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Kinetic and equilibrium study on uptake of iodide ion by calcined layered double hydroxides

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ABSTRACT

Iodide contamination removed using calcined MgAl-CO_3 layered double hydroxides (denoted as CLDH) was conducted in batch conditions. The equilibrium isotherms of uptake of iodide by CLDH were well fitted by the Langmuir equation, and thermodynamic parameters including ΔG^0, ΔH^0 and ΔS^0 were calculated from Langmuir constants. The negative value of ΔH^0 confirms the exothermic nature of adsorption. The negative values of ΔG^0 at 30, 40, 50 and 60°C indicate the spontaneous nature of adsorption. The negative value of ΔS^0 suggests the decreased randomness at the solid/solution interface for the uptake of iodide on CLDH. The influences of initial iodide ion concentration, dosage of CLDH, temperature of iodide removal have been tested in kinetic, respectively. Three kinetic models were used to fit the experimental data, and it was found that the pseudo-second order kinetics model could be used to describe the uptake process appropriately. The value of E_a was calculated to be 100.3 kJ mol^{-1}, which suggests that the process of uptake iodide ion is controlled by the reaction rate of iodide ion with the CLDH rather than diffusion. The reconstruction of CLDH to I-LDHs due to uptake of iodide ion has been confirmed by X-ray diffraction patterns, FT-IR spectroscopy and TG-MS measurements.

Keywords: Layered double hydroxides; Calcined; Equilibrium; Kinetic; Iodide; Uptake

1. Introduction

Although iodine is an essential trace element for human to avoid goitre that occurs in the case of inadequate iodine ingestion, excessive iodine supplementation is also harmful to the human body [1,2]. Iodine exists primarily as the anions iodide (I^-) and iodate (IO_3^-). At low to neutral pH values and positive redox potentials, iodide is the dominant species in freshwater [3]. The total iodine concentration in water resources is appropriate in the range of 10–125 µg l^{-1}, but it can exceed 2000 µg l^{-1} in certain groundwater near the sea coast at Shandong province in China. During oxidation and disinfection process, I^- is rapidly oxidized to IO_3^- [4].

On the other hand, radioactive iodide is widely used in biological experiments, medical treatments and in diagnosis [5,6]. During fission of uranium several iodide species are produced. All the short lived isotopes of iodide, including ^{131}I (half life 8.04 d), decay and only ^{127}I (stable) and ^{129}I (half life 1.59 × 10^7 y) remain as a problem. ^{129}I is especially considered as one of the key radionuclides that dominated the long-term radiation in underground radioactive waste stores. Iodide is one of the nuclides causing most concern

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among radioactive anions [7]. Significant precautions need to be taken when disposing of radioactive waste containing radioactive iodine into the environment, because radioactive iodine is readily absorbed by the body and represents a significant health hazard [8]. Different adsorbents such as zeolites [9], silica gel, anion exchange paper membrane [5], activated carbon [3] and activated carbon fibers [10], have been investigated as potential materials for elimination of iodide from liquid wastes.

Layered double hydroxides (LDHs), a class of synthetic anionic clays whose structure can be described as containing brucite-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively-charged sheets. This charge is balanced by intercalation of anions in the hydrated interlayer regions. The general formula is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\ mH_2O$, 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 $M^{3+}/(M^{2+} + M^{3+})$ and the layer charge will depend on the M^{2+}/M^{3+} ratio [11]. Carbonates are the interlayer anions in naturally occurring hydrotalcite.

LDHs act as sorbents of anionic species through two types of reactions, namely, anion exchange and reconstruction which further adds the possibility of recycling and reuse. The sorption of anions from aqueous solutions by structural reconstruction of calcined LDHs is based on a very interesting property of these materials, the so-called memory effect: Calcination of LDHs produces intermediate non-stoichiometric oxides (CLDH) which undergo rehydration in aqueous medium and give back the hydroxide structure with different anions in the interlayer [12]. Therefore, the CLDH can be used as potential ion exchangers/adsorbents for removal of toxic anions from contaminated water [13–15].

In light of this so-called "memory effect", calcined MgAl-CO_3 LDHs (CLDH) has been studied as a sorbent material to remove iodide or radioactive iodine contaminants in our group [16]. Although the influencing factors and mechanism on iodide removal have been reported, the uptake kinetics and equilibrium was not analyzed in detail [16]. It is necessary and significant to understand the variables which influence the adsorption of solutes, and the nature of interaction between the CLDH and iodide ions. The sorption of different forms of radioactive iodine on both LDH-Mg-Al-CO_3 and LDO has also been studied by Kulyukhin's laboratory in detail [17–19]. And the zinc aluminium LDHs has been studied to remove iodine and iodide from aqueous solutions in Frederick L. et al. [20].

In the present work, we primarily focus on the kinetics and equilibrium for iodide uptake by CLDH. The influences of various factors such as adsorbent quantity, initial iodide concentration, and temperature of uptake of iodide have been investigated, respectively. Three kinetics models were used to fit the experimental data, including first order kinetics model, pseudo-second order kinetics model and intraparticle diffusion model.

2. Experimental section

2.1. Materials

$Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, NaOH, Na_2CO_3, $NaNO_3$, KNO_3 and KI were A.R. grade and used as received without purification. All the water used was deionized (conductivity level < 0.05 µs cm^{-1}). The iodide aqueous solution used in this study was a synthetic wastewater. The standard iodide solutions used in the experiments were prepared from anhydrous KI.

2.2. Preparation of LDHs precursor and CLDH

LDHs containing carbonate as the interlayer anion was obtained by using a conventional coprecipitation method previously developed by our group [21,22]. The method involves very rapid mixing to complete the nucleation process, followed by a separate aging process. $Mg(NO_3)_2\ 6H_2O$ (0.36 mol) and $Al(NO_3)_3\ 9H_2O$ (0.09 mol) were dissolved in deionized water. A second solution containing NaOH (0.72 mol) and Na_2CO_3 (0.36 mol) in deionized water was prepared. The two solutions were simultaneously added to a colloid mill with rotor speed of 5000 rpm and stirred for 2 min. The resulting slurry was removed from the colloid mill and aged at 100°C for a specified period. The final precipitate was filtered, washed thoroughly, and dried at 80°C for 24 h to obtain Mg-Al-CO_3 LDHs. CLDH was obtained by calcining LDHs in a muffle furnace at 500°C for 3 h.

2.3. Characterization

X-ray diffraction pattern of the samples were obtained using a Shimadzu XRD-6000 diffractometer (precision: ±0.001) with Cu Kα radiation (40 kV and 30 mA) at a scanning rate of 5° min^{-1}. FT-IR spectra in the range 4000–400 cm^{-1} of samples as KBr pellets were recorded with a Bruker Vector 22 spectrometer (resolution: 1 cm^{-1}). TG-MS measurements were carried out on a Pyris Diamond TG/DTA instrument (PerkinElmer instrument) equipped with a mass spectrometer (ThermoStar TM) under N_2 atmosphere. The temperature-programmed rate was 10°C min^{-1}, and the measured range from 30°C to 1100°C. Gaseous emission was analyzed at intervals of 1 s. Elemental analysis was performed by inductively coupled plasma (ICP) emission spectroscopy with a Shimadzu ICPS-7500 ICP instrument using solutions prepared by dissolving the samples in dilute HNO_3.

2.4. Equilibrium study

Batch equilibrium isotherms studies were conducted with a range of different concentrations of iodide solutions by contacting a constant mass (0.05 g) of CLDH. The CLDH and iodide ion solutions were agitated in a series of 100 ml conical flasks with equal volumes of solution (50 ml) for a period of 24 h at 30°C, 40°C, 50°C, 60°C ± 1°C, using the maximum shaking rate of 200 rpm. The reaction mixture pH was not controlled after the initiation of experiments. After equilibration, CLDH was filtered from the solution, and the filtrate was analyzed for iodide using a selective electrode for iodide ions (PI-1, REX) at PHS-2F precision pH meter (Shanghai REX Instrument Factory. Intrinsic error, pH: ±0.01 pH; mV: ±2 mV ± 1), whose linear range is from 10^{-6} M to saturated solution.

The amount of the iodide ions loading (mg) per unit mass of CLDH, q_e, was obtained by the following equation:

$$q_\mathrm{e} = \frac{(C_\mathrm{i} - C_\mathrm{e})V}{m} \tag{1}$$

where C_i and C_e are initial and equilibrium concentrations in mg l^{-1}, m is the mass of adsorbent in grams, and V is the volume of solution in liters.

2.5. Kinetic study

CLDH samples (2.0 g) were dispersed in 2000 ml of iodide solutions with a concentration of 100 mg I^- l^{-1} and stirred for 6 h, in N_2 atmosphere. 5 ml aliquots were extracted at selected time intervals, separated by filtration, and diluted to 50 ml. Iodide ion concentration were measured in the solution using a selective electrode for iodide ion, and the solid remaining at the end of the experiment was characterized by X-ray diffraction, FT-IR and TG-DTA. Iodide ion uptake by the CLDH was calculated by the following equation:

$$q_\mathrm{t} = \frac{(\mathrm{C_i} - C_\mathrm{t})V}{m} \tag{2}$$

where q_t is the adsorption capacity of CLDH at time t in mg g^{-1}, V is the volume of solution in liters, C_i and C_t are initial and at time t concentration of iodide in mg l^{-1}, and m is the mass of adsorbent in grams.

3. Theory

The iodide ion uptake by CLDH can be divided into three consecutive stages. First, iodide ion migrates through the solution to the exterior surface of CLDH. Second, the iodide moves within the particles and CLDH reconstructed to LDHs within iodide and H_2O. Then, third, the iodide ion is moored at sites in the interlayer of LDHs. These stages are related with three controlling process: film diffusion, intraparticle diffusion, and chemisorption. Many factors can affect the uptake rate of iodide ion by CLDH, such as CLDH structure, initial iodide ion concentration, adsorbent quantity, and temperature. Generally, providing sufficient agitation to avoid particle and solute gradients in the batch reactor allows the bulk diffusion to be neglected, since in well-agitated adsorption studies, film diffusion is usually only rate-controlling for the first few minutes.

3.1. Equilibrium isotherms

For the liquid-solid system, the Langmuir and Freundlich isotherm equations usually are employed. The well-known Langmuir equation, which is obtained by combining the adsorption and desorption rate equations, can be described as following Eq. (3) when the adsorption process reaches equilibrium:

$$qe = K_\mathrm{L}\, q_\mathrm{m}\, C_\mathrm{e}/(1 + K_\mathrm{L}\, C_\mathrm{e}) \tag{3}$$

where $K_L = k_{ads}/k_d$ is the Langmuir constant related to the energy of adsorption; q_m the maximum loading capacity; q_e the adsorption loading at equilibrium (mg g^{-1}); and C_e is the equilibrium concentration of iodide ion in the solution (mg l^{-1}).

The Langmuir equation can be rearranged as follows:

$$C_\mathrm{e}/q_\mathrm{e} = 1/K_\mathrm{L}\, q_\mathrm{m} + C_\mathrm{e}/q_\mathrm{m} \tag{4}$$

The values of q_m and K_L can be calculated from the slope and the intercept of the linear plots C_e/q_e versus C_e.

The Freundlich isotherm is purely empirical and commonly presented as Eq. (5):

$$q_\mathrm{e} = K_\mathrm{F}\, \mathrm{C}_\mathrm{e}^{\,n} \tag{5}$$

where K_F and n are the Freundlich temperature-dependent constants, and q_e is the adsorption loading at equilibrium (mg g^{-1}), respectively.

3.2. Kinetic models

To identify the correct mechanism, several models must be checked for suitability and consistency over a broad range of system parameters. The key features of the three different kinetic models used to fit the experimental data can be summarized as follows:

First order kinetics model. The first order kinetics adsorption model was suggested by Lagergren [23] for the sorption of solid/liquid systems. It has been used by many authors [24–26] and can be expressed in integrated form:

$$\frac{dq_{\mathrm{t}}}{dt} = k_1(q_{\mathrm{e}} - q_{\mathrm{t}}) \tag{6}$$

where k_1 is the rate constant of adsorption (min^{-1}) and q_e and q_t are the adsorption capacity of iodide ion (mg g^{-1}) at equilibrium and at time t (min), respectively. The equilibrium capacity q_e (mg g^{-1}), is calculated from the Langmuir adsorption isotherm. After integration with the initial conditions $q_t = 0$ at $t = 0$, the equation becomes:

$$\ln(q_e - q_t) = \ln(q_e) - k_1\mathrm{t} \tag{7}$$

by plotting $\ln(q_e–q_t)$ against t, a straight line is obtained and the value of the rate constant k_1 can be calculated.

Pseudo-second order kinetics model. The pseudo-second order kinetics model [27,28] is expressed as:

$$\frac{dq_{\mathrm{t}}}{dt} = k_2(q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{8}$$

where k_2 (g · mg^{-1} · min^{-1}) is the rate constant of pseudo-second order adsorption. This model is based on the assumption that rate-limiting step may be chemisorption involving valency forces between sorbent and sorbate. The following form can be obtained:

$$q_{\mathrm{t}} = q_{\mathrm{e}}\left(1 - \frac{1}{k_2 q_{\mathrm{e}} t + 1}\right) \tag{9}$$

This former can be linearized as follows:

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \tag{10}$$

Plotting t/q_t against t, a line is obtained and the rate constant k_2 as well as q_e can be calculated.

Intraparticle diffusion model. In a liquid–solid system, the fractional uptake of the solute on a particle, F, varies [29,30] with the function $D_0 t^{0.5}/r^2$. Hence there is a linear relationship between F and $t^{0.5}$ for most of the adsorption process. F can be defined as:

$$F = (C_i - C_t)/C_i \tag{11}$$

The diffusion rate of the iodide ion in a particle, k_i, can be calculated from the following linear equation [31]:

$$q_t = k_i\, t^{0.5} \tag{12}$$

where k_i is the intraparticle diffusion rate (mg . g^{-1} . min$^{-0.5}$).

4. Results and discussion

4.1. Reconstruction of CLDH to LDHs after uptake of iodide ion

The XRD pattern of the MgAl-CO_3 LDHs (Fig. 1a) shows sharp and symmetric peaks at lower 2θ values, which are characteristic of hydrotalcite-like compounds, and the material consists of a single crystalline phase. After the material was calcined at 500°C the layered hydrotalcite-like structure is absent (Fig. 1b), leading to the formation of a mixed magnesium aluminum oxide. However, reconstruction of the structure (Fig. 1c) has been observed to take place after iodide ion adsorption, giving a material having a basal spacing of 0.812 nm, which is larger than that (0.769 nm) in the MgAl-CO_3 LDHs precursor and similar to that of I-LDHs (0.816 nm). This indicates that the reformed layered structure is MgAl-I LDHs.

The FT-IR spectrum of the MgAl-CO_3 LDHs precursor shows a band at 1359 cm^{-1} (Fig. 2a) attributed to the absorption of CO_3^{2-}, as reported previously [11]. It can be seen in Fig. 2b that the bands between 400 and 800 cm^{-1} could be due to the superposition of the vibrational absorptions of magnesium and aluminum oxides. The shoulders observed at 1628 and 1412 cm^{-1} are characteristic vibrational absorptions of reversibly sorbed H_2O and CO_2 on oxide surfaces (Fig. 2b). After adsorption of iodide ion, the band at 1359 cm^{-1} shifts to higher frequency 1394 cm^{-1} (Fig. 2c). This could be due to the reconstruction of the layered material in the presence of iodide ion.

The TG-MS measurements (Fig. 3a and b) show that the reconstructed LDHs has three stages of weight loss upon heating between 30 to 1100°C: the first one from

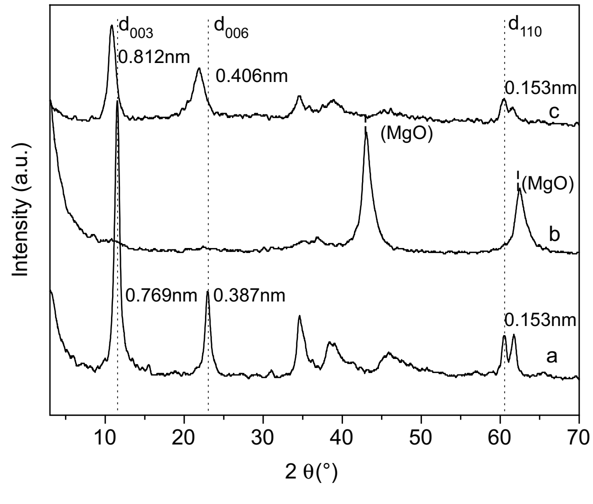

Fig. 1. Power XRD patterns for (a) MgAl-CO_3 LDHS, (b) CLDH, (c) CLDH after uptake of iodide ion.

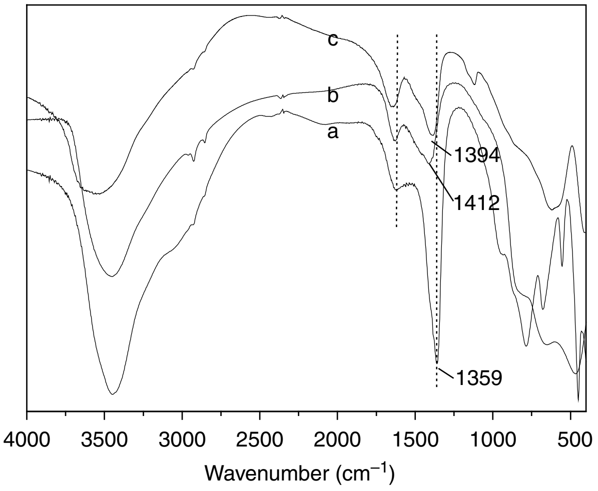

Fig. 2. FT-IR spectra for (a) MgAl-CO_3 LDHs, (b) CLDH, (c) CLDH after uptake of iodide ion.

room temperature to 230°C can be attributed to the removal of carbonate (MS: m/z 44), surface adsorbed water and interlayer water molecules (MS: m/z 18) (Fig. 3b), with one corresponding endothermic peak (212°C) in the DTA curve (Fig. 3a); the second step (230–500°C), involving a gradual weight loss, is the result of the deintercalation of carbonate (MS: m/z 44, 392°C) and dehydroxylation of the brucite-like layers (MS: m/z 18, 413°C), with a corresponding endothermic peak (422°C) in the DTA curve; the third step (500–110°C) is assigned to the deintercalation of iodide ion (MS: m/z 127, 128 and 129), corresponding endothermic peak (869°C).

Chemical analysis indicates that the material formed after reaction of CLDH with iodide ion has an Mg/Al molar ratio of 4.15:1, close to that of both the LDHs precursor (4.12:1) and CLDH (4.08:1).

Based on the results above, a mechanism of uptake of iodide ion by CLDH can be confirmed as follows: LDHs containing carbonate as the interlayer anion decomposes to afford mixed magnesium aluminum oxides when heated at 500°C. The calcined product–CLDH ($Mg_{0.80}Al_{0.20}O_{1.1}$) was rehydrated with incorporation of iodide ion from aqueous solution, to reform a layered structure.

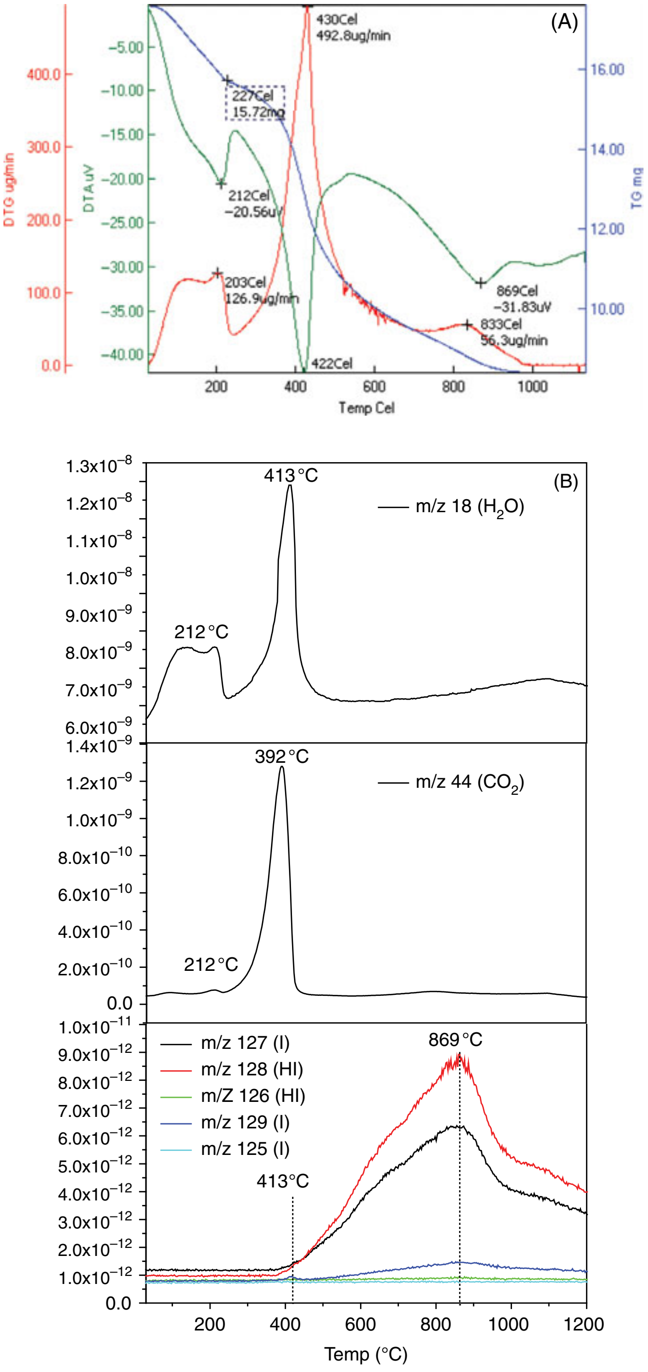

Fig. 3. TG-MS profiles for CLDH after uptake of iodide ion, (a) TG-DTA-DTG curves, (b) MS spectra of emission gas.

4.2. Equilibrium isotherms

Fig. 4a is the equilibrium isotherms of iodide ion on CLDH at different temperature, which indicates that the uptake capacity increases upon increasing equilibrium concentration of iodide ion and decreasing temperature. The observation shows that the interaction between adsorbate and adsorbent is exothermic in nature, even though the change in the temperature does not influence the equilibrium time and the removal curve is smooth and continuous.

The data were further fitted by the Langmuir and Freundlich equations respectively, and it was found that the Langmuir model gave a satisfactory fit to the experimental data, as shown in Fig. 4b and Table 1.

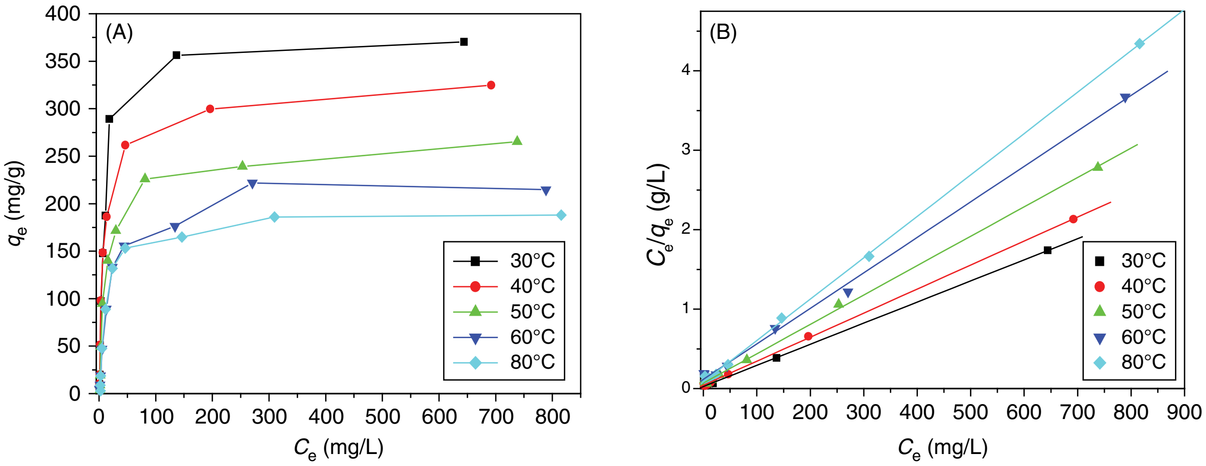

Fig. 4. Equilibrium isotherms of iodide ion on CLDH, (a) equilibrium isotherms, (b) Langmuir fitting.

Table 1
Langmuir constants and thermodynamic parameters associated with iodide ion removal onto CLDH

Temp (°C)	q_m(mg g^{-1})	K_L(l mol^{-1})	ln K_L	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J $^{-1}$mol^{-1} K^{-1})
30	375.9	12,805.9	9.458	–23.84		
40	331.1	9071.4	9.113	–23.73		
50	270.3	6835.9	8.830	–23.72	–25.84	–6.67
60	223.7	4910.8	8.499	–23.54		
80	200.4	3015.0	8.011	–23.52		

Thermodynamic parameters such as Gibbs free energy (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) for the process were calculated using the equations:

$$\Delta G^0 = -RT \ln K_L \qquad (13)$$

$$\ln K_L = \Delta S^0/R - H^0/(RT) \qquad (14)$$

where R is universal gas constant, T is temperature (K), and K_L is Langmuir constant. The values of ΔG^0, ΔH^0 and ΔS^0 are also listed in Table 1. The negative ΔG^0 value indicates the spontaneity of the removal of iodide ion process. ΔH^0 and ΔS^0 were calculated from a Van't Hoff plot (Fig. 5, correlation coefficient $R^2 = 0.999$) using the slope and intercept by regression method, respectively. The negative value of ΔH^0 confirms the exothermic nature of uptake of iodide ion by CLDH which has been predicted earlier from Fig. 4a. The negative value of ΔS^0 suggests the decreased randomness at the solid/solution interface for the removal of iodide ion on CLDH because of its reconstruction to I-LDHs.

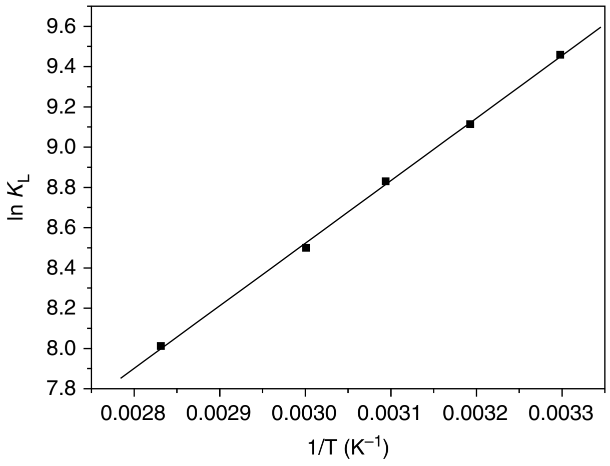

Fig. 5. Van't Hoff plot for uptake of iodide ion.

4.3. *Kinetic of uptake of iodide*

Fig. 6 displays the changes in the uptake capacity of CLDH with time for various initial iodide ion concentrations (20, 70, 100, 200, 800, 1000 and 2000 mg l^{-1}).

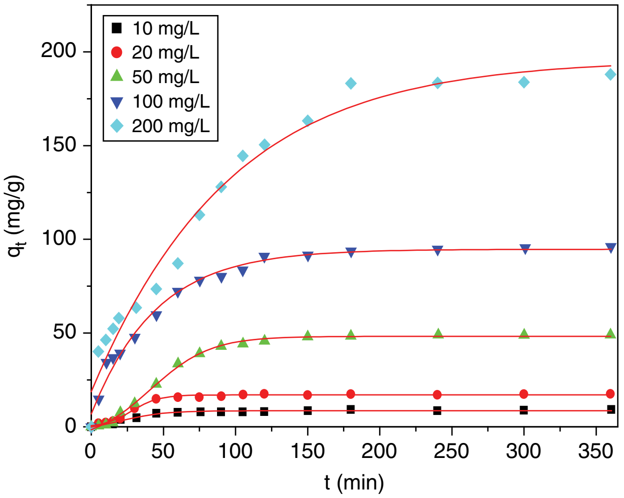

Fig. 6. Effect of initial concentration on the kinetics of uptake of iodide ion by CLDH (V = 2 l, T = 30°C, [CLDH] = 1.0 g l^{-1}).

For all the concentrations employed there is a monotonic increase in the uptake capacity with time. At low initial iodide ion concentration, iodide ion is almost completely removed from the aqueous solution. Thus, the overall adsorption process is not influenced by external mass transfer diffusion.

Fig. 7 shows the results of the kinetic studies using different amounts of adsorbent (0.5–3.0 g l^{-1}). An increase in the solid content generally results in an increase in the rate of abstraction of iodide ion, while the adsorption capacity with respect to iodide ion ions decreases. The results are listed in Table 1. The influence of increasing an adsorbent amount is mainly related to the resulting increase surface area, which results in higher numbers of adsorption sites. The adsorption rate decreases with an amount of adsorbent and hence more time is needed to reach equilibrium.

Temperature is a highly significant parameter in the adsorption process. Fig. 8 displays the adsorption curves obtained under different isothermal conditions. The rate of adsorption increases significantly while the time taken to reach equilibrium decreases with increasing temperature–whether this is due to a chemical reaction or diffusion control mechanism will be discussed later. In a similar manner, the rate of fluoride adsorption by CLDH was found to increase with temperature, but the observed rate of fluoride removal was higher than that of iodide ion removal found here.

Table 2 presents the results of fitting experimental data to first order, pseudo-second order and intraparticle diffusion models. It can be seen from Table 2 that the correlation coefficients (R^2) vary in the order: pseudo-second order > first order > intraparticle diffusion model under all experimental conditions, which indicates that the pseudo-second order model is the most satisfactory in describing the adsorption kinetics of iodide ion on CLDH. The calculated $q_{e\ cal}$ using this model is also agreement well with the $q_{e\ exp}$. The pseudo-second order equation is based on the uptake capacity of the solid phase and is in agreement with a chemisorption mechanism being the rate-determining step. Another advantage of the pseudo-second order model is that it predicts the behavior over the whole range of the adsorption process.

An Arrhenius plot (Fig. 9) of the adsorption rate against the reciprocal temperature was performed using the kinetic data of Table 2, giving a reasonably straight

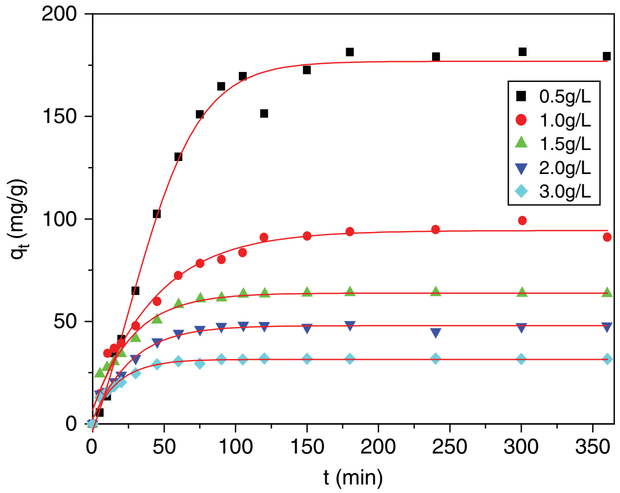

Fig. 7. Effect of CLDH mass on the kinetics of uptake of chloride ion by CLDH (V = 2 l, T = 30°C, [I^-] = 100 mg l^{-1}).

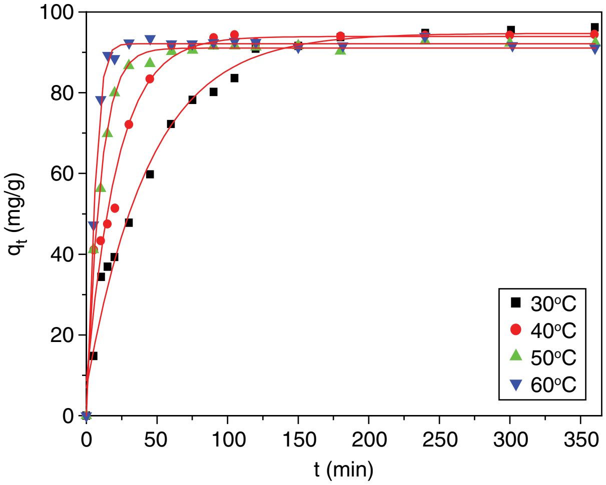

Fig. 8. Effect of temperature on the kinetics of uptake of iodide ion by CLDH (V = 2 l, [I^-] = 100 mg l^{-1}, [CLDH] = 1.0 g l^{-1}).

Table 2
Experimental conditions, kinetic parameters and regression coefficients (R^2) for the three kinetic models

Run No.	$[I^-]_0$ (mg/l)	[CLDH] (g/l)	T (°C)	$q_{e.exp}$ (mg/l)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
					$q_{e.cal}$ (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	$q_{e.cal}$ (mg/g)	$k_1 \times 10^{-4}$ (g/mg·min)	R^2	k_{i1} (mg/g·min)	k_{i2} (mg/g·min)	R^2
1	10	1.0	30	9.88	8.1	1.41	0.898	9.7	48.93	0.996	1.499	0.121	0.964
2	20	1.0	30	19.76	18.8	1.97	0.933	20.6	11.54	0.957	3.061	0.134	0.894
3	50	1.0	30	47.84	64.5	2.72	0.978	63.6	2.12	0.906	6.142	0.136	0.971
4	100	1.0	30	97.35	83.5	1.83	0.983	101.2	3.36	0.998	8.224	0.669	0.977
5	200	1.0	30	187.3	176.4	1.27	0.974	220.8	0.78	0.971	13.19	0.784	0.962
6	100	0.5	30	177.0	201.1	2.52	0.913	216.5	8.95	0.969	22.77	0.711	0.983
7	100	1.5	30	64.84	49.9	2.91	0.972	66.8	12.74	0.998	5.806	0.042	0.979
8	100	2.0	30	48.47	52.0	4.33	0.985	49.9	15.97	0.995	5.547	0.081	0.979
9	100	3.0	30	32.49	22.3	3.18	0.951	32.7	41.18	0.999	3.390	0.012	0.988
10	100	1.0	40	97.86	74.9	3.24	0.959	97.8	11.12	0.998	9.436	0.130	0.948
11	100	1.0	50	94.86	86.7	8.19	0.991	93.6	28.12	0.9998	14.69	0.353	0.967
12	100	1.0	60	89.07	94.6	18.13	0.969	92.1	210.2	0.9996	19.00	0.069	0.867

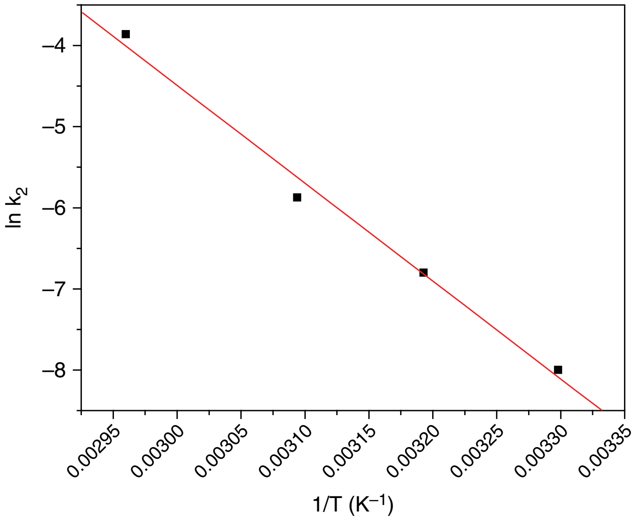

Fig. 9. Arrhenius plot for uptake of iodide ion.

line (R^2 = 0.990). The gradient of this plot is – (E_a/R), according to the well-known Arrhenius expression given in Eq. (15), and the activation energy can thus be calculated:

$$k_2 = Ae^{-(\mathrm{Ea}/\mathrm{RT})} \tag{15}$$

Ho and Mckay [27] and Lazaridis et al. [15] have shown in the case of diffusion-controlled processes the activation energy of adsorption is less than 25–30 kJ mol^{-1}. The calculated E_a value in our case, 100.3 kJ mol^{-1}, indicates that the process of iodide ion removal is controlled by the reaction rate of iodide ion with the CLDH rather than diffusion.

The Ea value obtained in this study is greater than those of reported by our group for Br^- (79.9 kJ mol^{-1}) [32], Cl^- (56.8 kJ mol^{-1}) [33] and F^- (39.73 kJ mol^{-1}) [34]. Although these values were obtained under different ranges of conditions, they can be useful in criterion of difficulty level of CLDH uptake anions.

5. Conclusions

Because calcined LDHs possessed a “memory effect” to reconstruct their layered structure in propriety anions solution, MgAl-CLDH had been studied to remove iodide contamination. The CLDH reconstructed to I-LDHs after uptake of iodide ion, even as we expected, confirmed by X-ray diffraction patterns, FT-IR spectra and elemental analysis data. Thermodynamic parameters including ΔG^0, ΔH^0, and ΔS^0 for the process were calculated from Langmuir constants. Uptake of iodide ion by CLDH follows the pseudo-second order model, which describes the chemisorption process. These studies have significant implications for efficient remediation of iodide pollutant from wastewater by CLDH.

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