potential feasibility of layered double hydroxides (LDH) intercalated with tartrate (tartrate-Mg–Al) for the removal of lead ions from aqueous solutions was investigated. The effects of various experimental parameters such as contact time, solution pH, and adsorbent dosage were also investigated. The extent of lead ions removal increased with the increase in contact time and amount of tartrate-Mg–Al used; however, the percentage removal decreased with the increase in pH. The shape of the isotherms that was obtained from the experimental data was well fitted to the Langmuir isotherm. The fundamentals of lead removal from aqueous solution with the use of tartrate-Mg–Al could be explained by the formation of complexes between the tartrate and Pb^{2+} ions and for Mg–Al–NO_3 it was the primary surface opposite charge precipitation reaction. The results from this study indicated that the LDH which intercalated with tartrate could be used as a potential adsorbent for the removal of lead ions from aqueous solution.

Keywords: Layered double hydroxide; Tartrate; Lead; Metal complexes

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1. Introduction

Layered double hydroxides (LDHs) are a class of anionic clay that has high anion-exchange capacities. The chemical composition of LDH can be described by the formula $[M^{2+}{}_{1-x}\ M^{3+}{}_{x}\ (OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$ where M^{2+} and M^{3+} are metal cations, for example Mg^{2+} and Al^{3+}, that occupy octahedral sites in the hydroxide layers. A^{n-} is an exchangeable anion, and x is the ratio of $M^{3+}/(M^{2+} + M^{3+})$. Carbonates are the interlayer anions in the naturally occurring mineral hydroxides, which is a member of this class of materials. Several studies have reported the use of LDH as an adsorbent for the preservation of aqueous environments, such as treatment of colored water [1,2], treatment of phenolic water [3], treatment of water polluted with heavy metals [4–6] and as nitrogen oxide storage [7].

Intercalation of organic compounds between the layers of LDH will produce composite materials that can be used in various areas of science and technology. The intercalation process of producing organic–inorganic LDH can be carried out with the use of two different methods namely co-precipitation, and ion exchange. Recently several studies on the intercalated compounds of LDH which can be used as an adsorbent for the removal of heavy metals have been reported.

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The LDH intercalated with ethylenediaminetetraacetate (EDTA) process was reported to rapidly take up heavy metals ions such as Cu^{2+} and Cd^{2+} from aqueous solution [8]. The group postulated that the main mechanism for the removal of the metal cations was through the formation of an EDTA–metal complex in the interlayer of Mg–Al–LDH. In another reported study, Mg–Al–LDH intercalated with citrate, malate, and tartrate was used as an adsorbent to examine the removal of Cu^{2+} and Cd^{2+} from the aqueous solution [9]. The group found that, the intercalated compounds rapidly took up heavy metals of Cu^{2+} and Cd^{2+} at a constant pH of 5 and the main mechanism of the process was attributed to the formation of complexes in the interlayers of the Mg–Al–LDH. The application of such materials in the removal of other heavy metals was also reported. Water-dispersible magnetite-graphene–LDH-composite was reported to have successfully remove arsenate from the aqueous solution [10]. The results of the studies showed an enhancement in the arsenate removal through the use of the composite as compared to the original Mg–Al LDH. Few-layered graphene oxide nanosheets material was also reported to have successfully removed lead ions from the aqueous solution [11]. A strong surface complexation was found to be the main removal process of the lead ions in their study.

Organic acids are present in natural and exist abundantly in nature. They have the ability to be used as a leaching agent for leaching heavy metals from fly ash [12]. The acids are found to have the ability to form chelate complexes with the metals on the surface of the fly ash. Our study concerns the intercalation of tartrate with Mg–Al LDH for the formation of composite material using the co-precipitation method. Although previous studies have examined the synthesis of tartrate-Mg–Al LDH [9] and the way in which the compound was used as an adsorbent for the removal of heavy metals, the application towards the removal of lead has not been examined previously. Therefore, the main objective of this present work is to synthesize, characterize, and study the removal efficiency of lead by using the tartrate-Mg–Al LDH.

2. Experimental

2.1. Synthesis of original Mg–Al LDH (Mg–Al–NO_3) and tartrate-Mg–Al LDH (tartrate-Mg–Al)

All chemicals used in this synthesis were of analytical grade and used without any purification. The original Mg–Al LDH (Mg–Al–NO_3) was prepared from Mg $(NO_3)_2{\cdot}6H_2O$ and Al $(NO_3)_3{\cdot}9H_2O$ at moderate conditions. The co-precipitation method was adapted to synthesis tartrate-Mg–Al LDH in this work. In the preparation of the Mg–Al solution, an aqueous solution of Mg $(NO_3)_2{\cdot}6H_2O$ and Al $(NO_3)_3{\cdot}9H_2O$ was dissolved in deionized water to give Mg^{2+}/Al^{3+} ratio of 4. The tartrate solutions were prepared by dissolving the required amount of organic salt of tartrate in deionized water according to the stoichiometric quantities defined by the following equation:

$$0.2\,Mg^{2+} + 0.05\,Al^{3+} + 0.1C_4H_4O_6^{2-} + 2OH^- \rightarrow Mg_{0.2}Al_{0.05}(OH)_2(C_4H_4O_6)_{0.1} \quad (1)$$

An aqueous solution of Mg–Al–NO_3 at a ratio of 4 was then added dropwise to a solution of tartrate under nitrogen atmosphere with vigorous stirring. The solution mixture was kept under nitrogen atmosphere throughout the synthesize process to minimize the effects of dissolved carbon dioxide. The pH of the solution mixture was kept constant at a pH of 10 by adding a sodium hydroxide solution. The resulting slurry was aged at 70°C for 24 h in an oil batch shaker. The resultant slurry was then filtered and washed with deionized water to remove free ions and excess organic salt. The material was then dried in an oven at 60°C for 24 h and was kept in sample bottles for further use and characterizations.

2.2. Characterization of original Mg–Al LDH (Mg–Al–NO_3) and tartrate-Mg–Al LDH (tartrate-Mg–Al)

The X-ray Diffraction (XRD) patterns of Mg–Al–NO_3 and tartrate-Mg–Al LDH before and after removal experiments were obtained by PANlytical X'pert Pro using Ni-filtered Cu k_α radiation, 60 KV, and 60 mA. The basal spacing (*d*-spacing) of the compounds was determined via the powder technique. All solid samples were mounted on PW18xx sample holder series and the scans were done at 5–90° 2θ/min at 0.003° steps. Fourier transformed infrared spectra of Mg–Al–NO_3 and tartrate-Mg–Al LDH were recorded by Perkin Elmer 1725X spectrophotometer in the range of 400–4,000 cm^{-1}. Finely grounded 1% samples in KBr powder were compressed to obtain a pellet and the pellet was then used to obtain the IR spectrum.

2.3. Removal of lead ions from aqueous solution

The batch method was employed in the removal experiment of lead ions from the aqueous solution using the original LDH (Mg–Al–NO_3) and tartrate-Mg–Al LDH (tartrate-Mg–Al). A sample of

0.05 g Mg–Al–NO_3 and tartrate–Mg–Al was placed in a 100 mL Schott Duran bottle and 25 mL of 20–40 mg/L lead solution was added to the bottle and agitated by the use of the shaker operating at room temperature with a speed of 150 rpm. The amount of lead ions removed (%) was calculated as follows:

$$\frac{C_o - C_t}{C_o} \times 100\% \tag{2}$$

where C_o is the initial concentration (mM) of the lead ions solution and C_t is the concentration equilibrium at the time, t. At predetermined time, the solutions were withdrawn and filtered through a 0.45 μm Whatman syringe filter. The remaining concentration of lead ions was then measured by using the Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrophotometer. All experiments were conducted in duplicate and controls were simultaneously carried out to ensure that the removal was by adsorbent and not by the wall of the glassware. Adsorption isotherms were also carried out by the use of a batch method. A sample of 0.05 g Mg–Al–NO_3 and tartrate-Mg–Al was placed in a 100 mL bottle and then filled with 25 mL of lead solutions at different concentrations. In order to avoid precipitation, the pH of the solution was kept below 6 since the solubility product of $Pb(OH)_2$ was recorded at 1.43×10^{-20} [13]. The amount of lead ions removed was calculated as eq. (2).

3. Results and discussion

3.1. Characterization of original Mg–Al LDH (Mg–Al–NO_3) and tartrate-Mg–Al LDH (tartrate-Mg–Al)

The structure of the LDH (Mg–Al–NO_3) synthesized at a ratio of 4 and the structures of intercalated compound before (tartrate-Mg–Al) and after the removal of lead (tartrate-Mg–Al–Pb) ions were characterized and their XRD patterns were shown in Fig. 1. As shown in the Fig. 1(a), original LDH (Mg–Al–NO_3) indicated fairly good crystallinity. This was proven by the *d*-spacing which was recorded at 7.6 Å that demonstrated the general features of the LDH [14–16]. The *d*-spacing showed the characteristic values for the trigonal structures with a strong sharp and symmetrical peaks assigned to (0 0 3) and (0 0 6) planes, respectively. The interlayer spacing of the sample corresponding to the (0 0 6) plane was found to be 3.8 Å.

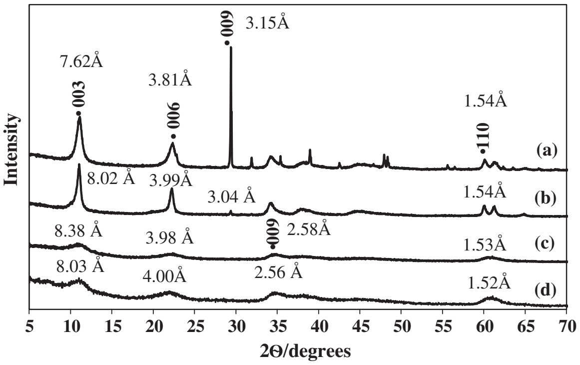

Fig. 1. XRD patterns of (a) original Mg–Al–NO_3, (b) Mg–Al–NO_3–Pb, (c) tartrate Mg–Al, and (d) tartrate-Mg–Al–Pb.

The original XRD patterns of tartrate-Mg–Al (Fig. 1 (c)) showed a broader pattern as compared to the original Mg–Al–NO_3 which suggested that tartrate-Mg–Al had the common structure of the Mg–Al–NO_3. The basal spacing for tartrate-Mg–Al recorded at 8.38 Å indicated that the interlayer spacing was larger than that of the Mg–Al–NO_3. The pattern revealed that the intercalation of tartrate ions in the interlayer of Mg–Al–NO_3 increased the basal spacing from 7.6 to 8.38 Å. The basal spacing recorded for the tartrate-Mg–Al suggested that the tartrate ions which were larger in size than the nitrate ions were intercalated into the interlayer of Mg–Al–NO_3 LDH [9]. The XRD patterns of tartrate-Mg–Al after the removal of lead ions (Fig. 1 (d)) showed that the basal spacing was slightly lower than that of the original tartrate-Mg–Al. The pattern showed that no additional peaks were detected for the precipitation products of lead which indicated that the main mechanism for the removal of the lead ion was not through the surface precipitation reaction between lead ions and hydroxide ions. Therefore, the results suggested that the main mechanism for the removal of lead was through the formation of metal complexes between the lead ions and tartrates which were formed in the interlayer of tartrate-Mg–Al LDH. For the removal of lead ions with the use of Mg–Al–NO_3, the precipitation reaction was expected to occur; however, there were no additional peaks for lead precipitation products detected as shown in Fig. 1(b) (Mg–Al–NO_3–Pb). The patterns still revealed that good crystallinity though the formation of the precipitate or metal adsorption did not have any virtual effect on the reflections as also previously reported in the heavy metals removal using intercalated LDH [8,16,17].

Fig. 2 shows the Fourier transform infrared (FTIR) spectra of LDH (Mg–Al–NO_3) and the intercalated compound before (tartrate-Mg–Al) and after the removal of lead ions (tartrate-Mg–Al–Pb). As shown in Fig. 2(a), the FTIR spectra of Mg–Al–NO_3 showed a broad band centered around 3,485 cm^{-1} which was due to the presence of OH stretching of the hydroxyl group of LDH that physically adsorbed water molecules. The band around 1,635 cm^{-1} was due to H–O–H bend vibrations and the intense absorption band

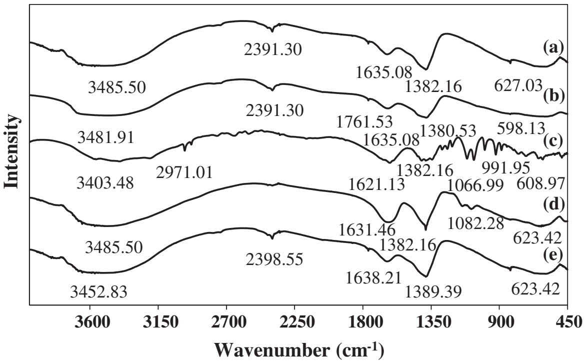

Fig. 2. FTIR spectra of (a) original Mg–Al–NO_3, (b) Mg–Al–NO_3–Pb, (c) tartrate, (d) tartrate Mg–Al, and (e) tartrate-Mg–Al–Pb.

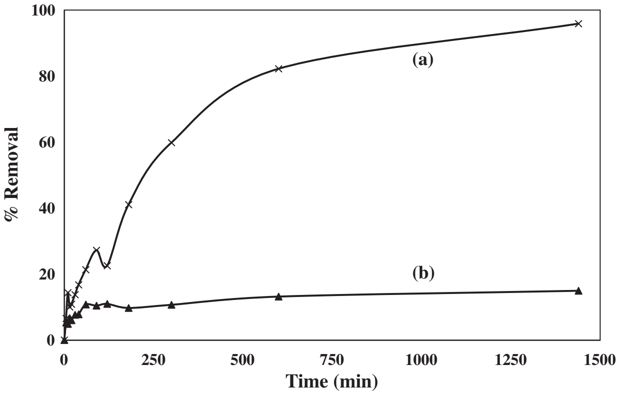

Fig. 3. Effects of contact time on the removal of lead ions with the use of (a) tartrate Mg–Al and (b) Mg–Al–NO_3.

around 1,382 cm^{-1} was due to the asymmetric stretching of NO_3^- in the interlayer of LDH. Fig. 2(b) shows the FTIR spectrum of tartrate-Mg–Al that was prepared using the co-precipitation method. As shown in the Figure, the tartrate-Mg–Al LDH was slightly similar in patterns as compared to the original Mg–Al–NO_3 which suggested that the tartrate-Mg–Al had the common structure of the Mg–Al–NO_3. A strong absorption band recorded at 1,631 cm^{-1} for tartrate-Mg–Al LDH was attributed to the symmetric and asymmetric vibration of coordinated –COO^- group from the tartrate. As also shown in the Figure, tartrate-Mg–Al–Pb showed a less strong absorption band that was recorded at 1,638 cm^{-1} which could be explained by the formation of complexes in the interlayer of tartrate-Mg–Al between the tartrate and lead ions which contributed to the decrease of the absorption which could also be supported by the XRD patterns that were mentioned earlier.

3.2. Effect of contact time on the removal of lead from aqueous solution

The effect of contact time on the removal of lead from aqueous solution using original Mg–Al–NO_3 and intercalated tartrate-Mg–Al LDH was carried out at a period of time ranging from 30 min to 12 h under the same conditions of 298 K of temperature, 0.05 g adsorbent (Mg–Al–NO_3 and tartrate-Mg–Al), and the concentration of lead 40 mg/L. As shown in Fig. 3, the percentage of lead removal with the use of tartrate-Mg–Al increased rapidly for the first 600 min with 82% removal recorded. The percentage removal has not changed for both concentrations when incubation time was further increased indicating an equilibrium state. Among the factors that may have contributed to this are as follows: (i) the adsorption has achieved an equilibrium state; and (ii) as the removal progressed, the concentration of lead ion solutions decreased which led to a fall in the percentage removal. The percentage removal of lead with the use of tartrate-Mg–Al was recorded larger than the original Mg–Al–NO_3. This was attributed to the function of tartrate in the layer of tartrate-Mg–Al which possibly forms complexes with aqueous solution of lead ions. However, this possibility was not supported with the XRD patterns of tartrate-Mg–Al due to the poor crystallinity and turbostatic effects which contributed to difficulty in the identification of accurate reflections. Similar results were also previously found in heavy metals adsorption by Mg–Al–EDTA, Li–Al–EDTA and Zn–Al–EDTA [8,16,18]. Furthermore, the pattern showed that no additional peaks were recorded due to the possible hydrolysis of $Pb(OH)_2$ that could have possibly been formed through the adsorption of lead ions on the surface of Mg–Al LDH. This result was supported by the previously reported paper in which the tartrate-Mg–Al–LDH loaded with Cu^{2+} ions showed a nearly the same the XRD pattern as the original Mg–Al–LDH with no peaks due to the hydrolysis product of $Cu(OH)_2$ recorded [9]. The recorded results from the XRD patterns of tartrate-Mg–Al–Pb suggested that the removal of lead from the aqueous solution was mainly due to the formation of complexes between tartrate and lead ions and not from the electrostatic binding reactions between lead ions and the opposite charged at the surface of Mg–Al LDH.

3.3. Effect of dosage on the removal of lead from aqueous solution

The effect of the dosage of Mg–Al–NO_3 and intercalated tartrate-Mg–Al LDH on the removal of lead from aqueous solution was carried out at different dosages ranging from 0.01 to 0.1 g with concentration

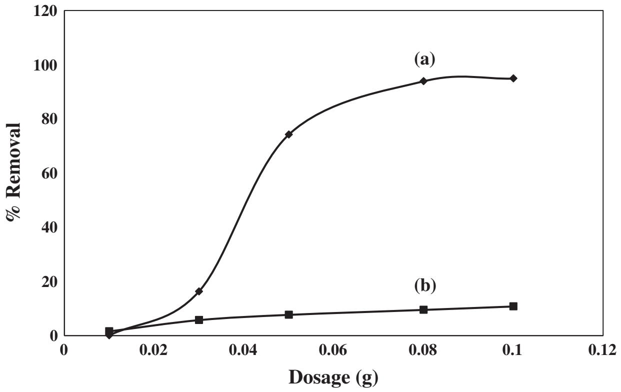

Fig. 4. Effects of dosage on the removal of lead ions with the use of (a) tartrate Mg–Al and (b) Mg–Al–NO_3.

aqueous solution of lead of 40 mg/L. The results in Fig. 4 follow the expected pattern, in which the percentage removal of lead increased with the increase of the dosage of Mg–Al–NO_3 and intercalated tartrate-Mg–Al LDH. As shown in the Figure, the percentage removal of lead increased rapidly and reached the maximum of 0.1 g dosage. This might have been due to the increase of sites available for lead to form complexes with tartrate and consequently allowing better removal to take place. The results also showed that the percentage removal of lead with the use of tartrate-Mg–Al was higher than the original Mg–Al–NO_3. The percentage removal increased almost linearly with the increase of dosage probably implying that the amount of tartrate-Mg–Al sites for possible complexes formation also increased.

3.4. Effect of pH on the removal of lead from aqueous solution

The effect of pH on the removal of lead from the aqueous solution with the use of Mg–Al–NO_3 and intercalated tartrate-Mg–Al LDH was carried out within the range of pH from 2 to 12. The initial pH values of lead solutions were adjusted using 0.1 mol/L hydrochloric acid (HCl) and 0.1 mol/L sodium hydroxide (NaOH) solutions. The experiment was carried out at a fixed concentration of lead solutions of 40 mg/L and dosage (Mg–Al–NO_3 and tartrate-Mg–Al) of 0.05 g. The removal of lead from the aqueous solution was found to be a function of a pH as shown in Fig. 5. As shown in the Figure, the percentage removal of lead from the aqueous solution decreased with an increase in pH and reached the maximum removal at a pH of around 2–4. Further increase of the pH would steadily decrease the percentage removal of lead. When the pH was steadily increased, the metal cations in the LDH layers began to dissolve which could also be explained by the dissolution of LDH that led to the decrease in the percentage removal of lead. It was obvious that the percentage of lead removed was higher at a moderate pH. At a too low pH, excess hydrogen ions could inhibit the removal process which corresponded to the formation of complexes between Pb^{2+} and tartrate at the interlayer of tartrate-Mg–Al LDH.

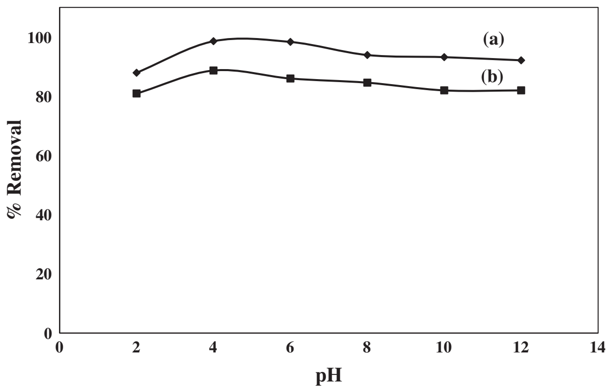

Fig. 5. Effects of pH on the removal of lead ions with the use of (a) tartrate Mg–Al and (b) Mg–Al–NO_3.

3.5. Adsorption isotherms

In order to determine the maximum sorption amounts of lead by Mg–Al–NO_3 and tartrate-Mg–Al, equilibrium isotherms studies had to be carried out. Two equilibrium models were used in isotherm studies to fit the experimental data which were the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) isotherms.

(i) Langmuir isotherm

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max b}} + \frac{C_e}{Q_{\max}} \tag{3}$$

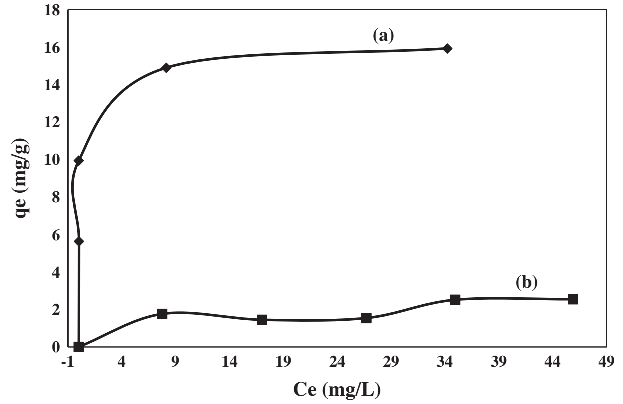

Fig. 6. Isotherm plot for the removal of lead with the use of (a) tartrate Mg–Al and (b) Mg–Al–NO_3.

Table 1
Isotherm parameters for Langmuir and Freundlich

	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Tartrate-Mg–Al	8.4	1.28	0.987	0.14	12.3	0.953
Mg–Al–NO_3	3.2	0.06	0.727	3.3	4.3	0.366

Table 2
Sorption capacities of lead ions with the use of various materials in wastewater treatment

Materials	Sorption capacity	
Oxidized multiwall carbon nanotubes	9.92×10^{-6} mol/g	Xu et al. [23]
Cyclodextrin multiwall carbon nanotubes/iron oxides	9.85 mg/g	Hu et al. [24]
Multiwall carbon nanotubes/polyacrylamide composites	29.71 mg/g	Yang et al. [25]
Hierarchical films of layered double hydroxides	2.0 mg/g	Zhao et al. [26]

where q_e (mg/g) is the sorption amount of lead, C_e (mg/L) is the equilibrium concentration of remaining lead in the solution, Q_{max} (mg/g) is the maximum sorption amount of lead, and b (L/mg) is a Langmuir constant.

(ii) Freundlich isotherm

$$\text{Log } q_e = \text{Log } K_f - \frac{1}{n}\text{Log } C_e \quad (4)$$

where K_f and n are Freundlich constants. The Freundlich isotherm however does not predict the maximum sorption amount of the adsorbent.

The adsorption isotherms of lead removal with the use of Mg–Al–NO_3 and tartrate-Mg–Al are shown in Fig. 6. As shown in the figure, the isotherms were of Langmuir H type according to the classification by Giles et al. [18] which suggested a very high affinity between the adsorbent and adsorbate [19]. These results contradicted with those previously reported on the removal of heavy metals with the use of such materials. Cruz-Guzman et al. [20] reported that only Hg^{2+} had high affinity towards adsorbent and Pb^{2+} was more efficiently adsorbed on carboxyl functionalized organo clays. Brown et al. [21] described that, low affinity of Pb^{2+} and Cd^{2+} cations towards thiol group in the pores of functionalized clay minerals was due to their thermodynamic inability to coordinate within the space of the adsorbent pore channels. Also in contrast with our results, Nakayama et al. [22] reported that only a small amount of Cu^{2+} and Pb^{2+} cations was absorbed on LDH intercalated with meso-2,3-dimercaptosuccinate which explained the low affinity of adsorbate towards adsorbent. Based on our results, the chelating agent of tartrate that intercalated between the layers of LDH seemed to be more accessible to lead cations that significantly increased the sorption amount of lead as compared to the original Mg–Al–NO_3.

The maximum sorption amount (Q_{max}) of lead ions on tartrate-Mg–Al and Mg–Al–NO_3 was recorded at 8.4 and 3.2 mg/g, respectively. The experimental data from the isotherm studies showed that the Langmuir isotherm was a better model than the Freundlich on the basis of the correlation coefficients (R^2) with 0.987 and 0.953 recorded for the Langmuir and Freundlich, respectively. The rest of the parameters for the adsorption study are listed in Table 1. As comparison, the sorption capacities of lead ions with the use of such materials in wastewater treatment are given in Table 2.

4. Conclusion

In this study, the removal of lead from aqueous solution was carried out by the original Mg–Al–NO_3 and intercalated tartrate-Mg–Al that was prepared by the co-precipitation method. The removal process was performed at variable contact times, variable pH, and variable dosages of adsorbents (Mg–Al–NO_3 and tartrate-Mg–Al). The percentage removal of both adsorbents increased with the increase in the contact time and adsorbent dosage but decreased with an increase in the solution pH. The percentage removal of lead with the use of tartrate-Mg–Al was higher than that of the original Mg–Al–NO_3 and this was mainly due to the formation of the chelate complex between Pb^{2+} and the intercalated tartrate ($C_4H_6O_6^{2-}$).

The maximum sorption of lead by tartrate-Mg–Al and original Mg–Al–NO_3 was 8.4 mg/g and 3.2 mg/g respectively obtained from the equilibrium data fitted with the Langmuir H type. These results suggested that tartrate-Mg–Al could be used as a potential adsorbent for the removal of heavy metals from aqueous solutions.

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