Treatment of gold ore cyanidation wastewater by adsorption onto a Hydrotalcite-type anionic clay as a novel adsorbent

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Abstract

The treatment of cyanide contaminated wastewater from a gold processing plant was performed by the synthesized nanostructured Layered Double Hydroxide (LDH) which has known as a Hydrotalcite-type anionic clay. LDH was synthesized by the co-precipitation process, characterized by *X-ray fluorescence* (XRF), X-ray powder diffraction (XRD), scanning electron microscope (SEM) Brunauer-Emmett-Teller (BET), Fourier-transform infrared spectroscopy (FTIR) and Wavelength Dispersive X-ray analysis (WDX) and applied for removal of free cyanide from both synthetic solution and mining effluent. The maximum particle size of synthesized LDH was determined to be 4 nm based on the Scherrer's equation. The maximum loading capacity of LDH, 60 mg/g, indicates that LDH is an interesting adsorbent for cyanide removal. The data modeling showed that the kinetic and equilibrium data best fitted by FPKM and RPIM, respectively, also, rate-controlling step in the adsorption process is intra-particle diffusion based on Weber–Morris plot, and the adsorption of CN^- onto LDH is a two-step process. The thermodynamic studies confirm that the adsorption of free cyanide on Mg/Al LDH is a spontaneous and endothermic process. The energy of activation for adsorption of free cyanide on Mg/Al LDH was determined to be 6.14 kJ/mol, which is in the range physicochemical sorption. The mining wastewater treatment was performed by the synthesized LDH. The adsorption experiments showed that more than 90% of free cyanide was removed from the real solution during a short period of contact time, which confirms the ability of LDH for the treatment of industrial cyanide contaminated wastewater.

Keywords Cyanide adsorption · Mining wastewater · Nanostructured layered double hydroxide · Kinetic data modeling · Thermodynamic studies

Nomenclature

EPA	Environmental Protection Agency.
LDH	Layered Double Hydroxide.
XRD	X-Ray Diffraction.
XRF	X-Ray Fluorescence.
SEM	Scanning Electron Microscopy.
WDX	Wave length dispersive X-ray.
FTIR	Fourier transform infrared.
BET	Brunauer-Emmett-Teller.
BJH	Barrett–Joyner–Halenda.
MPSD	Marquardt's percent standard deviation.
ARE	Average Relative Error.
R^2	Correlation coefficient.

LAIM	Langmuir Isotherm Model.
FRIM	Freundlich Isotherm Model.
TEIM	Temkin Isotherm Model.
RPIM	Redlich–Peterson Isotherm Model.
KCIM	Koble–Corrigan Isotherm Model.
ELKM	Elovich Kinetic Model.
FPKM	Fractional Power Kinetic Model.
PFOKM	Pseudo-First Order Kinetic Model.
PSOKM	Pseudo-Second Order Kinetic Model.
WMIDM	Weber and Morris Intaparticle Diffusion Model.
q_e	The adsorbed cyanide after equilibrium (mg/g).
q_t	The adsorbed cyanide at time t (mg/g).
D	Mean crystallite size (nm),
K	A constant value (usually 0.9, but varies based on the crystallite shape),
λ	X-ray wavelength (0.154 nm for K_α Cu),
θ	Bragg's angle in degrees,
β	Full width at half maximum of a diffraction peak.
C_0	Initial CN^- concentration (mg/L),

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C_e	CN^- concentration after equilibrium (mg/L).
C_t	CN^- concentration at time t (mg/L).
V	Solution volume (L).
W	Adsorbent mass (g).
q^{exp}	Experimental amount of CN^- adsorbed on the Mg/Al LDH (mg/g).
q^{cal}	Calculated amount of CN^- adsorbed on the Mg/Al LDH (mg/g).
N	Number of data point.
p	Number of model parameters.
T	Absolute temperature (K).
R	Ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).
k_1	PSOKM Type (I) rate constant ($\text{g mg}^{-1} \text{ h}^{-1}$).
A	Temperature-independent factor (min^{-1}).
E_a	Adsorption activation energy (kJ mol^{-1}).

Introduction

Cyanide is a very poisonous chemical compound. Hence, EPA has set an enforceable regulation for cyanide at 0.2 mg/L. Large volumes of wastewaters annually produced by various industrial activities such as mining (extraction of gold, silver, etc.), electroplating, and production of synthetic fibers, plastics, organic chemicals and pharmaceuticals [1–3]. They usually contain high concentrations of free and metal-complexed cyanide species and must be treated before they are released into the environment [4, 5]. Electrowinning, Acidification–Volatilisation–Reneutralisation, hydrolysis distillation, precipitation, oxidation of cyanate, flotation, reverse osmosis, alkaline-chlorination oxidation, electrodialysis, Caro's acid and biodegradation [6, 7] are the main technologies for cyanide removal [8]. Adsorption is one of the most important technologies for cyanide removal as it is simple to operate, and no hazardous chemicals are required in this process [9–11]. Various adsorbents have been used for cyanide removal from aqueous solutions such as activated carbon [8], bentonite [12] and zeolites [13]. The loading capacity of these adsorbents for free cyanide is relatively low, and therefore, there is a research interest to find new materials with higher loading capacity and greater ease of regeneration than carbon for water treatment while their adsorptive characteristics are still desirable.

Anionic clays, normally named as LDH or hydrotalcite-like compounds, form part of a family of natural or synthetic clays [14, 15]. LDH can be usually showed by the formula $[M_{(1-x)}^{2+}M_x^{3+}(OH)_2] [An_{x/n}^- \cdot mH_2O]$, where M^{2+} can be a divalent cation such as Mg^{2+} , Co^{2+} or Zn^{2+} , and M^{3+} can be a three-valent cation such as Al^{3+} , Ga^{3+} , Fe^{3+} , Mn^{3+} or Gd^{3+} and An^- denotes the interlayer anions that balance the positive charges on the layers for example, NO_3^- or Cl^- , and x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio ($0.20 \leq x \leq 0.33$) [16]. An

excess positive charge is introduced in the octahedral layers as a result of isomorphic substitution of divalent cations by three-valent cations which is normally balanced by exchangeable anions located in the interlaminar space [17]. The positive charge can also be balanced by other anions from solution, which is why LDH can be used as an anion exchanger [18]. LDH is a novel potential adsorbent for the removal of anionic pollutants due to Low-cost and simple preparation, high sorption efficiency and many other advantages [19]. For example, LDHs can take up sulfate [20], arsenate [16, 21], chromate [22], selenite [23], bromate [24], Antimonate [25], fluoride [26] and phosphate [27] from aqueous solutions.

The adsorptive properties of LDH nanoclays for the removal of various anionic pollutants from aqueous solutions has been proved, but its ability for the removal of free cyanide anion (CN^-) has not been received any attention up to now and it is the main focus of this research. Hence, Mg/Al LDH was synthesized by a coprecipitation method, characterized by various experimental tools and used for the removal of free cyanide from aqueous solutions. The adsorption mechanism of free cyanide on LDH was assessed through equilibrium, kinetic and thermodynamic studies. For industrial applications, it is important to test the ability of an adsorbent for the removal of an adsorbate from real wastewaters, since various anionic and cationic species are present in real wastewaters which can affect the adsorption process. Hence, a real wastewater was taken from a gold ore processing plant and its treatment was performed by the synthesized LDH.

Materials and methods

Reagents

Analytical grade reagents including $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, NaOH, KI, NaCN and $AgNO_3$ were obtained from Merck Co., Germany.

Synthesis of LDH

A co-precipitation method was applied for the synthesis of Mg/Al LDH [28–30]. Initially, 48.076 g (0.75 mol) of $Mg(NO_3)_2 \cdot 6H_2O$ and 23.446 g (0.25 mol) of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved into 250 mL of deionized water (It is named as solution A). Furthermore, 20 g (2 mol) of NaOH was dissolved in 250 mL of deionized water (It is named as solution B). Afterward, 250 mL of suspension B was added dropwise to the 250 mL of solution A with constant agitation at ambient temperature. As the caustic solution was added, hydrotalcite immediately formed as a white precipitate. The mixture was covered and left overnight. The precipitate was collected by filtration, washed with deionized water (50 mL), dried in an

oven overnight at 80 °C and reduced in size by grinding in a mortar.

Characterization

SEM images were taken from LDH samples after gold coating by using a Philips XL30 SEM. WDX studies were carried out with a WDX 3PC, MICROSPEC Corp., USA. The chemical composition of LDH was analyzed by the Philips PW1480 XRF instrument. The mineralogical composition of the synthesized LDH sample was determined by X'Pert PRO XRD instrument (Philips Company). Crystallite dimensions were estimated according to full width half maximum values for the outstanding XRD peaks using the Debye Scherrer equation (Eq.1) [31].

$$D = \frac{\lambda K}{\beta \cos \theta} \quad (1)$$

FTIR spectra of LDH sample before and after free cyanide adsorption were recorded using the KBR pellet technique with a Bruker Tensor 27 FTIR spectrometer over the 4000–400 cm^{-1} wavenumber range.

The N_2 adsorption/desorption isotherms were determined at liquid nitrogen temperature (−196 °C) and relative pressure interval between 0.025 and 0.9936 on a Belsorp mini II, Microtrac Bel Corp. Japan. The samples were degassed at 110 °C for 2 h. The surface area was calculated from the adsorption data in the relative pressure range of 0.05–0.35 according to the BET method. The pore size distribution was determined according to BJH model.

Adsorption experiments

In equilibrium studies, a cyanide stock solution was used to prepare the required working solutions at CN^- concentrations of 13.3, 26.6, 53.1, 79.7, 106.3, 159.4, 212.6, 265.7, 318.9, 372 and 425.2 mg/L. The pH of solutions was pre-adjusted to 10 by diluted NaOH solution. The CN^- concentration of solutions was analyzed in triplicate and averaged by the titration method. The stock silver nitrate solution was prepared by dissolving 2.16 g of silver nitrate salt in 500 ml distilled water. 10 mL of the stock silver nitrate solution was poured into 1 L volumetric flask and brought to the volume by distilled water. It was transferred to a burette as titrant solution. 2 ml of a solution with an unknown concentration of free cyanide was transferred to a beaker and 2–3 drops of 10 g/L KI solution as indicator was added into it. The titrant solution was added dropwise into the beaker until the color of solution change to light yellow which is easily recognized. Finally, the concentration of free cyanide in solution was determined by the following equation:

$$C_{\text{CN}} = \frac{V_{\text{AgNO}_3} * 2.5 * 1000}{V_{\text{CN}} * 100} * 0.531 \quad (2)$$

Where C_{CN} (mg/L) is the cyanide concentration in the sample, V_{CN} (mL) is the volume of cyanide solution, and V_{AgNO_3} (mL) is the volume of standard silver nitrate solution.

For adsorption experiments, 500 mL of a working solution and 1 g Mg/Al LDH was added into 2.5 L Merck glass bottles and agitated for 72 h at ambient temperature (25 ± 1 °C) and at a stirrer speed of 100 rpm. Sampling and analyzing of CN^- concentration was performed at the end of experiments. The q_e value was determined by Eq.3.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (3)$$

Kinetic studies were performed as the same procedure with the equilibrium tests. Sampling was done at the predetermined time intervals. The q_t values were determined by Eq.4.

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (4)$$

Various kinetic and equilibrium models were compared by MPSPD and ARE error functions apart from R^2 . ARE and MPSPD can be calculated by Eq. 5 and Eq.6, respectively [32].

$$ARE = \frac{100}{N} \sum_{i=1}^N \left| \frac{(q_{\text{exp}} - q_{\text{cal}})}{q_{\text{exp}}} \right| \quad (5)$$

$$MPSPD = 100 \sqrt{\frac{1}{N-p} \sum_{i=1}^N \left(\frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}} \right)^2} \quad (6)$$

Thermodynamic studies

A solution at initial CN^- concentration of 265 mg/L, pH of 10 and a volume of 500 mL was poured into a beaker and placed within a water bath. In order to determine the thermodynamic parameters and activation energy of cyanide adsorption on LDH, the tests were conducted at three different solution temperatures of 30, 40 and 50 °C. A certain amount of Mg/Al LDH (1 g) was added to the solution and stirred for 72 h at a constant rotation speed of 250 rpm by a mechanical stirrer. Some samples were taken at certain time intervals for the CN^- concentration analysis.

Treatment of real cyanide contaminated aqueous solution

A real cyanide contaminated wastewater was taken from a gold processing plant in the northeastern of Iran. In this plant,

Fig. 1 a) An image from a gold processing plant in the northeastern of Iran, b. An image from its tailing dam.

the gold-bearing ore after crushing and milling with particle size less than $75\ \mu\text{m}$ is transferred to the leaching tanks as pulp with a solid content of 40%. In these tanks, the solution pH is set at 10 by adding an appropriate amount of slaked lime. Afterward, sodium cyanide is added to the pulp as gold leaching lixiviant. During cyanidation, the gold is leached from the ore and entered to the pulp as gold-cyanide complexes. They are adsorbed by activated carbon. The gold loaded activated carbons are separated from the pulp through screening, and the barren pulp is transferred to the tailing dam. An image from the gold processing plant and its tailing dam has been shown in Fig. 1a and b, respectively.

Nearly 5 L pulp was taken from the place where the barren pulp was poured into the tailing dam. The pulp was filtered by a laboratory vacuum filter, and the clear solution was used in the adsorption experiments. It was analyzed for free cyanide concentration by the standard titration method, and the solution pH was recorded by pH-meter. 500 mL solution was fed to the glass bottle and 10 g synthesized LDH was added to the solution. The glass bottle was placed on the bottle roller mixer. It was agitated by a constant rotation speed of 100 rpm for 48 h at ambient temperature. Sampling was performed at designated times and the samples were sent for analysis.

Results and discussion

Mg/Al LDH characterization

The XRD spectra of prepared LDH is presented in Fig. 2. The peaks at $2\theta = 12^\circ, 22^\circ, 32.5^\circ, 57^\circ$ and 58.3° are related to the planes of (003), (006), (009), (110) and (113), respectively, which corresponds to the typical Miller-Bravais indices of Mg/Al LDH [33]. Since the formation of alumina and magnesium hydroxide can occur during the synthesis procedure, we have checked the XRD spectra (Fig. 2) by the standard one for aluminum hydroxide and found that there is no $\text{Al}(\text{OH})_3$ in the synthesized LDH; however comparing the standard peak for magnesium hydroxide and LDH spectra, the peak at $2\theta = 34^\circ, 39^\circ, 50^\circ$ and 59° which show in blue triangle can be contributed to $\text{Mg}(\text{OH})_2$ formation. Using the Scherrer Eq. 1, the mean diameter of the LDH crystal was estimated to be 4.3361 nm, which indicates that the synthesized LDH is a nano-adsorbent.

The chemical composition of the synthesized LDH was analyzed by the XRF analyzing method and the main constituents of the sample were determined to be MgO 32.36%, Al_2O_3 14.15%, Na_2O 4.01%, and LOI 49.02%. The transition

Fig. 2 XRD patterns of LDH

Fig. 3 (a) SEM photograph of synthetic synthesized LDH. (b) and (c) Elemental distribution maps of aluminum and magnesium over scanned area

metals (magnesium and Aluminum) were detected in the LDH sample and their molar ratios were very close to the nominal ($\text{Mg}/\text{Al} = 1/3$) based on XRF analysis.

Figure 3.a shows the surface morphologies of Mg/Al LDH. Figures 3b and c show the elemental distribution maps of Al and Mg over the scanned area, respectively. It found that the relative proportion of Mg element is more than the Al element. The ratio of Mg/Al from synthesis LDH is close enough to the initial 3:1 M ratio of the salts.

Figure 4a shows the N_2 gas adsorption/desorption isotherms onto Mg/Al LDH. The adsorption isotherm resembles to the Type IV of the six main types of adsorption isotherms which proposed by IUPAC [34]. The characteristic feature of Type IV

isotherm is its hysteresis loop, which is due to capillary condensation taking place in mesopores. The hysteresis loops or desorption isotherms in different adsorbents show several forms based on the shape of pores which have been classified by IUPAC to four main groups [34]. The hysteresis loop for the Mg/Al LDH in Fig. 4a resembles to the Type-H3 hysteresis loops which are the main feature of aggregates of platelike particles forming slit-like pores. Figure 4b shows the pore size distribution curve of Mg/Al LDH. As can be seen, most of the pores in Mg/Al LDH fall in the category of mesopores (i.e., pores with diameter in the range of 2–50 nm), since the pores with diameter of 12.24 and 7.98 nm have the highest frequency in the adsorbent. Furthermore, there are a considerable amounts of micropores (i.e., pores with diameter less than 2 nm) in the adsorbent. The BET surface area for the Mg/Al LDH was determined to be $0.51 \text{ m}^2/\text{g}$.

Equilibrium studies

Figure 5 shows the loading capacity of Mg/Al LDH for free cyanide at different initial cyanide concentrations. The loading capacity of Mg/Al LDH increases from 2.66 mg/g to 13.29 mg/g with increasing the initial cyanide concentration from 13.29 mg/L to 531.49 mg/L. The uptake capacity of activated carbon as the most widely used adsorbent for free cyanide is around 10 mg/g [9]. The loading capacity of the other adsorbents (Fig. 6) for free cyanide usually is less than 10 mg/g [35] which indicate that Mg/Al LDH is potentially an interesting adsorbent for cyanide removal since its loading capacity is sharply higher than the other current adsorbents. The initial cyanide concentration has a direct effect on the loading capacity of Mg/Al LDH for free cyanide which may be due to this fact that the activity of CN^- ions in solution increasing by increasing the initial concentration.

The removal percentage of free cyanide by Mg/Al LDH at different initial cyanide concentrations has also illustrated in Fig. 5. The removal percentage can be determined by Eq. 7.

$$\text{Removal percentage} = 100 \times \left(1 - \frac{C_e}{C_0} \right) \quad (7)$$

Fig. 4 a N_2 gas Adsorption/Desorption isotherms, and b) corresponding BJH pore size distribution curve

Fig. 5 The effect of initial cyanide concentration on loading capacity (q_e) and removal percentage of CN^- by Mg/Al LDH

It found that the adsorption of CN^- by Mg/Al LDH decreases at high cyanide concentration. It decreases by about 60% by increasing the beginning concentration of free cyanide from 13.29 to 531.49 mg/L.

The equilibrium data for adsorption of CN^- by Mg/Al LDH were modeled by various isotherm models including LAIM, FRIM and TEIM, RPIM and KCIM. The isotherm models, their linear forms, the model parameters and the approach to get the isotherm parameters are presented by Behnamfard et al. [8].

The LAIM is based on some assumptions including a uniform surface, a single layer of adsorbed material and uniform sorption energies among the adsorption sites and adsorbed molecules [36, 37]. This model may be simplified into four different linearized forms as given in Table 1. The FRIM is an empirical isotherm model. It assumes that the energy of adsorption sharply decreases when the adsorption sites of an adsorbent completed, and the adsorption occurs as multilayer. $1/n$ and K_F are constant parameters of FRIM, and they are related to adsorption intensity and capacity, respectively [8]. The indirect adsorbate-adsorbate

interactions are considered in the TEIM [38]. The KCIM and RPIM models are three-parameter isotherms and hybrid of both features of LAIM and FRIM [39]. The parameters, the R^2 , ARE, and MPSD values for all tested isotherm models are given in Table 1. The ARE and MPSD values for the three-parameter isotherm models are lower than that of the two-parameter isotherm models which indicates that the equilibrium data best fitted by these isotherm models. Furthermore, the equilibrium data better fitted by LAIM than FRIM, suggesting that the surface of adsorbent is homogeneous and the adsorption of CN^- on the LDH surface is monolayer.

Figure 7 shows the plot of experimental versus calculated q_e values by various isotherm models for adsorption of CN^- on Mg/Al LDH. This figure illustrates the feasibility of different isotherm models for representing the equilibrium data. As can be seen, the difference between the calculated and experimental equilibrium data for RPIM is lower than that of the other isotherm models. Hence, the best isotherm model for prediction of the loading capacity of free cyanide on Mg/Al LDH is RPIM.

Fig. 6 The loading capacity of different conventional adsorbents for free cyanide [2]

Table 1 Isotherms models and their linearized expressions for the cyanide sorption on LDH

Isotherm	Main Equation	Linear Form	Plot	Parameters	R ²	ARE	MPSD
FRIM	$q_e = L n K_F (C_e)^{1/n}$	$\ln q_e = L n K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs $\ln C_e$	$K_F = 3.7247 \text{ mg g}^{-1} (\text{L mg}^{-1})^{1/n}$ $n = 2.0734$	0.968	11.16	1.3
LAIM	$q_e = \frac{(q_m K_L C_e)}{(1 + K_L C_e)}$	Type(I) $\frac{C_e}{q_e} = \left(\frac{1}{K_L} \frac{q_m}{q_e} \right) + \left(\frac{C_e}{q_e} \right) \text{ vs } C_e$		$q_m = 64.9351 \text{ mg g}^{-1}$ $K_L = 0.0167 \text{ L mg}^{-1}$	0.985	9.99	3.28
		Type(II) $\frac{1}{q_e} = \left(\frac{1}{K_L} \frac{q_m}{C_e} \right) + \left(\frac{1}{q_m} \right) \text{ vs } \frac{1}{C_e}$		$q_m = 40.6504 \text{ mg g}^{-1}$ $K_L = 0.05244 \text{ L mg}^{-1}$	0.901	18.47	7.13
		Type(III) $\frac{q_e}{C_e} = q_m - \left(\frac{1}{K_L} \right) \frac{q_e}{C_e} \text{ vs } \frac{q_e}{C_e}$		$q_m = 52.058 \text{ mg g}^{-1}$ $K_L = 0.03445 \text{ L mg}^{-1}$	0.750	13.81	3.8
		Type(VI) $\frac{q_e}{C_e} = K_L q_m - K_L \text{ vs } q_e$		$q_m = 57.7946 \text{ mg g}^{-1}$ $K_L = 0.0258 \text{ L mg}^{-1}$	0.750	12.35	3.37
TEIM	$q_e = q_m \ln(K_T C_e)$	$q_e = q_m \ln K_T + q_m \ln C_e$	q_e vs $\ln C_e$	$q_m = 11.423 \text{ mg g}^{-1}$ $K_T = 0.3162 \text{ L mg}^{-1}$	0.963	19.43	5.1
RPIM	$q_e = \frac{A_{RP} C_e}{1 + B_{RP} C_e}$	$\ln \left[\left(\frac{A_{RP}}{B_{RP}} \right) \frac{C_e}{q_e} - 1 \right] = g \ln C_e + \ln \left[\left(\frac{A_{RP}}{B_{RP}} \right) \frac{C_e}{q_e} - 1 \right] \text{ vs } \ln C_e$		$g = 0.7207$ $B_{RP} = 0.2320 (\text{L mg}^{-1})^g$ $A_{RP} = 2.72 \text{ mg g}^{-1} (\text{L mg}^{-1})$	0.962	6.48	1.84
KCIM	$q_e = \frac{A_{KC} C_e^p}{1 + B_{KC} C_e^p}$	$\frac{1}{q_e} = \left(\frac{1}{A_{KC} C_e^p} \right) + \frac{B_{KC}}{A_{KC}} \text{ vs } \frac{1}{C_e^p}$		$A_{KC} = 2.9430 \text{ mg g}^{-1} (\text{L mg}^{-1})^p$ $B_{KC} = 0.02178 (\text{L mg}^{-1})^p$ $P = 0.61$	0.956	7.77	0.5

Kinetic studies

The kinetics of free cyanide adsorption on Mg/Al LDH was modeled by different kinetic models including ELKM, FPKM, PFOKM and PSOKM. The kinetic models, their linear expression, the model parameters are summarized in Table 2. The correlation coefficients values (R²), MPSD, ARE, and the constants of various kinetic models for adsorption of free cyanide by LDH at 265.7 mg/L initial CN[−] concentration also has presented in the table. The adsorption kinetic data were fitted in the best way by the FPKM because of a much higher R² (0.9763) and an lower MPSD (0.13%) and ARE (3.53%). Moreover, the model-predicted q_e value is quite similar to the experimental data. These firmly offer that

the adsorption of CN[−] onto LDH is best represented by the FPKM.

Figure 8 illustrates experimental data (symbols) and calculated values by FPKM (lines) at various cyanide concentrations versus time. It found that the adsorption of cyanide by LDH depends on time. At all initial cyanide concentrations, the adsorption rate was rapid at the beginning of the reaction, which 30% of the total amount adsorbed in 3 h done. Over time, the absorption capacity increases and the absorption rate decreased gradually during the 72 h to reach equilibrium. After this time, the adsorption rates reach a constant value by increasing the time where adsorption does not change anymore. Note that increasing the initial cyanide concentration leads to higher adsorption capacity.

Fig. 7 The calculated q_e from various models vs. experimental q_e (conditions: sorbent dosage = 2 g/l; agitation rate = 100 rpm; Temp. = 25 ± 2 °C; pH = 10)

Table 2 Kinetic models parameters by linear regression method for the cyanide sorption on LDH at initial cyanide concentration of 265.3 mg/L)

Kinetic models	Equations	Linear expression	Plot	Parameters	R ²	ARE	MPSD
ELKM	$q_t = \beta \ln(\alpha/\beta t)$	$q_t = \beta \ln(\alpha/\beta) + \beta \ln t$	q_t vs $\ln t$	$\alpha = 3.7899$ mg/g.h $\beta = 5.6941$ g/mg	0.930	6.02	0.06
FPKM	$q_t = kt^v$	$\ln q_t = \ln k + v \ln t$	$\ln q_t$ vs $\ln t$	$v = 0.2$ $k = 18.2799$ mg/g.h	0.976	3.53	0.13
PFOKM	$q_t = q_e [1 - \exp(-k_1 t)]$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs t	$q_e = 29.3855$ mg/g $k_1 = -0.0367$ 1/h	0.947	52.62	60.72
PSOKM	$q_t = \frac{k_{2P} q_e^2 t}{(1 + k_{2P} q_e t)}$	Type(I) $\frac{t}{q_t} = \left(\frac{1}{k_{2P} q_e^2} \right) + \left(\frac{t}{q_e} \right)$	$\left(\frac{t}{q_t} \right)$ vs t	$q_e = 45.45455$ mg/g $K_{2P} = 0.004667$ g/mg.h	0.980	18.1	10.69
		Type(II) $\frac{1}{q_t} = \left(\frac{1}{k_{2P} q_e^2} \right) \left(\frac{1}{t} \right) + \left(\frac{1}{q_e} \right)$	$\frac{1}{q_t}$ vs $\frac{1}{t}$	$q_e = 34.7222$ mg/g $K_{2P} = 0.04168$ g/mg.h	0.804	13.05	0.63
		Type(III) $q_t = q_e - \left(\frac{1}{k_{2P} q_e} \right) q_t$	q_t vs q_t/t	$q_e = 36.924$ mg/g $K_{2P} = 0.03192$ g/mg.h	0.628	12.68	2.58
		Type(VI) $\frac{q_t}{t} = k_{2P} q_e^2 - k_{2P} q_e q_t$	q_t/t vs q_t	$q_e = 40.07426$ mg/g $K_{2P} = 0.01848$ g/mg.h	0.628	12.73	3.14
WMIDM	$q_t = k_P t^{0.5}$	$q_t = k_P t^{0.5}$	q_t vs $t^{0.5}$	$K_P = 19.331$ mg/g.h ^{0.5} $K_P = 3.495$ mg/g.h ^{0.5}	0.980	—	—

Figure 8 also shows that the equilibrium time increases with increasing the initial cyanide concentration. Due to the fact that, at low initial concentration the cyanide ions has a good access to sorption sites, while at higher cyanide contents,

the ions find no way but to diffuse to the inner sites of the LDH.

The curves in Fig.8 (lines) show that the FPKM at different initial concentrations of cyanide is fitted to the data. It is

Fig. 8 Temporal variation of cyanide adsorption at different initial cyanide concentrations. (a) 26.5 and 106.3 mg/L; (b) 265.7 and 531.5 mg/L. Symbols and lines represent experimental (exp.) and the calculated values (cal.) by FPKM, respectively (conditions: agitation rate = 100 rpm; sorbent dosage = 2 g/l Temp. = 25 ± 2 °C; pH = 10)

Fig. 9 Application of Weber and Morris-suggested plots for cyanide removal by LDH versus beginning concentration (agitation rate = 100 rpm; sorbent dosage = 2 g/l; Temp. = 25 ± 2 °C; pH = 10)

difficult to describe the diffusion mechanism with the FPKM, for this reason, Weber-Morris model for intraparticle diffusion was employed to assess the diffusion mechanism.

If intraparticle diffusion is dominated, Weber and Morris model, the plot of $t^{0.5}$ versus q_t , should be linear and intraparticle diffusion will be rate-controlling step if graphs pass through origin [40]. Figure 9 represents the plot of q_t versus $t^{0.5}$ for the cyanide concentrations of 26.5, 106.3, 265.7 and 531.5 mg/L. Non-linear behavior was observed in all plots for the entire sorption period; thus the intraparticle diffusion was not dominated in the whole adsorption process. The plots consisted of two linear sections with different slopes. The first step may be the diffusion of cyanide ions onto Mg/Al LDH and reaching the adsorption sites, and the second step may be the adsorption of CN^- on the adsorption site. Given that first step lines pass through the origin; therefore particle diffusion was deduced to be the adsorption rate-limiting step.

Thermodynamic studies

Figure 10 shows the kinetics of free cyanide adsorption onto Mg/Al LDH at four different temperatures of 303.15, 313.15, 323.15 and 333.15 K at initial cyanide concentration of 265.7 mg/L. From the graph, the adsorption kinetics accelerates with raising the solution temperature. It reveals that raising the solution temperature favors the adsorption process due to the increasing of cyanide activity in the solution.

Thermodynamic parameters can give valuable information about the adsorption process [41, 42]. The following equation used for the calculation of standard free energy:

$$\ln K_d = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (8)$$

K_d is the distribution coefficient which can be calculated as [43]:

$$K_d = (C_0 - C_e)V / C_e W \quad (9)$$

Fig. 10 Kinetics of cyanide adsorption onto the LDH at four different temperatures of 303.15, 313.15, 323.15 and 333.15 K (at a cyanide concentration of 265.7 mg/L, conditions: sorbent dosage = 2 g/l; agitation rate = 250 rpm; Temp. = 25 ± 2 °C; pH = 10)

Fig. 11 Graphical determination of ΔH° , ΔS° and adsorption activation energy

The experiments were carried out at 303.15° K, 313.15 K, and 323.15 K at the initial cyanide concentration of 265.7 mg/L. The values of ΔH° and ΔS° for the adsorption were calculated from the slope and intercept of the plot of $\ln K_D$ versus $1/T$ (Fig. 11).

After the calculation of ΔH° and ΔS° values, the ΔG° value can be determined through Eq. 10.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

The values of ΔH° and ΔS° for adsorption of CN^- on Mg/Al LDH were about $21.16 \text{ kJ.mol}^{-1}$ and 59.04 J.mol^{-1} , respectively. The positive value of enthalpy reveals the endothermic nature of the adsorption process. The affinity of Mg/Al LDH for CN^- ions was confirmed by positive entropy of adsorption. The negative free energy values (at temperature 303, 313 and 323 K were about -17.87 , -18.46 and $-19.05 \text{ kJ.mol}^{-1}$, respectively) indicated that the adsorption process is spontaneous.

Activation energy is defined as the used energy for the reaction of adsorbate ion with adsorbent in adsorption studies, [44]. The adsorption activation energy, E_a was obtained by

using the Arrhenius equation:

$$\ln K_I = \ln A - \left(\frac{E_a}{RT} \right) \quad (11)$$

The values of $\text{Log } k_1$ were plotted versus $1/T$ and the linear regression equation was shown in Fig. 11 (secondary vertical axes). The intercept of the plot is equal to $-E_a/RT$. The type of an adsorption process may be determined based on the magnitude of its activation energy. Typically, physisorption processes require lower activation energies ($0\text{--}4 \text{ kJ mol}^{-1}$), while in case of chemisorption, as stronger chemical bonds are formed, higher activation energies apply ($15\text{--}800 \text{ kJ mol}^{-1}$). Among these is the extent of physicochemical adsorption [45]. The activation energy for the adsorption of CN^- on Mg/Al LDH is determined to be 6.4 kJ/mol which suggests a physicochemical adsorption.

Treatment of real cyanide contaminated aqueous solution

As previously mentioned, cyanide is used as a common gold leaching lixiviant all over the world. Hence, annually a

Fig. 12 The FTIR spectra of LDH before (a) and after (b) adsorption of free cyanide

Fig. 13 The kinetics of cyanide adsorption onto LDH from real cyanide contaminated wastewater

massive amount of cyanide contaminated wastewaters are produced by the gold processing plants. In order to evaluate the applicability of the synthesized LDH for the treatment of real cyanide contaminated wastewaters, a sample was taken from a gold processing plant in the northeastern of Iran. The initial free cyanide concentration of the sample was determined to be 98.3 mg/L (NaCN concentration = 185 mg/L) and the solution pH was 10.1. In this case, 10 g synthesized LDH was added to the 500 mL real solution and it was agitated for 48 h by bottle roller mixer at ambient temperature. At the end of the experiment, two samples were taken and analyzed for free cyanide concentration. The equilibrium cyanide concentration was determined to be 7.97 mg/L which indicates that the synthesized LDH has removed 91.89% of cyanide. It confirms the ability of LDH for the treatment of industrial cyanide contaminated wastewaters. The FTIR spectra of LDH before and after adsorption of free cyanide are illustrated in Fig. 12. The distinct difference between the two spectra is the prominent peak at 2411 cm^{-1} (after CN^- adsorption) which can be assigned to CN triple bond stretching vibrations. It confirms the adsorption of CN^- by LDH [47].

The loading capacity of LDH was determined to be 4.52 mg/g regarding the presence of various anionic species in the industrial wastewaters rather than synthetic solutions. It is not a restriction

for the industrial applications of LDH since the quality of the effluent increases by removing all of the anionic species.

In order to evaluate the kinetics of cyanide adsorption onto the LDH from real cyanide contaminated wastewaters, 10 g synthesized LDH was added to the 500 mL real wastewater and agitated by bottle roller apparatus. Samples were withdrawn at certain time intervals and analyzed for free cyanide concentration. The results have been presented in Fig. 13. As can be seen, the kinetics of cyanide adsorption onto the LDH is very fast during the first 30 min of adsorption, so that 75.68% of free cyanide is adsorbed during this period. The removal percentage of free cyanide increases to 85.14% after 5 h. After that, the removal percentage increases gradually and reaches 91.89% at the end of experiment. Hence, LDH is a very powerful adsorbent for the treatment of the ore processing wastewaters.

Figure 14 compares the loading capacity of LDH for removal of free cyanide from real and synthetic solutions. As can be seen, the loading capacity of LDH for removal of free cyanide from the real solution is lower than that of the synthetic solution. It is due to this fact that in real wastewaters there are several anionic species such as CO_3^{2-} and Cl^- . The LDH has low selectivity for anionic species and it can adsorb most of anionic species which result in lowering loading capacity for free cyanide adsorption.

Fig. 14 Comparison between the loading capacity of LDH for removal of free cyanide from real and synthetic solutions

Conclusions

The main conclusions are as follows.

- (I) LDH was synthesized by the co-precipitation process using a 3:1 ratio of magnesium nitrate and aluminum nitrate and the chemical and mineralogical compositions of LDH were investigated using XRD, XRF and SEM (WDX) analysis.
- (II) The maximum loading capacity of LDH for free cyanide was determined to be 60 mg/g which is significantly more than the other conventional adsorbents.
- (III) RPIM fitted the equilibrium data in the best way. It suggested that the surface of LDH for adsorption of cyanide is homogeneous.
- (IV) The results show that the kinetic data best fitted by FPKM.
- (V) Weber–Morris plots indicate that the adsorption of CN^- onto LDH is a two-step process. Also, rate-controlling step in the adsorption process is intra-particle diffusion.
- (VI) The negative value of ΔG and positive enthalpy (ΔH) indicated that the adsorption was a spontaneous and endothermic process. The activation energy was found to be 6.14 kJ/mol, which refers to the physicochemical sorption.
- (VII) The treatment of a real cyanide contaminated wastewater from a gold processing plant in the northeastern of Iran was performed by the synthesized LDH. The cyanide concentration of the real solution was reduced from 98.30 to 7.97 mg/L by adding 10 g LDH to 500 mL solution and the removal percentage reached to more than 90%. The adsorption kinetics was very fast so that 75.68% of free cyanide was removed during the first 30 min of contact time. Hence, the synthesized LDH has a great potential for the treatment of industrial cyanide contaminated wastewaters, specially the tailings of the cyanidation process.

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