Adsorption of metallic ions by layered double hydroxides (LDH) intercalated with the chelating agents EDTA or EDDS

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Contents

Chapter 1 General Introduction

1.1 Background

Recently, environmental pollution is one of the most serious problems in the world due to its deep effect on future of human being. Then it began to draw major public attention how to resolve the problem of the environmental pollution in the world [1, 2]. It is well known that the major forms of environmental pollution include air pollution, water pollution, soil pollution and so on. Among them, water pollution is the most seriously due to its liquidity which may bring other pollution. Water is an important substance in all part of the environment. Water covers about 70% of the earth's surface. It occurs in all spheres of the environment including vast reservoir of salt water in the ocean, surface water on the land, rivers in lake, groundwater in underground, water vapor in the atmosphere, and solid ice in the polar ice caps. Water is an essential part of all living systems as is the medium from which life evolves and in which life exists. It is a liquid having unique characteristics. It is a universal solvent, that is, it is able to dissolve, absorb, adsorb and suspend many different compounds (WHO, 2007).

Surface water pollution and groundwater contamination are some of the environmental problems today. One of the cases of environmental pollution is due to heavy metal contaminants such as copper, lead, cadmium, chromium, arsenic, and zinc etc. Also, heavy metals are concerned because of their strong toxicity even at low concentration. With the rapid development of industry, the water pollution by metallic ions are becoming more and more serious. Based on the type of mining, the kinds and the concentrations of metal ions are many and varied. Heavy metal ions have high toxicity and poor biodegradability for plants and animals at higher concentrations [3, 4].

On the other hand, over the past years, commercial market remands for Rare Earth Elements (REEs) have arisen due to it can be widely applied in industry and agriculture [3,4]. However, the shortage of it has been attractive for many years due to its limited resource. It is expensive and difficult to obtain based on the recent price. So, the shortage of trace metals including REEs and the problem of stable supply for these metals has been concerned [5,6].

There are several methods to remove metal ions in aqueous solutions. In these methods such as precipitation, adsorption and ion exchange, metal ions can interact with a solid surface [7]. However, these technologies become expensive or inefficient for the treatment of metal ions with high concentrations. Then, it is important to develop new methods for the removal and recovery of metals from such effluents, and thus reduce the concentration of these metal ions to low levels. One effective way of removing metals is adsorption on various materials such as activated carbon, biomaterials and clay minerals [8-14].

In recent years, clay minerals found increasing interest as adsorbents by virtue of their properties, which make them attractive materials for adsorbing heavy metal ions. Their abundance in nature, low cost and good cation adsorptive properties, a result of their negatively charged layers and high specific surface areas make them suitable for adsorption of metal ions [15,16]. LDH used in this paper are the antitypes of clay minerals.

Layered double hydroxides (LDHs) are typical intercalation compounds with the general formula $\{M^{II}_{1-x}M^{III}_{x}(OH)_2\}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metals, A^{n-} denotes compensating for the positive charger of the metal hydroxide layers. The structure and their high anionic exchange capacity make LDHs suitable for many applications including pollutant sorbents, catalysts and anionic exchangers. Chelation is a type of bonding of ions and molecules to metallic ions. It involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand (multiple bonded) and a single central atom. EDTA (Ethylenediaminetetracetic Acid) is a chelating agent widely used in industry and agriculture. It forms strong complexes with the ratio 1:1 between heavy metal ions and ligand. EDDS (N, N'-1, 2-Ethanediylbis-1-Aspartic Acid) is also a chelating agent, which may offer a biodegradable alternative to EDTA, and is currently used on a large scale in numerous applications [17, 18].

Considering the structure of LDHs and the properties of chelating agents, LDHs modified with chelating agents has been studied as the potential adsorbents of heavy metals from the aqueous solution [19, 20]. The potential adsorbents for these compounds may be due to the stability of the chelates formed by ligands and metals.

Based on the above-mentioned, the removal of harmful pollutants such as heavy metals in water environment is very significant to protect the environment from the adverse effects of pollution. Furthermore, the establishment of the new recovery method for the rare earth elements can release the commercial demand of REEs.

1.2 Toxic Heavy Metal

Toxic Heavy Metal is a series of relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. They are found naturally in the earth. Heavy metals exist in nature at certain levels under normal circumstances [21,22]. However, they become concentrated as a result of human caused activities and can enter plant, animal, and human tissues via inhalation, diet, and manual handling. Then, they can bind to and interfere with the functioning of vital cellular components. Their high toxicity and poor biodegradability for plants and animals make the removal from aqueous solutions become a hot issue in the world.

Heavy metals enter plant, animal and human tissues via air inhalation, diet and manual handling. Water sources (groundwater, lakes, streams and rivers) can be polluted by heavy metals leaching from industrial and consumer waste [23]. Among heavy metals found at contaminated sites, most commonly are lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and arsenic (As). Plants are exposed to heavy metals through the uptake of water; animals eat these plants; ingestion of plant- and animal-based foods are the largest sources of heavy metals in humans. Absorption through skin contact, for example from contact with soil, is another potential source of heavy metal contamination [23-25]. For humans, long-term exposure to toxic heavy metals can have carcinogenic, central and peripheral nervous system and circulatory effects. Toxic heavy metals can accumulate in organisms as they are hard to be biodegrade. **Table1-1** shows the typical presentations of toxic heavy metals (Cu, Pb, Cr, Cd, As) [25-29].

For living things, some metals such as iron (Fe), chromium (Cr) and copper (Cu) are essential in small quantities to keep people and animals healthy, whereas some heavy metals such as lead (Pb) and mercury (Hg) are dispensable in any amount. At any case, any heavy metal can be toxic to living things at an elevated level. In this study, the following heavy metallic ions were studied as adsorbate. [23,25]

1.2.1 Copper (Cu)

Copper is a chemical element with symbol Cu and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. In addition, it is one of the few metals that occur in nature directly with a usable metallic form, so it is widely used by human being, such as conductor of heat and electricity, building material, constituent of various metal alloys, and constant used in strain gauges and thermocouples for temperature measurement.

As one of the great metals of commerce, it is not surprising that copper released by humans into the environment is in significant excess over what might be found naturally. Copper pollution has occurred in the vicinity of copper mines and smelting operations since mankind began the activity several millennia ago. The excavation of Cu-containing earth at open pit copper mines can produce copper rich dusts which are spread around the mine site by the wind. Most of these ores are sulfide minerals, and oxidize in the air to sulfates, producing sulfuric acid, which renders the copper in the mineral highly soluble. For human being, copper toxicity can occur from eating foods cooked in uncoated copper cookware, or from exposure to excess copper in drinking water or other environmental sources [24, 25].

In addition, the above mentioned heavy metals, others metallic elements are toxic in excessive amounts to environment and human health. As a whole, the connection between soil contamination and metal uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops. Soils contaminated with heavy metals may pose both direct (i.e. through negative effects of metals on crop growth and yield) and indirect (i.e. by entering the human food chain with a potentially negative impact on human health) threats.

1.2.2 Lead (Pb)

Lead is a chemical element with atomic number 82. It is used in building construction, lead-acid batteries, bullets and shot, weights, as part of solders, pewters, fusible alloys, and as a radiation shield. If ingested or inhaled, lead and its compounds are poisonous to animals and humans. Lead is a neurotoxin that accumulates both in soft tissues and the bones, intestines, kidneys, damaging the nervous system and causing brain disorders. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders [21].

Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., corn, beans, tomatoes, strawberries, and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g., lettuce) and on the surface of root crops (e.g., carrots). Generally, the risk of lead poisoning through the food chain increases as the lead level in soil rises above 300 ppm [23, 26, 27]. Then it is necessary to remove the water or soil contaminated by lead.

1.2.3 Cadmium (Cd)

Cadmium is located at the end of the second row of transition elements. Cadmium occurs as a minor component in most zinc ores, and therefore is byproduct of zinc production. Cd is one of the most poisonous heavy metals (together with Hg and Pb) and is not known for any essential biological function. Cadmium contamination are arised from many common industrial such as fossil fuel combustion, battery production, phosphate fertilizers, cadmium pigments and coatings iron and steel production, and electroplating [27-29].

The application of agricultural inputs (such as fertilizers, pesticides, and biosolids sewage sludge), and the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils. The bioavailability of Cd determines whether Cd is uptaken by plant to a significant degree. The main routes entering cadmium into the body are inhalation of fine dust and fumes (tobacco smoking) or ingestion of highly soluble cadmium compounds (food intake) [30-32]. The major threat to human health is chronic accumulation in the kidneys which lead to kidney dysfunction.

1.3 Rare earth elements (REEs)

Rare Earth Elements are a collection of seventeen chemical elements in the periodic table, which a set of fifteen lanthanides, and yttrium (Y) and scandium (Sc). They can be an excellent natural probe of many fundamental geochemical processes taking place in both of the interior and at the surface of the earth [33].

In recent decades, geochemical processes controlling metal migration and deposition in the earth`s surface environment has been intensively and increasingly attracting much interests of scientists. The lanthanide elements traditionally have been divided into two groups, the heavy rare earth elements (HREEs) and the light rare earth elements (LREEs). Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, and Samarium (Lanthanum through Europium) are the light rare earth elements. Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium (gadolinium through lutetium) are the heavy rare earth elements. [34-36].

REEs have been widely used in many fields such as automobiles, electronics, computers and portable equipment. With growth of demands in such fields, the requirement of rare earths is expected to increase fast. Future growth is forecasted for rare earths in rechargeable batteries, fiber optics, medical applications as magnetic resonance imaging contrast agents, scintillation detectors, medical isotopes and dental and surgical lasers. so the shortage of trace metals including REEs (and the problem of stable supply for these metals) has been concerned. Therefore, it is requiring us to remove these radionuclides within the scope of permissible concentration before discharge into subsurface environments. Considering the technical, economical and health-related points, the adsorption process seems to be a more appropriate technology for the removal of REEs from pollutants [38-41].

1.4 Adsorbents

Metallic ions in aqueous solution can interact in various ways with solid surface including precipitation, adsorption and ion exchange. Among these methods, adsorption have been found as an efficient possess to remove metallic ion in aqueous solution. Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. It is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. The materials which can be used as absorbent are activated carbon, chitosan, and so on. Because adsorption is a consequence of surface energy, adsorbent must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high capacity for adsorption. Most of the adsorbents also have a distinct pore structure that enables fast transport [44, 45].

In recent years, clay minerals found increasing interest as adsorbents by virtue of their properties, which make them attractive materials for adsorbing heavy metal ions [44-47]. Their abundance in nature, low cost and good cation adsorptive properties, make them suitable for adsorption of metal ions. Layered double hydroxide (LDHs) used in this study are the antitypes of clay minerals [47-49].

1.4.1 Layered double hydroxide (LDHs)

LDHs or anionic clays is lamellar ionic compound containing a postively charged layer and exchangeable anions in the interlayer. They consist of brucite-like layers, and are represented by the general formula $[M_{1-x}^{II}M_x^{III}(OH)_2]\ (A^{n-})_{x/n}\cdot mH_2O$, where cationic M^{II} and M^{III} are divalent and trivalent metals and occupy the octahedral holes in the brucite-like layer. A^{n-} is the interlayer exchangeable anions, which is located in the hydrate layered galleries, and x is the layer charge density $\mathrm{x} = [M^{II}]/([M^{III}]+[M^{III}])$ [50-52]. The layered structure of LDHs is shown in **Fig.1-1**.

In this compound, the positive charge excess is produced by isomorphic substitution of divalent for trivalent cations and compensated by the introduction of anions (usually together with water) in the interlayer space [53, 54]. The layer structure, the positive charge of layer and the kinds of anion make LDHs has multiple properties, which make LDHs suitable for many applications. There are several prominent features: (1) the main laminated chemical composition can be adjusted; (2) the type and quantity of guest anion can be adjusted; (3) the intercalation assembly size and size distribution can be adjusted. Based on this, the property of LDHs includes interchangeability of interlayer anions, thermal stability, and memory effect. LDHs usually were used as adsorbent materials, for the removal process of metallic ions from aqueous solutions, they have large surface area, which lead to a high adsorption capacity, high anion-exchange capacities, and flexible interlayer space. The uptake of the anion species onto LDHs from aqueous solutions can involve three different mechanisms: surface adsorption, interlayer anion exchange and reconstruction of a calcined LDH by the memory effect [55].

For example, LDH intercalated with CO_3^{2-} can be transformed into Mg-Al oxides (LDO) by calcination at 500 °C, as follows:

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + x/2\ CO_2 + H_2O \quad (1)$$

Calcination treatment provides an effective way of enhancing surface defects of derivatives and improving internal reactions. LDO can rehydrate and combine with anions to reconstruct the LDH structure by means of the so-called “memory effect”, as follows:

$$Mg_{1-x}Al_xO_{1+x/2} + x/n\ A^{n-} + (1 + x/2)\ H_2O \rightarrow Mg_{1-x}Al_x(OH)_2A_{x/n} + xOH^- \quad (2)$$

LDO showed a higher adsorption capacity, due to the synergism of the “memory effect” and the “size effect”. Based on this, there is an efficient method for the synthesis of new kinds of LDHs [49,55].

Moreover, since the interlayer anions are easily exchangeable, various types of anions can be intercalated in its structure. This property not only makes LDHs suitable for many applications including pollutant remediation sorbents, antacids, catalysts and anionic exchangers [51, 52, 56]. Intercalation of anion such as anionic ligands is also an efficient way to incorporate different metal cations to LDHs, and there are some reports about the adsorption of anions such as phosphate anions. The capacity of LDHs as adsorbents of pollutant has been extensively reported both for inorganic [57] and organic [58, 59] anions. LDHs also can be intercalated with different polydentate ligands as scavengers of these solids to metal cations and lanthanides [60-62].

1.4.2 Chelation

Chelation is a type of bonding of ions or molecules to metal ions. It involves the formation or presence of two or more separate coordinate bonds between a single central atom and ligand within two or more separate binding sites. Most of these ligands are organic compounds, and are called chelates, chelators, chelating agents, or sequestering agents. The terms bidentate, tridentate or multidentate are used to indicate the number of potential binding sites of the ligand. The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating ligands for the same metal.

Chelation is useful in applications such as providing nutritional supplements, in chelation therapy to remove toxic metals from the body, as contrast agents in MRI scanning, in manufacturing using homogeneous catalysts, in chemical water treatment to assist in the removal of metals, and in fertilizers [52, 57, 64, 65].

In this thesis, two typical chelating agents were used as anionic ligands for intercalation reaction. The first one is Ethylenediaminetetraacetic acid (EDTA) and it is conjugate base is ethylenediaminetetraacetate It is an aminopolycarboxylic acid and colorless; and can be used for both industrial and medical purposes. Since EDTA cannot be dissolved in aqueous solution, it usually produced as several salts, notably disodium EDTA and calcium disodium EDTA. It is widely used in industry and agriculture. It forms strong complexes with the ratio 1:1 between heavy metal ions and ligand.

As a structural isomer of EDTA, the second one is ethylenediamine-N,N′-disuccinic acid (EDDS). It can exist as three isomers: (S,S), (R,S)/(S,R) and (R,R), but only the S,S-isomer is readily biodegradable. The (R,S) and (R,R) isomers are less biodegradable, whereas the (S,S) stereoisomer has been shown to be very effectively biodegraded even in highly polluted soils [65]. EDDS exhibits a surprisingly high rate biodegradation at 83% in 20 days. Biodegradation rates also varies the different metal ions chelated. For example, the complexes of lead and zinc with EDDS have relatively the same stability but the lead complex biodegrades more efficiently than the zinc complex [66]. As of 2002, EDDS has been commercially prominent in Europe on a large scale with an estimated demand rate increase of about 15% each year. Since EDDS offers a biodegradable alternative to EDTA, and is currently used on a large scale in numerous applications [67, 68]. **Figure 1-2** shows the structure of EDTA and EDDS.

1.5 Data Analysis

For data analysis, various equilibrium, kinetic, and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorption. The metallic ions uptake by each adsorbent was calculated using the Eq. (3):

$$Q = \frac{(C_0 \text{-} C_e)}{W} \cdot V \quad [\mu\text{g}\cdot\text{g}^{-1}] \qquad (3)$$

where Q is the adsorption capacities at equilibrium (μg·g^{-1}), C_o and C_e are the initial and equilibrium concentrations of metallic ions in a batch system respectively $[\text{mg}\cdot\text{L}^{-1}]$, V is the volume of the solution (L), and W is the weight of each adsorbent (g) [69, 70].

1.5.1 Adsorption Isotherms

In adsorption processes, it is necessary and critical the equilibrium isotherm studies to predict the behavior of pollutant adsorption onto the sorbent surfaces. Two common adsorption model, Langmuir and Freundlich isotherm model was applied to evaluate the adsorption data obtained in this study.

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to saturated monolayer of solute molecules on the adsorbent surface [71, 72]. Langmuir model assumes monolayer sorption onto a surface and is given by eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \qquad (4)$$

where C_e is the concentration of metallic ions in batch system at equilibrium ($mg \cdot L^{-1}$), q_e is the amount of adsorption of metallic ions at equilibrium ($mg \cdot g^{-1}$), q_{max} is the maximum adsorption capacity on the surface of adsorbent ($mg \cdot g^{-1}$), K_L is the equilibrium adsorption constant ($L \cdot mg^{-1}$). A plot of C_e/q_e versus C_e gives a straight line ($Y=A+BX$) with slope of $1/q_{max}$, and intercept is $1/ (K_L\, q_{max})$; and K_L *is* Langmuir adsorption constant related to the free energy constant (L/g).

The equilibrium constant [72,73] K_L can be calculated from equation (5)

$$K_L = q_e / C_e \qquad (5)$$

where C_e and q_e were the same as mentioned above in Eq.(3).

The favorable adsorption of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L. This factor can indicate whether the sorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), and is given by following equation (6):

$$R_L = \left(\frac{1}{1 + K_L C_0}\right) \qquad (6)$$

where C_0 ($mg \cdot L^{-1}$) is the initial concentration[74, 75].

The Freundlich isotherm is employed to describe heterogeneous system, and it is not restricted to the formation of monolayer. The Freundlich equation predicts that the concentrations on the adsorbent will increase so long as there is an increased in the metallic ions concentration in the liquid. The linearized Freundlich model isotherm is represented by the following equation:

$$\lg q_e = \lg K_F + (1/n) \lg C_e \qquad (7)$$

where, K_F and $1/n$ indicate the adsorption capacity and the adsorption intensity of the system, respectively. The plots of q_e versus C_e in log scale can be plotted to determine values of $1/n$ and K_F depicting the constants of Freundlich model. The greater the value of the n, the more favorable is the adsorption [69, 70, 75].

1.5.2 Kinetic Model

The rate equation for a chemical reaction is an equation that links the reaction rate with concentrations or pressures of reactants and constant parameters (normally rate coefficients and partial reaction orders). For many reactions the rate is given by a power law such as

$$r = k[\mathrm{A}]^x[\mathrm{B}]^y \qquad (8)$$

where *[A]* and *[B]* express the concentration of the species *A* and *B*, respectively (usually in moles per liter (molarity, *M*)). The exponents x and *y* are the partial reaction orders and must be determined experimentally; they are often not equal to the stoichiometric coefficients [72-75]. The constant *k* is the rate coefficient or rate constant of the reaction. The value of this coefficient *k* may depend on conditions such as temperature, ionic strength, surface area of an adsorbent or light irradiation.

The kinetic data can be used to determine the time required for adsorption equilibrium and provide useful data to improve the efficiency of the adsorption model and develop predictive models [76, 78]. In this work, four adsorption isotherm models pseudo-first-order, pseudo-second-order, intra particle diffusion, and Elovich) were applied for modeling the adsorption process.

The pseudo first-order model is expressed as the Eq. (9):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (9)$$

where q_t and q_e (µg·g^{-1}) are the metal amount adsorbed at time at t (h) and equilibrium, respectively, and k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}).

The linear form of the pseudo-second-order rate equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (10)$$

where k_2 (g·µg^{-1}·h^{-1}) is the pseudo-second-order rate constant of the adsorption [69, 70, 78].

The intra-particle diffusion model which was developed by Weber and Morris mostly is utilized to understand the adsorption process mechanism [77]. The initial rate of intra-particle diffusion is calculated by linearization of equation:

$$q_t = k_{ip} t^{0.5} + C_{ip} \qquad (11)$$

Where k_ip (µg /g h$^{0.5}$) is the constant rate of the intra-particle diffusion, and C_ip (µg /g) is the constant depicting the boundary layer effects (intercept).

For Elovich model, α (mg/g min) and β (g/mg) parameters denote the initial adsorption rate and activation energy for chemical adsorption, respectively. The Elovich model is expressed as Eq. (12):

$$q_\mathrm{t} = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \qquad (12)$$

where q_t and t is the same as the above equation, the constants α and β were obtained from the slope and intercept of the linear plot of q_t versus $\ln t$ [71, 79].

1.5.3 Adsorption Thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change (ΔG^0) is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both standard enthalpy (ΔH^0) and standard entropy (ΔS^0) can be considered to determine the Gibb's free energy of the process [75-78]. The free energy of an adsorption process is related to the equilibrium constant by Van't Hoff equation (Eq. 13):

$$\Delta G^0 = \text{-}RT \ln K_d \qquad (13)$$

where R is the universal gas constant (8.314Jmol^{-1} K^{-1}), T is the temperature (K). The value of ln K_d can be obtained by plotting ln (q_e/C_e) vs. q_e for adsorption of metallic ions onto LDHs and extrapolating q_e to zero [80,81]. The thermodynamic parameters of the adsorption for the equations were also calculated by using the Langmuir constant (K_L) or Freundlich constants (K_F) instead of K_d.

$$\ln K_d = \frac{\Delta S^0}{R} \text{-} \frac{\Delta H^0}{RT} \qquad (14)$$

The slope and intercept of Van't-Hoff plot of lnK_d vs. $1/T$ were used to determine the values of ΔH^o and ΔS^o based on eq. 14. The plot of ΔG^0 vs. T also can give ΔH^0 and ΔS^0 by the following equation [80-82].

$$\Delta G^0 = \Delta H^0 \text{-} T\Delta S^0 \qquad (15)$$

1.6 The Purpose and Outline of the Thesis

In this thesis, the objective elements are mainly lead (Pb), copper (Cu), cadmium (Cd) and REEs (lanthanides); and the adsorbent are LDHs intercalated with chelating agents EDTA or EDDS.

The purpose of present study is at first to synthesize and characterize LDHs intercalated with EDTA or EDDS, and then to investigate the efficiency of the materials as adsorbent for metallic ions and REEs ions from aqueous solution for more practical use in the future. On the other hand, in order to obtain the potential adsorption mechanism, the batch experimental data were fitted via different isotherm models. Moreover, the rate kinetic and thermodynamic of the adsorption process was also performed.

The following five kinds of compounds synthesized in present work are MgAl-NO_3 (L1), MgAl-EDTA (L2), MgAl-EDDS (L3), ZnAl-NO_3 (L4) and ZnAl-EDTA (L5),

There are 5 chapters in this thesis.

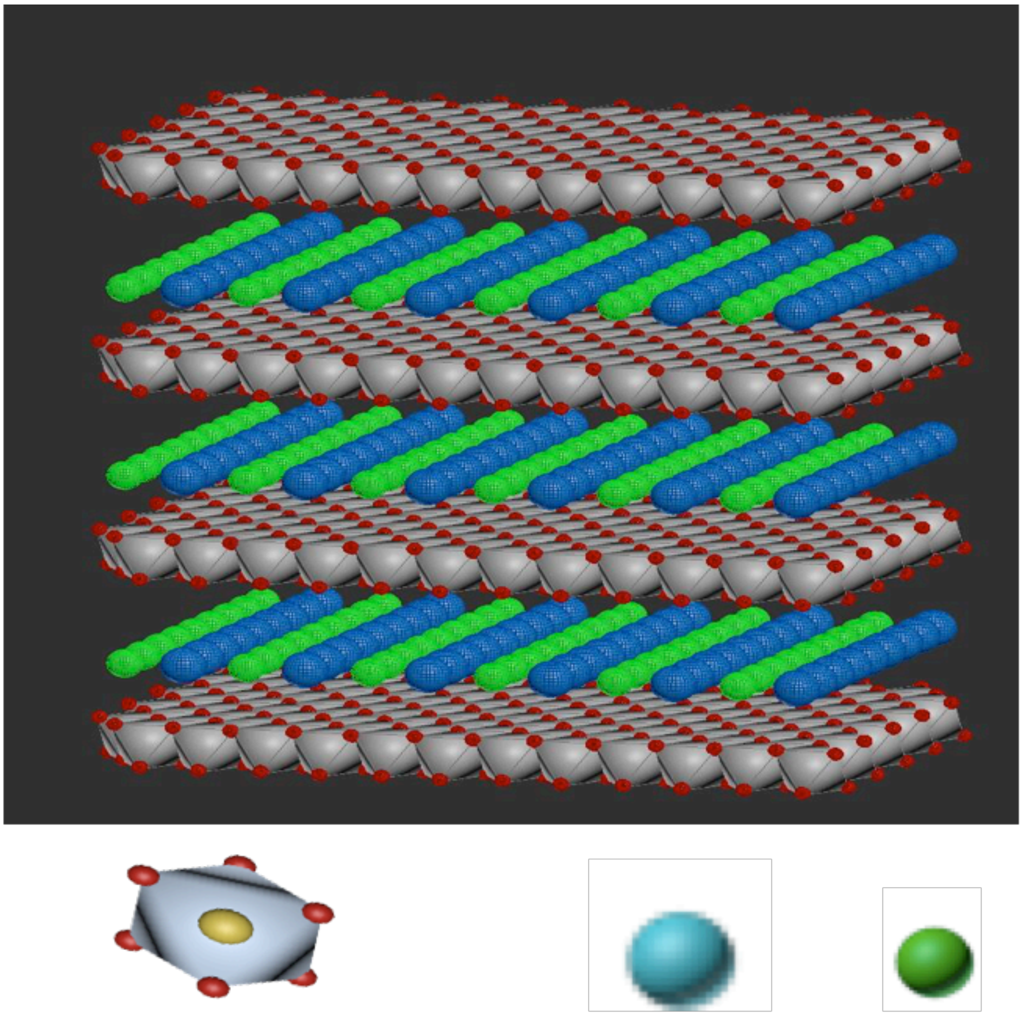
In Chapter 1, the general introduction for this work was described.

In Chapter 2, LDHs intercalated with EDTA or EDDS was synthesized and all the LDHs was characterized. The structure, the composition and the surface properties of precursor-LDHs and intercalated-LDHs (intercalated with the chelating agents) were characterized by chemical analysis, Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD) and a physical adsorption analyzer. Comparative experiments were also carried out with commercially available LDH adsorbent (L0) (i.e., Kyowa DHT-4A).

In Chapter 3, the adsorption experiment of heavy metallic ions from aqueous solution onto LDHs intercalated with chelate agents has been investigated in a batch system. In order to obtain the optimum conditions for the adsorption process, the amount of heavy metallic ions adsorbed at different pH, temperature, and the dosage of adsorbent was determined by Atomic absorption spectrometry (AAS) or Inductively coupled plasma atomic emission spectrometer (ICP-AES). Adsorption isotherms of adsorption experiments were measured at varying initial concentrations under optimized condition. Kinetic models as well as adsorption isotherm models were employed to describe the mechanism involved in the sorption process.

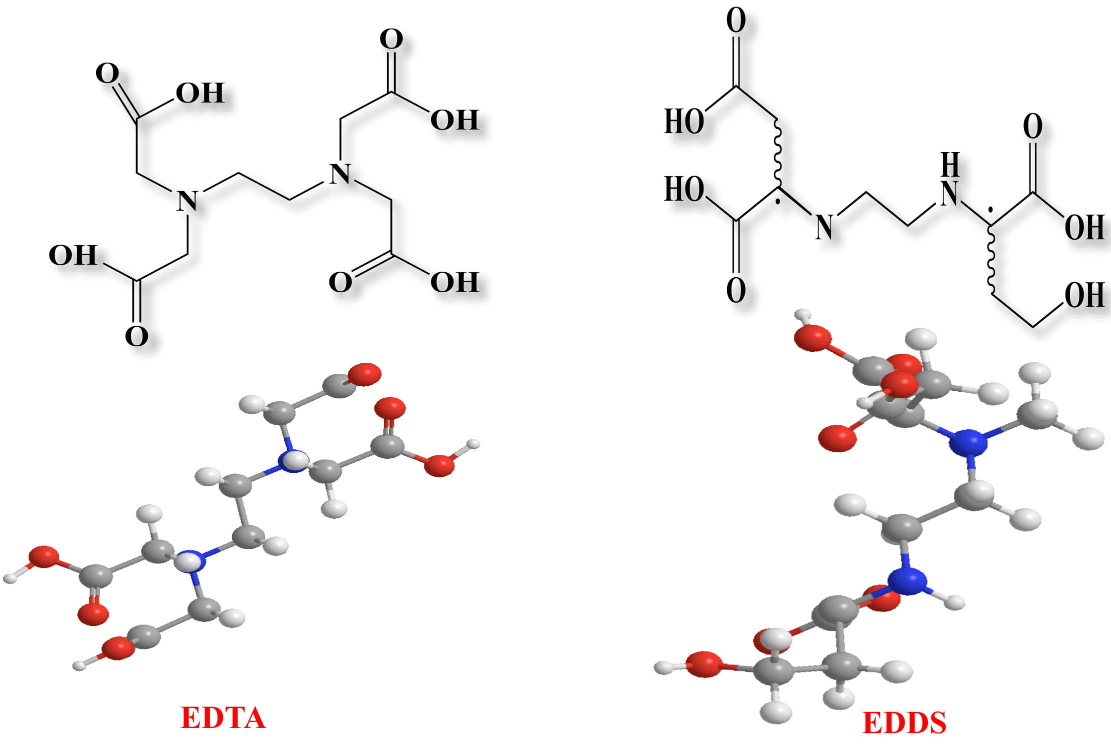
In Chapter 4, the recovery of REEs from aqueous solution by LDHs intercalated with chelate agents was investigated. The amount of REEs absorbed onto these adsorbents was determined with ICP-AES. The data of adsorption experiments were also analyzed by adsorption isotherms and the kinetics models.

Chapter 5 describes general remarks and conclusion of this thesis.



$$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\cdot mH_2O$$

Fig. 1-1 The layered structure of LDHs



EDTA

EDDS

Fig. 1-2 The structure of EDTA and EDDS

Table 1-1 the typical presentations of toxic heavy metals [25-29]

Element	Acute exposure usually a day or less	Chronic exposure often months or years
Cadmium	Pneumonitis (lung inflammation)	Lung cancer Osteomalacia (softening of bones) Proteinuria (excess protein in urine; possible kidney damage)
Lead	Encephalopathy (brain dysfunction) Nausea Vomiting	Anemia Encephalopathy Foot drop/wrist drop (palsy) Nephropathy (kidney disease)
Chromium	Gastrointestinal hemorrhage (bleeding) Hemolysis (red blood cell destruction) Acute renal failure	Pulmonary fibrosis (lung scarring) Lung cancer
Arsenic	Nausea Vomiting Diarrhea Encephalopathy Multi-organ effects Arrhythmia Painful neuropathy	Diabetes Hypopigmentation/Hyperkeratosis Cancer
copper	ngestion include vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), jaundice gastrointestinal distress	liver and kidneys damage milder symptoms

Chapter 2 Synthesis and Characterization of LDHs Intercalated with EDTA or EDDS

2.1 Introduction

LDHs (Layered Double Hydroxides) or anionic clays is lamellar ionic compound containing a postively charged layer and exchangeable anions in the interlayer. They consist of brucite-like layers, and are represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]\,(A^{n-})_{x/n}\cdot mH_2O$, where cationic M^{II} and M^{III} are divalent and trivalent metals and occupy the octahedral holes in the brucite-like layer. A^{n-} is the interlayer exchangeable anions, which is located in the hydrate layered galleries, and x is the layer charge density $x = [M^{II}]/([M^{III}] + [M^{III}])$ [50-52].

In this compound, the positive charge excess is produced by isomorphic substitution of divalent for trivalent cations and compensated by the introduction of anions (usually together with water) in the interlayer space [53,54]. Since the interlayer anions are easily exchangeable, various types of anions can be intercalated in its structure. This property makes LDHs suitable for many applications including pollutant remediation sorbents, antacids, catalysts and anionic exchangers [51,52,56].

Intercalation of anionic ligands is also an efficient way to incorporate different metal cations to LDHs, and there are some reports about the adsorption of anions such as phosphate anions. The capacity of LDHs as adsorbents of pollutant has been extensively reported both for inorganic [57] and organic [58, 59] anions. LDHs also can be intercalated with different polydentate ligands as scavengers of these solids to metal cations and lanthanides [60-62].

EDTA (Ethylenediaminetetracetic Acid) is a chelating agent widely used in industry and agriculture. It forms strong complexes with the ratio 1:1 between heavy metal ions and ligand. EDDS (N, N'-1, 2-Ethanediylbis-1-Aspartic Acid) is also a chelating agent, which may offer a biodegradable alternative to EDTA, and is currently used on a large scale in numerous applications [67, 68].

Considering the structure of LDHs and the properties of chelating agents, LDHs modified with chelating agents has been studied as the potential adsorbents of heavy metals from the aqueous solution. The potential adsorbents for these compounds may be due to the stability of the chelates formed by ligands and metals [83-85].

The following five kinds of compounds synthesized in present work are MgAl-NO_3 (L1), MgAl-EDTA (L2) MgAl-EDDS (L3), ZnAl-NO_3 (L4) and ZnAl-EDTA (L5),. Comparative experiments were also carried out with commercially available LDH adsorbent (L0) (i.e., Kyowa DHT-4A).

2.2 Experimental Section

2.2.1 Materials and Reagents

Chemical reagents including $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Na_2H_2EDTA \cdot 2H_2O$, NaOH, HNO_3 and Zn(II) Mg(II), Al(II) standard solution were purchased from Kanto Chemical Co., Inc.; EDDS (35%) was purchased from Sigma Co. Ltd.; and all reagents used were of analytical grade. CO_2 free water (> 18.2 MΩ) which was treated as an ultrapure water system (RFU 424TA, Advantech Aquarius) was employed throughout the work. The pH meter (HORIBA F-72) was used for measurement of pH while adjusting the pH by using 0.01 $mol \cdot L^{-1}$ or 0.1 $mol \cdot L^{-1}$ NaOH aqueous solution and 0.01 $mol \cdot L^{-1}$ or 0.1 $mol \cdot L^{-1}$ HNO_3 aqueous solution.

2.2.2 Synthesis of the Adsorbents

The synthesis of LDHs intercalated with EDTA or EDDS includes two steps: (1)

the preparation of the precursor LDHs (L1 or L4), and (2) the anion-exchange reaction of this compound with chelating agents [86]. All the synthesis was purged with N_2 to avoid CO_2 uptake from atmosphere.

- **Synthesis of Precursor L1 and L4**

L1 was prepared by dropping addition of 100 mL aqueous solution of 0.02 $mol \cdot L^{-1}$ $Zn(NO_3)_2 \cdot 6H_2O$ and 0.01 $mol \cdot L^{-1} Al(NO_3)_3 \cdot 9H_2O$ to 100 mL NaOH / $NaNO_3$ solution. Then, the solutions were agitated at 70 °C for 8h by maintaining the pH, separated by centrifugation and washed until neutral. L4 was also synthesized by using Mg $(NO_3)_2 \cdot 6H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$ as the similar method [69, 70].

- **Synthesis of L2, L3 and L5**

L2 was synthesized as follows. Under a N_2 atmosphere, 0.015 mol of EDTA or EDDS was added to the 150 mL of suspended solution of L1. Then, the mixing solutions were agitated at 70 °C for 8 h under a certain pH degree, then separated by centrifugation, washed until neutral and then dried at 60 °C overnight [60, 87]. L5 was synthesized by L4 as the similar method for L2.

2.2.3 Characterization of These Adsorbents

Elemental chemical analyses of C, H and N in LDHs were carried out using an elemental analyzer instrument (JMC10, J-SCIENCE LAB CO., Ltd.). After dissolving the sample by HNO_3, the amount of metallic ions in LDHs was obtained by ICP-MS(Agilent HP4500, Thermo). **Table 2-1** shows the operating conditions of ICP-MS. Infrared spectra were obtained using the KBr disc method, with wavenumbers from 400 to 4,000 cm^{-1} on a FT-IR (FTIR-4200, Jasco, Japan). XRD (X-ray Powder Diffraction) of LDHs samples were carried out on a RINT2500HR-PC (RIGAKU Corporation) using Cu *Kα* radiation in the scanning range of 2-80°. N_2

adsorption and desorption isotherms were employed to determine the specific surface area by the specific surface area determinator (AUTOSORB-1, Quabtachrome Inc., USA). The surface morphology of LDHs was surveyed using scanning electron microscopy (SEM; JSM-5800, JEOL, Japan). The element distribution and the component analysis were also analyzed by Electron probe micro analyzer (EPMA; 1600, Shimadzu Corporation).

2.3 Results and Discussion

2.3.1 Chemical analysis

The chemical analysis of LDHs samples is shown in **Table 2-2**. The molar ratio of M^{II} / M^{III} in L1 or L4 is nearly 2 which is well fitted to the expected formula. However, L2, L3 or L5 has lower M^{II} / M^{III} ratio than L1 or L4. The presence of polydentate ligand (Zn-EDTA or Al-EDTA complex) can result in this decrease of the ratio. Moreover, the decrease suggests that octahedron in hydroxyl layer has a partial dissolution (pK_{sp} ($Zn(OH)_2$ = 13.7, pK_{sp} ($Al(OH)_3$) = 32.7, pK_{sp} ($Mg(OH)_2$ = 12.7) during the anion exchange reaction which is performed at pH 5-6 [60,87,88]. The C/N of L5 is 4.35, while that of EDTA ligand is 5; and the little gap between them may be mainly due to the registration of nitrate ions in the interlayer. The more nitrate ions are included in LDHs, the lower C/N value is [89].

2.3.2 FT-IR spectra

The FT-IR spectra of L1 and L2 and L3 are shown in Fig.2-1, and that of L4, L5 are shown in Fig. 2-2. Typical M-OH (M: metallic ions) vibration modes due to the hydroxide layer between 400 and 1,000 cm^{-1} [90] are found in both Fig. 2-1 and Fig.

2-2.

The very sharp peak at 1,385 cm^{-1} in **Fig. 2-1(a)** and **Fig. 2-2(a)** are attributed to the NO_3^- stretching vibration. The NO_3- stretching vibration at 1,385 cm^{-1} is not observed from **Fig. 2-1(b)** and **Fig. 2-2(b).** It may be due to the group which is hidden by the band at 1,394 cm^{-1} [88, 91]. The absorption bands at 1,600 and 1,394 cm^{-1} are characteristics of the symmetrical and asymmetrical vibration of COO- groups. The position of these bonds is similar to the spectrum of LDHs which is reported by Park et al. [92, 93]. It is found that EDTA has been intercalated into the interlayer successfully, although a certain amount of -NO_3 may still retain in the compound judging from the results of chemical analysis. The wide band at around 3,450 cm^{-1} may be attributed to the -H bonding stretching vibrations of -OH groups and water molecules. The band at 1,623 cm^{-1} of L1 and L4 are assigned to water bending vibration [51, 88].

2.3.3 XRD patterns

XRD patterns of L1 and L2 and L3 are shown in **Fig. 2-3**, and those of L4 and L5 are shown in **Fig. 2-4**. They are typical XRD patterns of LDHs. The strong diffraction peaks at low angle, assigned to basal planes (003), (006), (009), were sharp and symmetric compared to the peaks at high angle, which are characteristics of clay mineral shaving a layered structure [92-94]. From the XRD pattern, the basal spacing (d) values of sample were calculated by using Bragg equation and the angle of peak (003).

Then the gallery height was obtained by subtraction from the basal spacing to the layer width (0.48 nm) [93]. The basal spacing and the gallery height of L1, L2, L4 and L5 are shown in Table 2. It indicates that the intercalation of EDTA into NO_3-LDHs gives rise to an increase of basal spacing. This basal spacing could identify the existence of EDTA, because it is close to the dimensions of EDTA complexes (0.9 nm-1 nm) founded by single crystal XRD of M-EDTA (M: metallic ions) compound [60, 87, 93, 95].

2.3.4 SEM micrographs

SEM images of all composite synthesized in this work are shown in **Fig. 2-5**. These adsorbents have clear plate-like morphology, which is typical for LDHs [96]. The intercalated product particles are more homogeneous than the precursor product which may be due to the hydrogen bonding on the layer. Hydrogen bonding makes soft agglomeration occurred on the surface of the LDHs, and after the chelating agent anion replaces the nitrate ions between the layers, the hydrogen bonding between the hydroxyl groups is reduced and the aggregation is weakened to a certain extent.

The inhomogeneous surface of the adsorbent indicated that a large amount of metal salt attached to the surface of the hydrotalcite in an excessive state, its unique layered structure, resulting in removal of heavy metal ions in the aqueous solution not only by Interlayer anion and heavy metal cation interaction, but also rely on the role of surface adsorption and sedimentation.

2.3.5 Specific surface area

Fig. 2-6 shown the specific surface area of the product. Specific surface area of L2 and L3 are bigger than that of L1, and that of L5 is bigger than L4 which may be attributed to intercalation of EDTA or EDDS. Specific surface area of L0 is bigger than that of L1, it is due to the difference of their particle size.

2.3.6 Electron probe micro analyzer (EPMA)

Element distribution analyzed of L1, L2, L4 and L5 by EPMA is shown in **Fig. 2-7**. After the ion exchange, the element distribution of N decreased obviously (by comparing red parts in these pictures), and this decrease is observed in both MgAl-LDHs (a, b) and ZnAl-LDHs (c, d). Furthermore, it is found that the moles of divalent metals are at least equal to or greater than that of the trivalent metals [59, 97], which is consistent with the results of chemical analysis.

2.4 Conclusions

In present study, the precursor LDHs $[Zn_2Al\cdot(OH)_6]$ $NO_3\cdot nH_2O$ and $[Mg_2Al\cdot(OH)_6]$ $NO_3\cdot nH_2O$ (shorted as ZnAl-NO_3 and MgAl-NO_3) was intercalated with the chelating agent EDTA (Ethylenediaminetetraacetic Acid) and EDDS (N, N'-1, 2-Ethanediylbis-1-Aspartic Acid) by anion exchange. The following five kinds of compounds synthesized in present work are MgAl-NO_3 (L1), MgAl-EDTA (L2) and MgAl-EDDS (L3), ZnAl-NO_3 (L4), ZnAl-EDTA (L5). These five kinds of synthesized samples are characterized by some instruments, such as chemical analysis, FT-IR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy) and XRD (Powder X-ray Diffraction) to confirm their properties. The result from characterization suggests that the intercalation into layered double hydroxide is performed successfully. The decrease of M^{II} / M^{III} molar ratio suggests that hydroxyl layer has a partial dissolution during the reaction process. The intercalated product particles are more homogeneous than the precursor product which may be due to the hydrogen bonding on the layer.

Zn-Al LDHs intercalated with EDTA were synthesized by anion exchange reaction and characterized. The results from characterization suggest that EDTA were intercalated into layered double hydroxide successfully. The decrease of Zn/Al molar ratio suggests hydroxyl layer has a partial dissolution during the reaction process. Based on the adsorption experiments which not shown in this chapter, LDHs modified with chelating agents has been studied as the potential adsorbents of heavy metals from the aqueous solution.

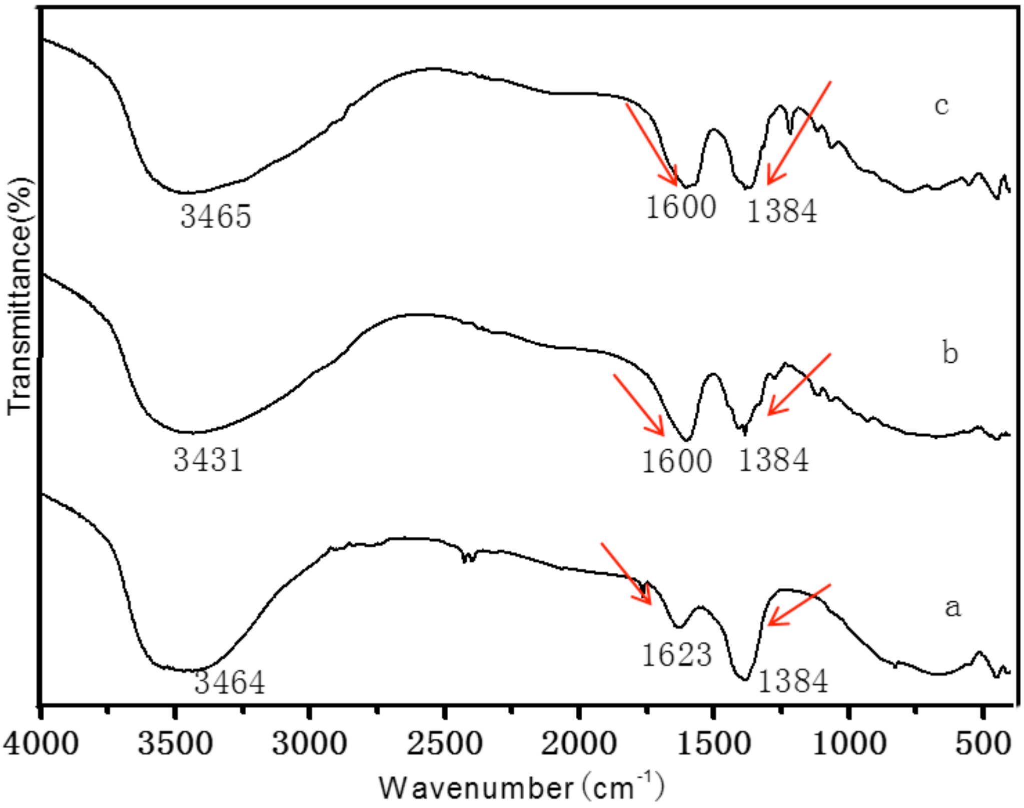


Fig. 2-1 FT-IR spectra of (a) L1, (b) L2 and (c) L3

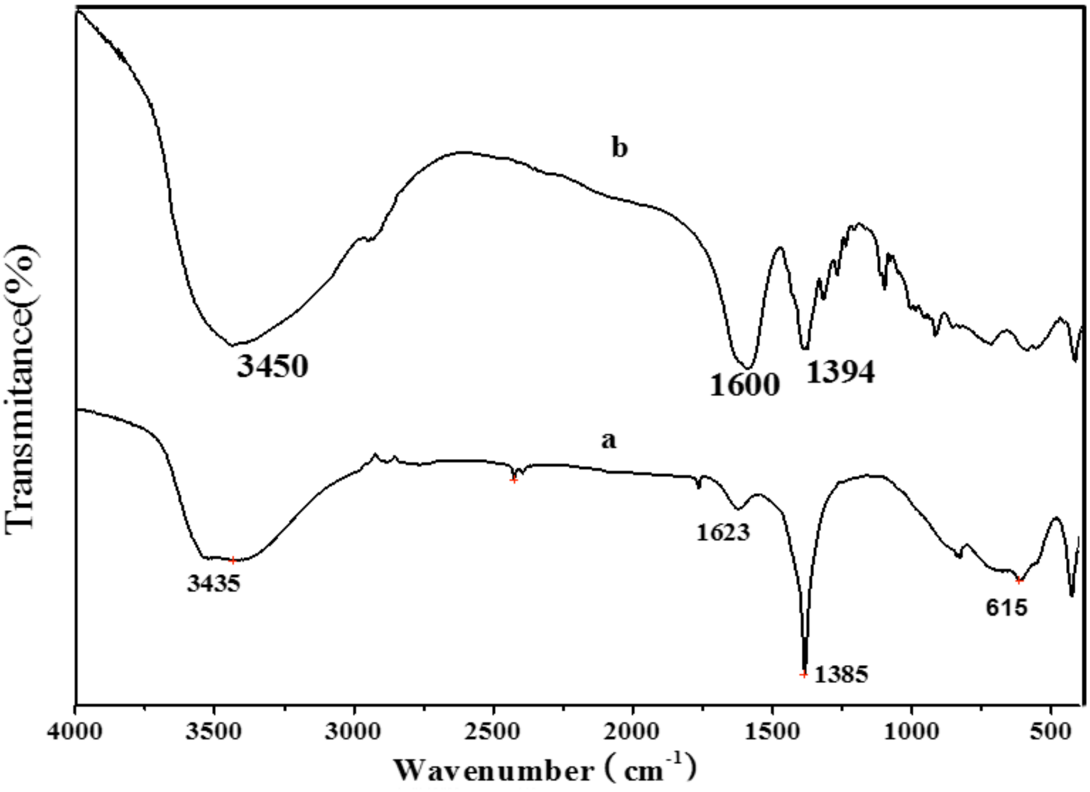


Fig. 2-2 FT-IR spectra of (a) L4 and (b) L5

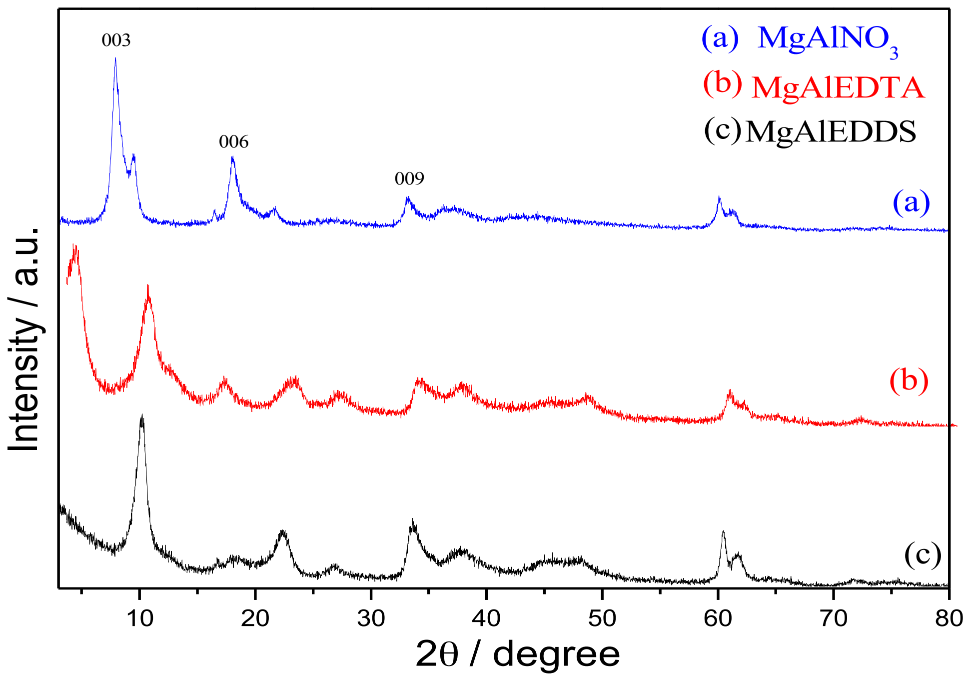


Fig. 2-3 XRD patterns of (a) L1, (b) L2 and (c) L3

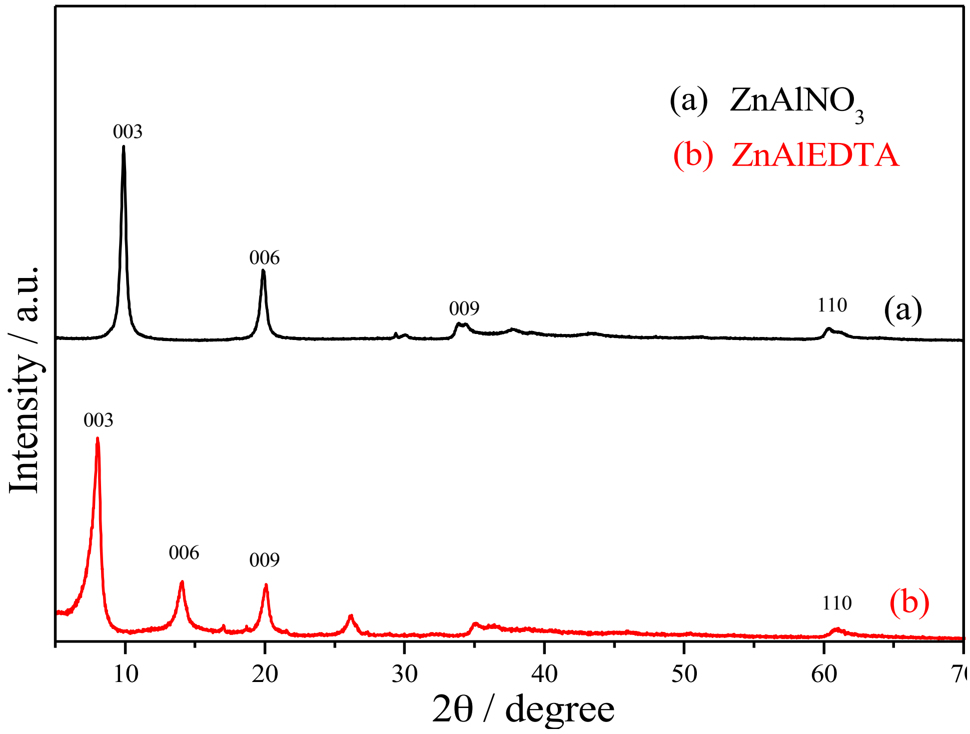


Fig. 2-4 XRD patterns of (a) L4 and (b) L5

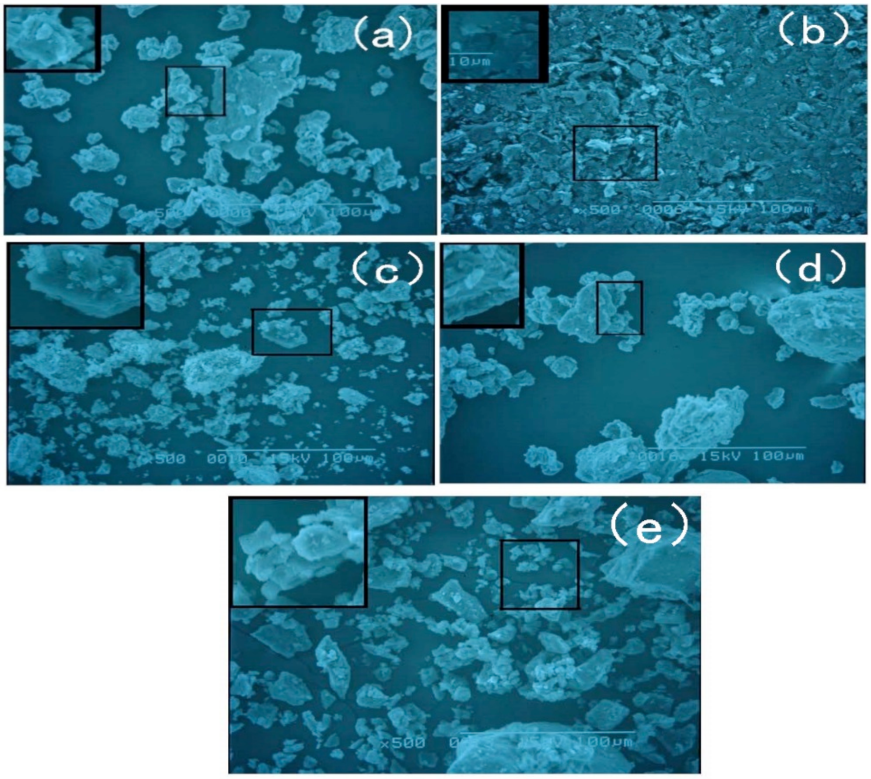


Fig. 2-5 SEM image of (a) L1, (b) L2, (c) L3, (d) L4 and (e) L5

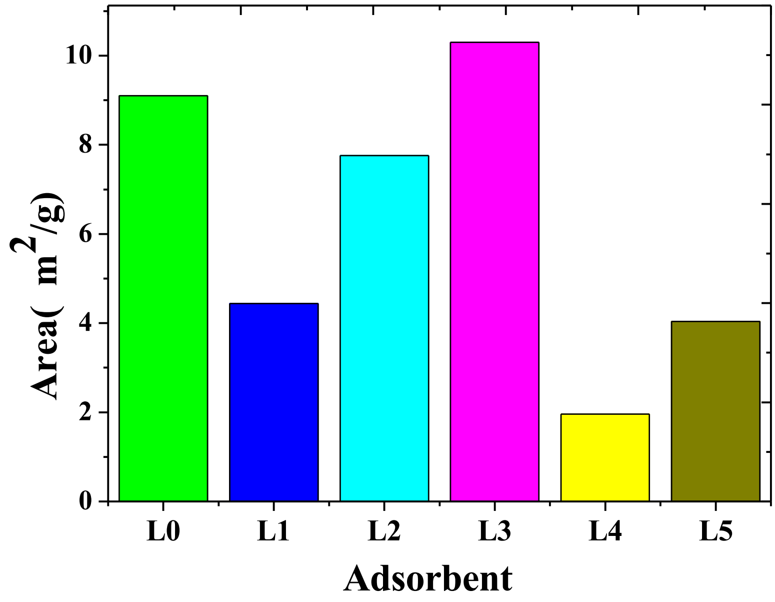
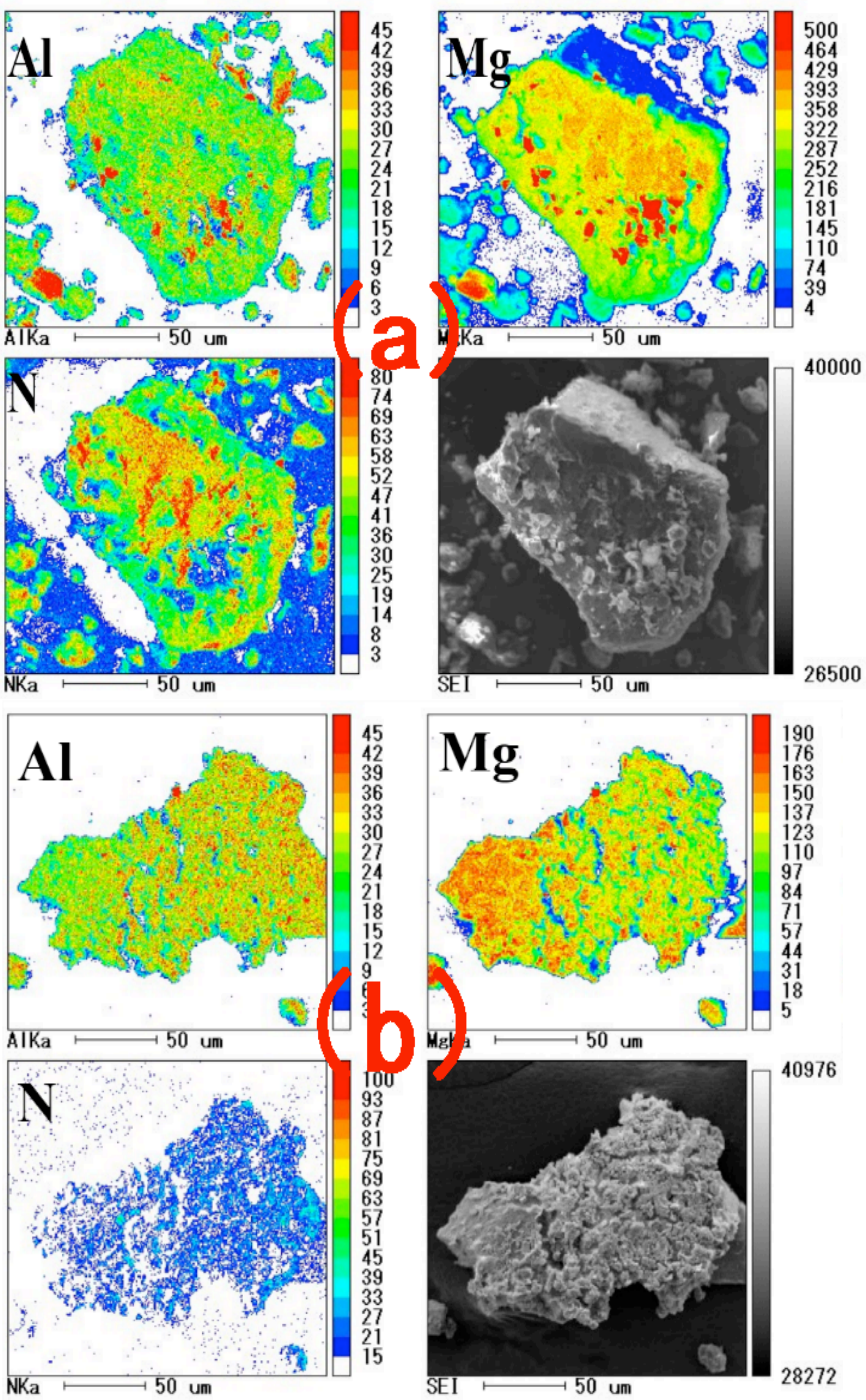


Fig. 2-6 specific surface area of L0, L1, L2, L3, L4 and L5 by BET method


Al
45 42 39 36 33 30 27 24 21 18 15 12 9 6 3
AlKa 50 um
Mg
500 464 429 393 358 322 287 252 216 181 145 110 74 39 4
MgKa 50 um
(a)
N
80 74 69 63 58 52 47 41 36 30 25 19 14 8 3
NKa 50 um
40000
26500
SEI 50 um
Al
45 42 39 36 33 30 27 24 21 18 15 12 9 6 3
AlKa 50 um
Mg
190 176 163 150 137 123 110 97 84 71 57 44 31 18 5
MgKa 50 um
(b)
N
100 93 87 81 75 69 63 57 51 45 39 33 27 21 15
NKa 50 um
40976
28272
SEI 50 um

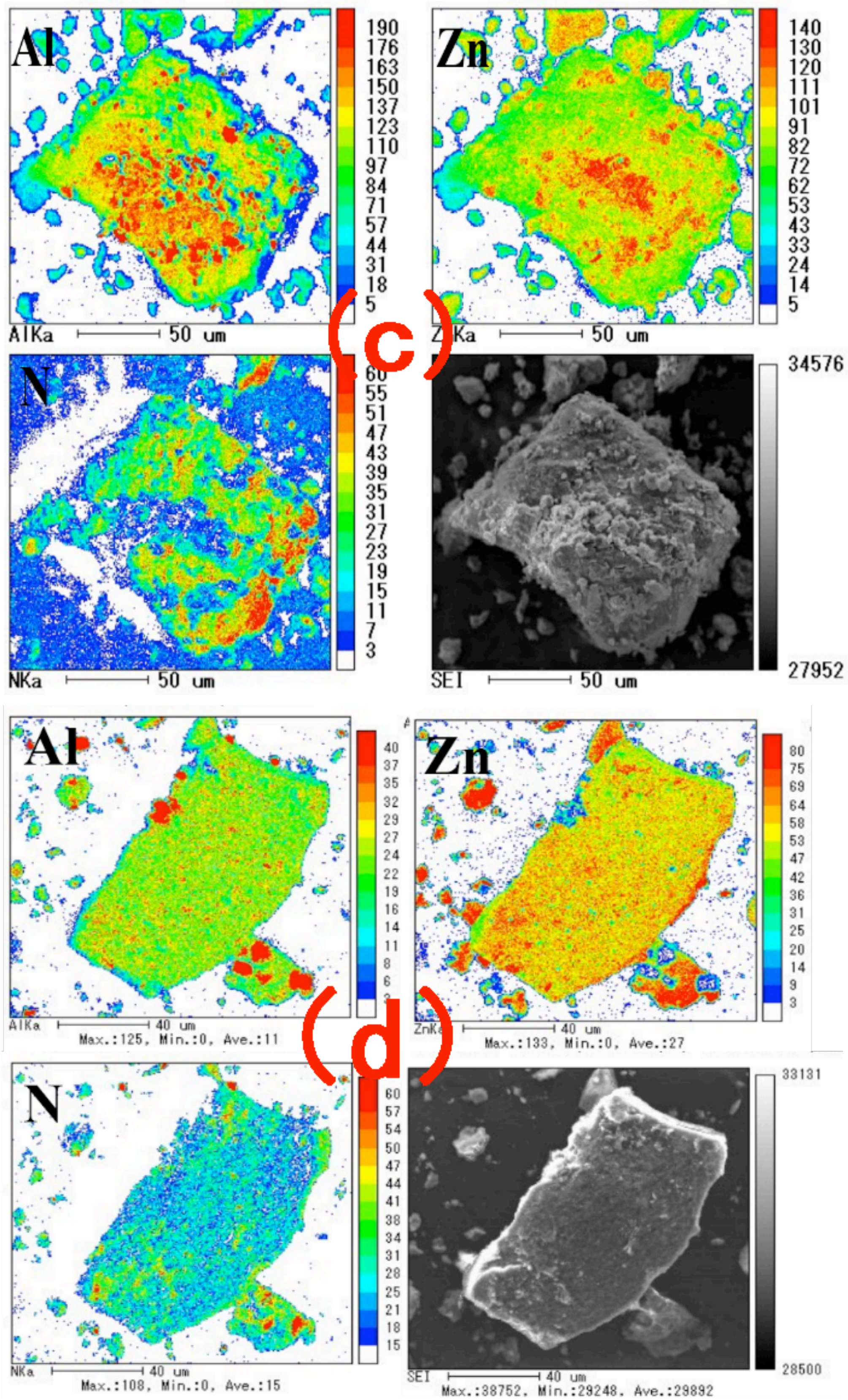


Fig. 2-7 Element distribution analyzed by EPMA of (a)L1, (b)L2, (c)L4 and (d)L5

Table 2-1 Operating conditions of ICP-MS

RF power	1400 W
Plasma gas flow	15 l·min^{-1}
Carrier gas flow	1.2 l·min^{-1}
Sampling depth	6.5 mm
Sample uptake rate	0.5 ml·min^{-1}
Measurement point	3 points/peak
Integration time	1.0 sec/point
Measured Isotope	

Table 2-2 Chemical analysis results of L1, L2, L3, L4 and L5

	wt%			Atomic ratios			Proposed formula
	C	N	H	M^{II}/M^{II}	C/H	H/N	
L1	0.54	5.17	3.24	2.23	0.01	8.79	$[Mg_2Al(OH)_6]NO_3$
L2	11.2	3.83	4.19	1.19	0.36	18.2	$[Mg_2Al(OH)_6]_2[C_{10}H_{14}N_20_8]$
L3	9.82	2.21	4.15	1.49	0.31	26.3	$[Mg_2Al(OH)_6]_2[C_{10}H_{13}N_2Na0_8]$
L4	0.06	4.26	2.38	2.10	0.00	5.72	$[Zn_2Al(OH)_6]NO_3$
L5	13.4	3.08	3.60	0.97	4.35	10.6	$[Zn_2Al(OH)_6]_2 [C_{10}H_{14}N_20_8]$

Table 2-3 the basal spacing of L1, L2, L4 and L5 calculated from XRD by using Bragg's equation

	L1	L2	L4	L5
Basal spacing	0.91	1.42	0.89	1.47
Gallery height	0.43	0.94	0.41	0.99

Chapter 3 Adsorption of heavy metals by chelating agents intercalated LDHs

3.1 Introduction

With the rapid development of industry, water pollution has been becoming a more serious problem in the world; especially heavy metal ions mostly derived from the mining industry is large. The kinds and the concentrations of metal ions are dependent on the type of mining. Heavy metal ions have an effect on plants and animals due to high toxicity and poor biodegradability at higher concentrations. There are several methods to remove metal ions from aqueous solutions. In these methods such as precipitation, adsorption and ion exchange, metal ions can interact with a solid surface. One effective way of removing metals is adsorption on various materials such as activated carbon, biomaterials and clay minerals [21-25].

Lead (Pb) is a non-essential element of the human body. It can enter the human body through the food chain and respiratory system, causing an inadequate supply of nutrients and oxygen, thus resulting in brain tissue damage. Especially children are more sensitive to lead than the adult in the growth and development stage. Excessive Pb in their bodies will lead to the developmental delay, loss of appetite, hearing disorders, and so on [24, 25].

Cadmium (Cd) is one of extremely toxic metal which commonly found in industrial places such as batteries and electroplating industry. The drinking water guideline value in World Health Organization (WHO) for Cd is 0.003mg/L. For human, extended exposure by Cd can lead to the damage for mental and central nervous function, blood composition, bone, liver and other vital organs. Thus the treatment of waste water including Cd has become a hot topic of environment science and technology [61, 95].Cd is one of the most poisonous heavy metals (together with Hg and Pb) and is not known for any essential biological function. Cadmium contamination are arised from many common industrial such as fossil fuel combustion, battery production, phosphate fertilizers, cadmium pigments and coatings[27-29] iron and steel production, and electroplating.

Copper (Cu) pollution has occurred in the vicinity of copper mines and smelting operations since mankind began the activity several millennia ago. The excavation of Cu-containing earth at open pit copper mines can produce copper rich dusts which are spread in the wind around the mine site. Most of these ores are sulfide minerals, and are oxidized in the air to sulfates, producing sulfuric acid, which renders the copper in the mineral highly soluble. For human being, copper toxicity can occur from eating acid foods cooked in uncoated copper cookware, or from exposure to excess copper in drinking water or other environmental sources [21,22].

LDHs are typical intercalation compounds with the general formula $\{M^{II}_{1-x}M^{III}_{x}(OH)_2\}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metals, A^{n-} denotes compensating for the positive charger of the metal hydroxide layers. The structure and their high anionic exchange capacity make LDHs suitable for many applications including pollutant sorbents, catalysts and anionic exchangers [50-51].

Considering the structure of LDHs, it is suggested that these compounds can be intercalated with different polidentate ligands. Recently, the study using LDHs modified with chelating agents as the potential adsorbents of heavy metals from aqueous solution has been reported [60,83]. The potential adsorbents for these compounds may be due to the stability of the chelates formed between ligands and metals. The advantage of LDHs modified with EDTA or EDDS are low cost, extensive range for application and simple operation. The aim of this work is at first to synthesize and to characterize LDHs intercalated with EDTA or EDDS, and to study the uptake of heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+}) by these hybrid compounds. The following five kinds of compounds synthesized in this work are ZnAl-NO_3 (L1), ZnAl-EDTA (L2), MgAl-NO_3 (L3), MgAl-EDTA (L4) and MgAl-EDDS (L5). To confirm the effect of intercalation with EDTA, the adsorption of metallic ions onto L1 and L2 are also compared.

This study investigated the adsorption ability of LDHS as adsorbent for Pb, Cu, and Cd from aqueous solution. Finally, the further developments of LDHs as useful adsorbent with the future of application in the environmental chemistry are metioned.

3.2 Experimental section

3.2.1 Materials

Chemical reagents including $Cu(NO_3)_2$, $Pb(NO_3)_2$ $Mg(NO_3)_2 \cdot 6H_2O$ and NaOH were purchased from Kanto Chemical Co., Inc. Cd(II) standard solutions were prepared by diluting a standard solution (1,000 $mg \cdot L^{-1}$). All reagents used were of analytical grade, and CO_2 free water (> 18.2 MΩ) which was treated by an ultrapure water system (RFU 424TA, Advantech Aquarius) was employed throughout the work. All synthesis should be performed under a N_2 atmosphere condition to avoid carbonate contamination.

3.2.2 Apparatus

The suspension containing the adsorbent and each of the above metallic solution was filtered through a 0.10 μm membrane filter (Mixed Cellulose Ester 47 mm, Advantec MFS, Inc.) to remove each metallic ion that have been adsorbed into the adsorbent. Then, the concentration of Cu(II) or Pb(II) in the filtrate was determined with an atomic absorption spectrophotometer (AAS), and the concentration of Cd(II) in the filtrate was determined by inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (SPS 1500, Seiko Instrument Inc). The operation condition of ICP-AES was shown in **Table 3-1**.

3.2.3 Adsorption experiments

For obtaining the optimum conditions regarding the adsorption of heavy metal, the batch experiments were studied by varying pH, contact time, adsorbent dose, and initial concentration on the adsorption of heavy metal.

The adsorption experiments of Cu(II) and Pb(II) *u*sing L2 and L3 were carried out. A certain amount of L2 or L3 were contacted with 30 mL of an aqueous solution containing known initial each metal ion (nitrate salts) ranging from 0.1 to 2 $g\cdot L^{-1}$. Sorption experiments were conducted in the pH range of 2–6, contact time from 30 min to 6 h, temperature from 25 to 40°C, and adsorbent dosage 5–40 mg. The pH of each solution was adjusted using 0.1 $mol\cdot L^{-1}$ NH_4OH and 0.1 $mol\cdot L^{-1}$ HNO_3.

The adsorption capacities of Cu(II) or Pb(II) on L1, L2 and L3 were compared with that of commercial LDHs: DHT-4A ($[Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O]$, Kyowa Chemical Industry Co., Ltd), which is abbreviated as L0 below. The properties of DHT-4A based on the Examination Report (technical information data) by Kyowa Chemical Industry Co., Ltd. are listed in **Table 3-2**.

The adsorption experiments of Cd(II) using L4 and L5 were also carried out. Cd(II) solution and standard solutions used in this study were prepared by diluting the standard solutions (XSTC-13 for heavy metals; 1000$mg\cdot dm^{-3}$ 5% HNO_3 solution) purchased from SPEX Certi. Prep., Inc. (USA).A certain amount of L4 or L5 were contacted with 30 mL of an aqueous solution containing known initial Cd(II) ranging from 0.05 to 1 $mg\cdot L^{-1}$. Sorption experiments were conducted from 30 min to 8h, temperature from 25 to 40°C. The experiment using Cd(II) solution without the adsorbent was also performed to identify potential loss of Cd ion during the process such as precipitation. To confirm the effect of intercalation with EDTA, the adsorption of Cu(II), Pb(II) Cd(II) onto L1 and L2 are also compared.

Following each adsorption experiment, the suspension containing the adsorbent and each of the above metallic solutions was determined by AAS or ICP-AES The metal uptake by the adsorbent was calculated using the Eq. (3).

3.2.4 Data Analysis

Adsorption isotherms of adsorption data were studied at varying initial concentration of metallic ions under optimized conditions of contact time and the dosage of adsorbents in this work. Based on other previous study, two common adsorption models, Langmuir (eq. (4)) and Freundlich isotherm (eq. (7))models, were applied to evaluate the adsorption data obtained for Cu(II), Pb(II) and Cd(II).

Furthermore, in order to describe the adsorbate-adsorbent interaction, the kinetic isotherms were analyzed by fitting experiments data into pseudo-first-order (eq. (9)), pseudo-second-order (eq. (10)), intra particle diffusion (eq. (11)), and Elovich equation (eq. (12)) to find out the suitable model that may be used for design consideration.

3.3 Results and Discussion

3.3.1 Optimum conditions of adsorption

For obtaining the optimum conditions regarding the adsorption of metallic ions, the effects of pH, contact time and dosage of adsorbents on the removal of metallic ions from the aqueous solution were investigated.

Effect of pH

With the aim of obtaining the optimum pH conditions, the effects of pH value, the adsorption experiments with a certain amount of L2 or L3 were contacted with 30 mL of an aqueous solution containing known initial each metal ion (nitrate salts) were conducted in the pH range of 2–6. Effect of pH on Cu(II) or Pb(II) adsorption onto L2 and L3 are shown in **Fig. 3-1**. The ordinate in **Fig. 3-1** (i.e., Qe) is the amount of solute adsorbed in the solid at the equilibrium (expressed as ug·g^{-1} or mg·g^{-1}).

From **Fig 3-1,** With the increase of pH, the adsorption efficiency increased under our experimental conditions. Then, a pH of 6 was selected in the following experiment, although the optimum range of pH may be regarded as 4 to 6, which is also necessary for the chelating process. It was pointed out that the adsorption capacities decrease at low pH due to the competition of protons with metal ions for active binding. On the other hand, at higher pH, the subject metals precipitated from the solution as its hydroxides [98, 99].

Effect of contact time

The effect of contact time on Cu(II), Pb(II) adsorption onto L2 and L3 are shown in **Fig 3-2**. At the beginning of the reaction, the adsorption rate is large. However, when the contact time exceeded more than 120 min, the adsorption efficiency became approximately constant. It is indicated the reaction reached equilibrium at 120 min, so the contact time was selected as 120 min in the following experiment.

Effect of adsorbent dosage

Under optimized condition of pH and contact time, the adsorption behaviors onto adsorbents at different dosages from 10mg to 40mg have been studied and, the results are shown in **Figure 3-3**. With the increasing of the dosage, the adsorption efficiency increases while the dosage is reached 20mg, When the dosage of adsorbent are more than 20mg, the rate becomes slow, and no remarkable increase is observed. With the increase of the adsorbent, the adsorbent site is increasing, and the overmuch adsorbent make the aggregation occurred between the adsorbent. Then it might reduce the adsorption capacity. Therefore, 20mg was considered as optimum dosage for the Cu(II), Pb(II) adsorption onto L2 and L3 in our study.

3.3.2 Adsorption of Cu(II) or Pb(II)onto L1, L2, L3 and L0

The adsorption capacities of Cu(II) or Pb(II) onto L1, L2, L3 and L0 are compared in **Figure 3-4**. The adsorption efficiency of Cu^{2+} was larger than that of Pb^{2+} for the same absorbent, which could be attributed to their stability constant (EDTA-Cu: 18.7; EDDS-Cu: 18.4; EDTA-Pb: 18.0; EDDS-Pb: 12.7) [60, 88]. That is to say, it can be considered that the large adsorption capacity is obtained when the stability constant of chelate-metal is high. By comparing among adsorbents used in this work, the order of the adsorption capacity is L2＞L3＞L0＞L1. The higher the adsorption efficiency of L0 than L1 may be attributable to its high specific surface area.

3.3.3 Adsorption of Cd(II) using L4 and L5

The effect of contact time on the adsorption is shown in **Fig.3-5**. Based on the previous studies of L5, the increased removal of heavy metal cation is produced by three parts: an exchange reaction of chelated zinc and heavy metal cation; the reaction of heavy metal cation with EDTA ions in the interlayer; and the metal cation hydroxide precipitation occurred at higher pH [83]. As the first two reactions both occur when the adsorbent was added in the solution, these two reactions are not distinguishable during the adsorption process.

From the chemical analysis of samples, it is suggested that the chelated zinc was released into the solution when the adsorbent was dispersed in the solution. Then the chelated zinc may be consumed by reacting with Cd(II) in aqueous solution. However, the presence of chelated zinc does not affect the adsorption process in this case, because the stability constants of Zn-EDTA complexes and Cd-EDTA complexes are similar. The fast removal rate in the beginning may be attributable to more available sites at the initial stage [90, 101].

The pH diminution generally occur as the time goes on during the reaction, which may cause by the increase of released zinc ions when the sorbent was dispersed into the solution, and also by the buffering effect of L5. The optimum range of pH can be regarded as 4 to 6 based on the other previous studies [60], which is good for the liberation of EDTA ion during the reaction. The lower pH may lead to the increase of the zinc ions in the solution by the partial dissolution of layer. On the other hand, at higher pH, the hydroxyl ions compete with EDTA for the precipitation of $Cd(OH)_2$. Both the initial pH and the final pH were observed around 5-6 during the reaction in this work. It is indicated that the pH may not vary so much when the concentration of metal ion is low (100ppb in this case) [90, 97, 100, 101], then the adsorption experiment was conducted without adjusting pH in this study.

3.3.4 Adsorption of Cu(II), Pb(II) Cd(II) onto L4 and L5

In order to confirm the effect of the intercalation with chelate agents on the adsorption capacity of metals, the adsorption experiments of some metallic elements onto L1 and L2 are compared. The adsorption of Cd(II), Cu(II) and Pb(II) onto these LDHs under the optimum condition are shown in **Fig. 3-6**, **Fig. 3-7** and **Fig. 3-8**, respectively.

Both LDHs were found to take up Cd(II), Cu(II) and Pb(II) from aqueous solutions, and the uptake was found to increase with time. The adsorption capacity of both LDHs for Cd(II), Cu(II) and Pb(II) increased rapidly during the initial stages, and thereafter it increased gradually. It is generally found that the time needed to be reached equilibrium for L2 was shorter than that for L1. From the adsorption experiment, the improvement of adsorption capacity by intercalation was observed. On the other hand, the adsorption capacity of Cu(II) and Pb(II) at equilibrium was higher than that of Cd(II). It is considered that heavy metal was removed by LDHs including two mechanisms: chemical precipitation and chelation [70]. In the first case, the hydroxyl anions compete with chelating agents for the precipitation of metal hydroxides at higher pH, and divalent ions are usually selectively dissolved. In the second case, the adsorption affinity is generally determined by the stability constant of the corresponding complex [31, 32, 61].

3.3.5 Adsorption isotherms

The Adsorption isotherms for Cu(II) or Pb(II) were obtained under the optimum adsorption conditions (i.e. pH 6, contact time 120 min, temperature 25°C and adsorbent dosage 10 mg). The adsorption isotherms of Cu(II) or Pb(II) onto L2 and L3 were analyzed using Langmuir and Freundlich equations and were shown in **Fig. 3-9**. and **Fig. 3-10**, respectively. From **Fig. 3-9**, the linear correlation coefficient (R^2) of L2 (Pb^{2+}), L3 (Pb^{2+}), L2 (Cu^{2+}) and L3 (Cu^{2+}) and other parameter for Langmuir and Freundlich isotherms model were shown in **Table 3-3**, respectively. That is, L2 and L3 synthesized in this work are well fitted by Freundlich adsorption isotherms models.

In order to verify the L5 as feasibility of process scale-up for more practical use, fitting the experimental data to the isotherm models and the kinetic models is significant.

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. The adsorption data obtained for Cd(II) using L5 were analyzed by Langmuir and Freundlich equations, and the results are shown in **Fig. 3-11** and **Fig. 3-12**, respectively.

In this case, the Freundlich equation is more satisfactorily for Cd(II). The Freundlich isotherm model allows for several kinds of adsorption sites onto the adsorbent, and represents the adsorption data properly at low and intermediate concentrations on heterogeneous surface. The correlation coefficients (R^2) of Langmuir and Freundlich isotherm are shown in **Table 3-4** along with other relevant parameters. K_F is a measure of adsorption capacity, and $1/n$ refers to the adsorption intensity of the system. It is shown that $1/n$ values between 0.1 and 1.0 refers to an interaction between exchange sites in the adsorbent and Cd(II) cations[73,91,101,102]. The K_F and $1/n$ in Table 3-4 indicates the adsorption process is favorable.

3.3.6 Kinetic model

The Kinetic isotherms for Cu(II) or Pb(II) were obtained under the optimum adsorption conditions (i.e. pH 6, concentration 200ppm, temperature 25°C and adsorbent dosage 10 mg). In **Table 3-5**, the parameters for two kinetic models of adsorption of Cu(II) or Pb(II) on L2 or L3 are presented. The data presented in Table 3-5 showed that adsorption process followed pseudo-second order rather than pseudo-first order model. Then the second order kinetic models plot for the adsorption of Cu(II) or Pb(II) on L2 or L3 is shown in **Fig 3-13**. The experimentally calculated values of q_e at various concentrations were in a good agreement with theoretical calculated values. Also, the values of correlation coefficients (R^2) for the pseudo-second-order kinetic model was nearly 1, indicated that pseudo-second-order kinetic model was better obeyed.

The Pseudo-first-order kinetic and second-order models were applied to test the experimental data of Cd(II) absorbed on L5 and to explain the kinetics of the layered double hydroxide adsorption process. **Table 3-6** shows the linear regression coefficients (R^2) and other parameters for two kinetic models of adsorption of Cd(II)) on L5, and the kinetic model is shown in **Fig. 3-14**. From **Table 3-6**, it is found that pseudo-second-order kinetic model fit the experimental data because R^2 value for pseudo-second-order kinetic model is comparatively large, whereas the value for pseudo-first-order kinetic model is fairly small. The q_e value calculated from the pseudo-second-order models is very consistent with the experimental q_e value ($q_{\mathrm{e\ EXP}}$) [70-72].

3.4. Conclusions

MgAl-LDHs (L1, L2, L3) synthesized in this work were very effective for removing Cu(II) and Pb (II) from water solutions. The adsorption efficiency of Cu(II) was higher than that of Pb(II) for the same absorbent. Higher adsorption efficiency is obtained by intercalating chelating agent (i.e. EDTA or EDDS) into LDHs. The adsorption capacity is in the order of L2 ＞ L3 ＞ L0 ＞ L1.

The adsorption experimental data of Cu(II) and Pb (II) onto L2 and L3 were well fitted by the Freundlich adsorption isotherms model. The results suggest that MgAl-LDHs synthesized in this work could be suitable as sorbent materials for the adsorption and removal of heavy metal ions from aqueous solutions.

The isotherm models such as Langmuir and Freundlich were used to analyze the adsorption data. The adsorption of Cd(II) by the ZnAl-EDTA was well fitted to

Freundlich isotherms, which suggests that the adsorption occurred for several kinds of adsorption sites onto the adsorbent.

The kinetic studies of Cd(II) adsorption by the L5 was analyzed using the pseudo-first order and pseudo-second order kinetic models, and it shows better fitting for the pseudo-second order model in this work. Zn(II) released in aqueous solution may affect the removal percentage (maximum 66.7%, not shown) by competing with Cd(II), which may be attributable to the similar stability constants between chelated zinc and chelated cadmium. More detailed research about the stability of adsorbent will be needed.

The uptake process of heavy metal ions onto LDHs includes the chelation with EDTA and the precipitation. This complex mechanism enables LDHs intercalated with EDTA to have high affinity for removing Cd(II). Based on the adsorption efficiency of this adsorbent, ZnAl-EDTA synthesized in this work can be an efficient adsorbent for heavy metal ions.

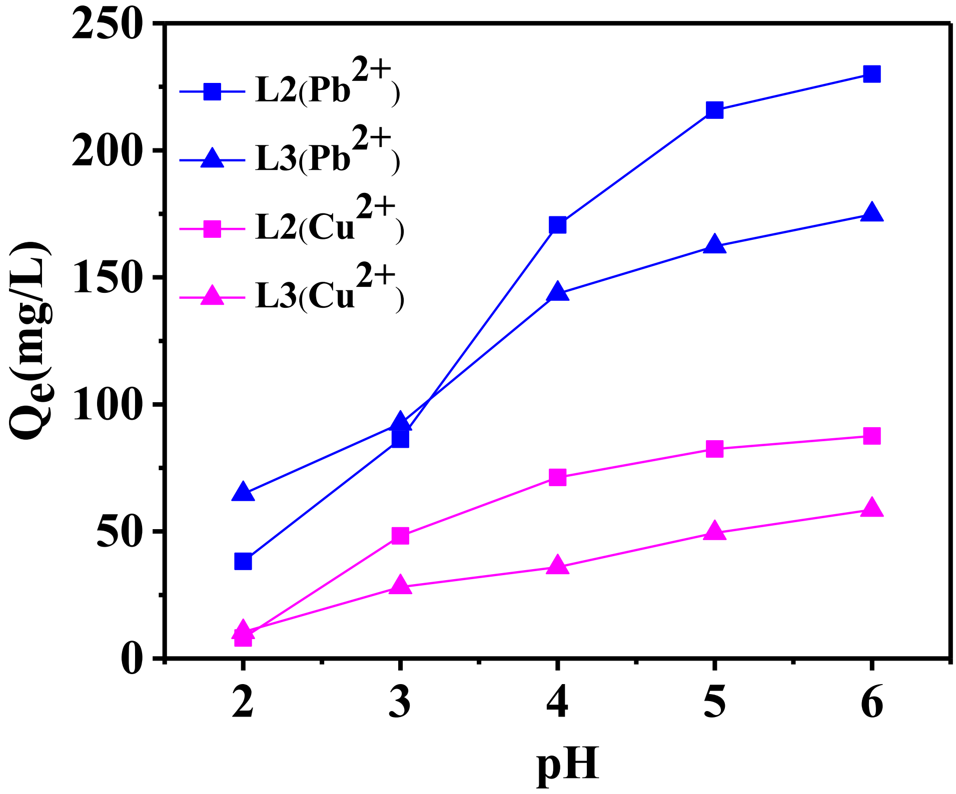


Fig. 3-1. Effect of pH on Pb^{2+} and Cu^{2+} adsorption onto L2 and L3

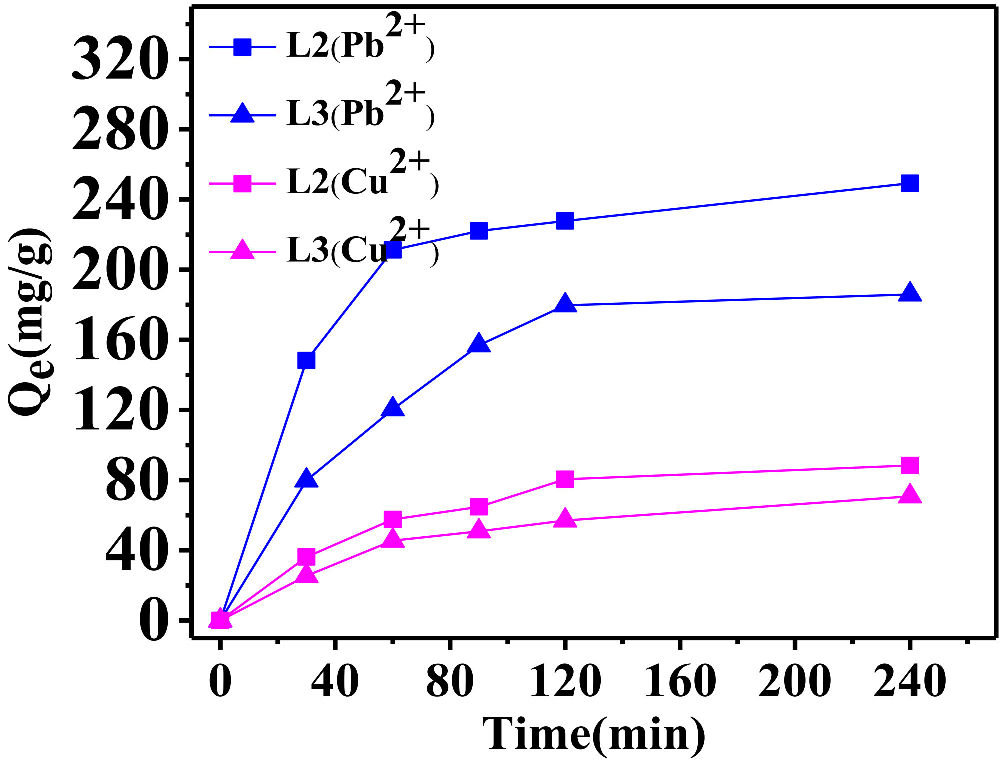


Fig. 3-2. Effect of connect time on Pb^{2+} and Cu^{2+} adsorption onto L2 and L3

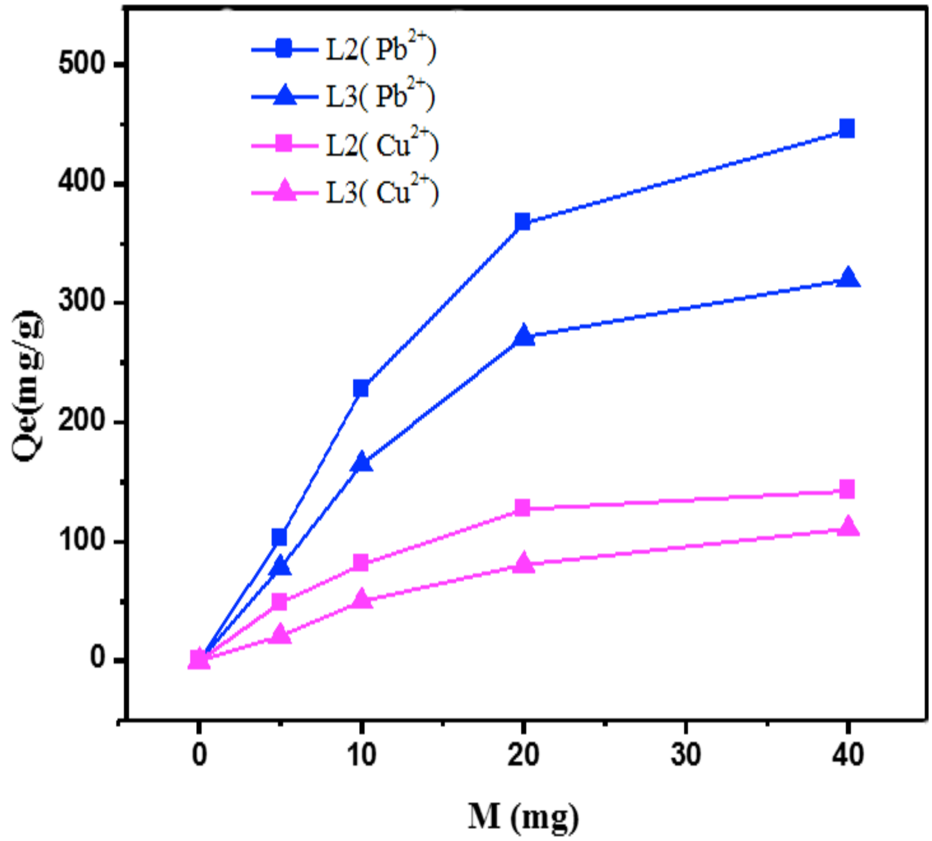


Fig. 3-3. Effect of adsorbent dosage on Pb^{2+} and Cu^{2+} adsorption onto L2 and L3

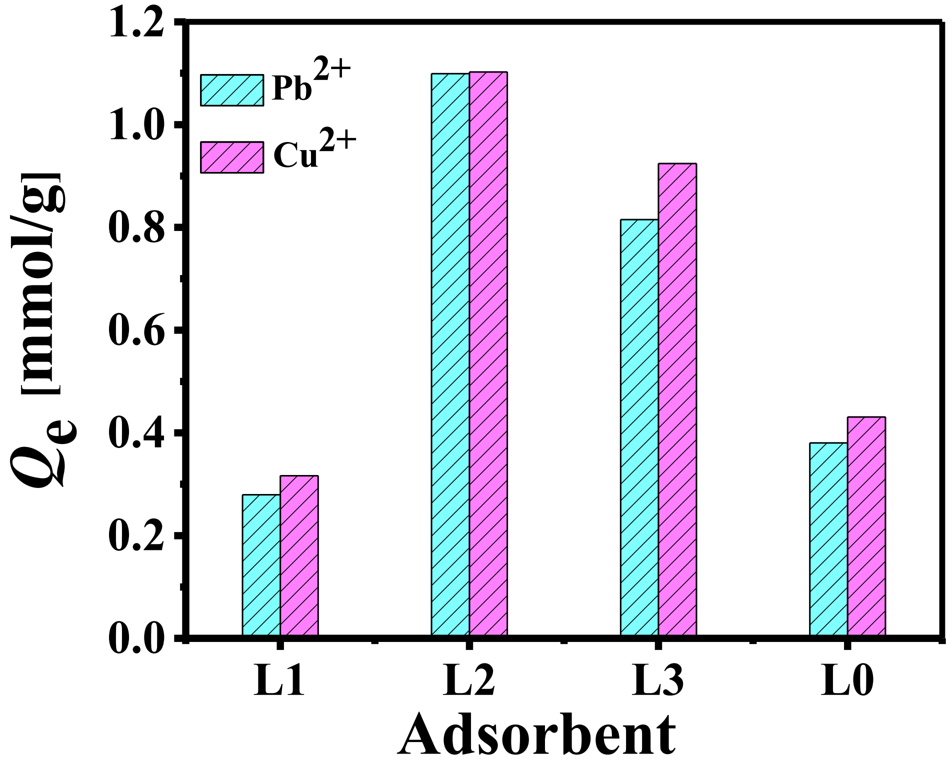


Fig. 3-4 The adsorption capacity of Pb^{2+} and Cu^{2+}onto L1, L2, L3 and L0

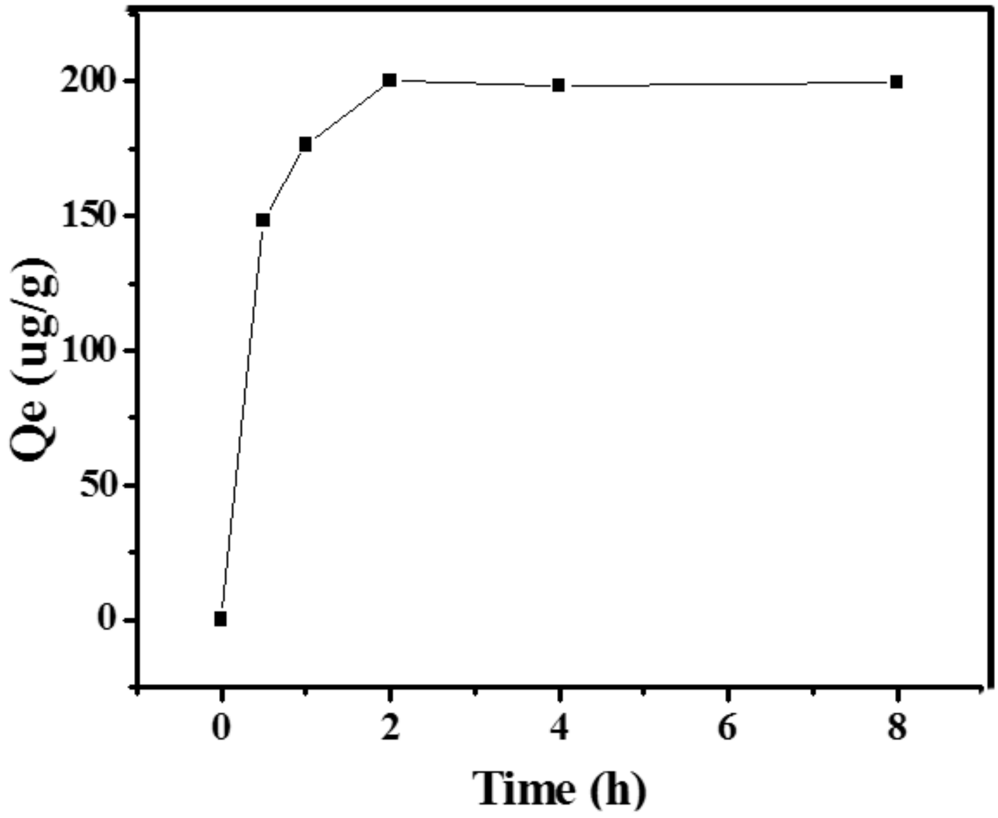


Fig. 3-5 Effect of time on adsorption of Cd (II) onto L5

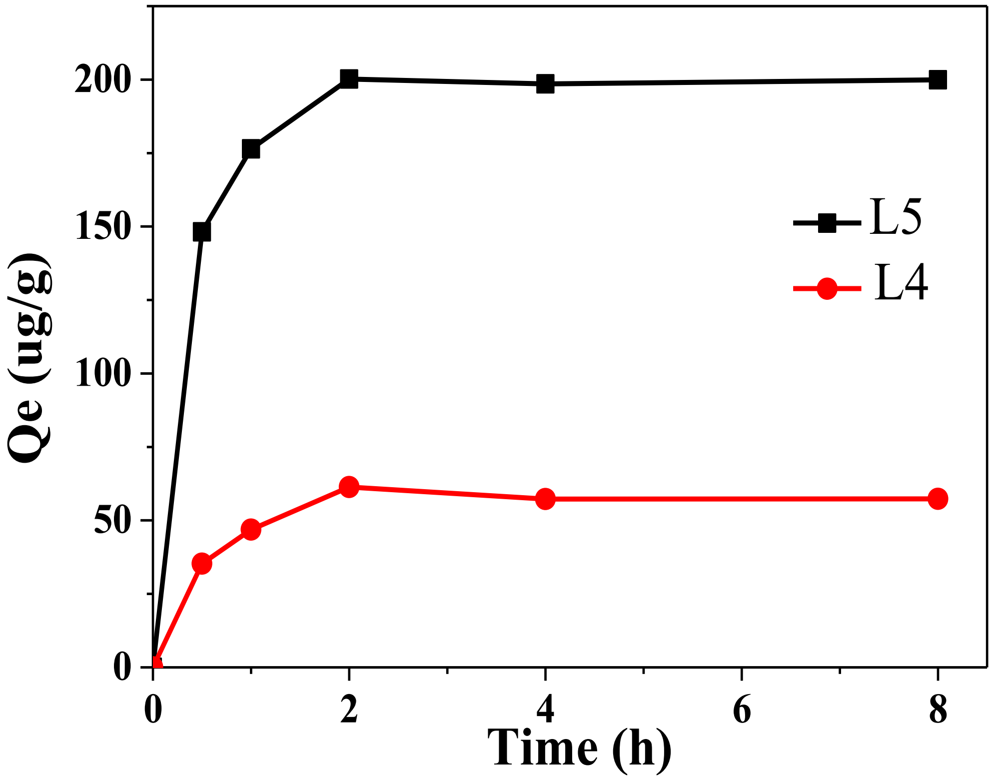


Fig. 3-6 Adsorption of Cd(II) onto L4 and L5.

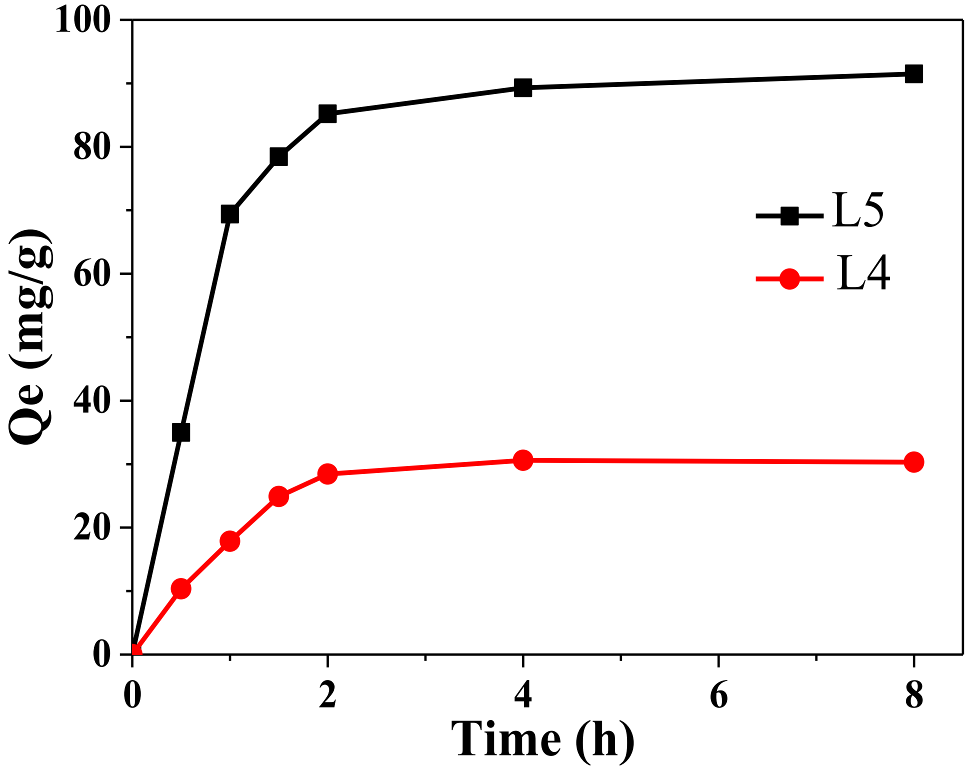


Fig. 3-7 Adsorption of Cu(II) onto L4 and L5.

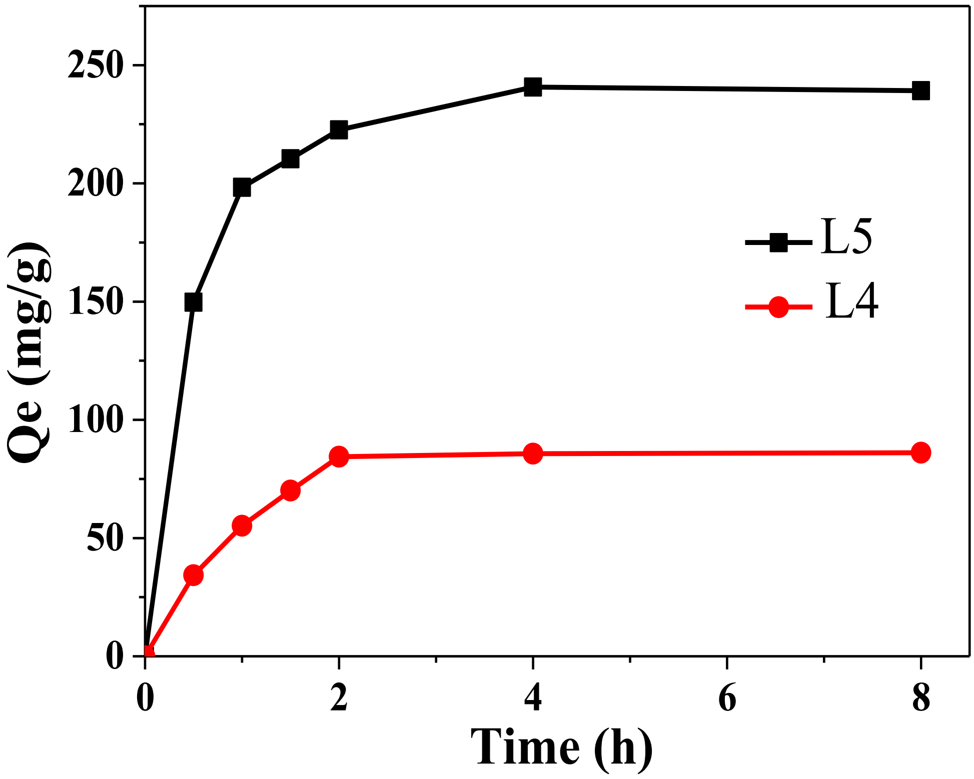


Fig. 3-8 Adsorption of Pb(II) onto L4 and L5

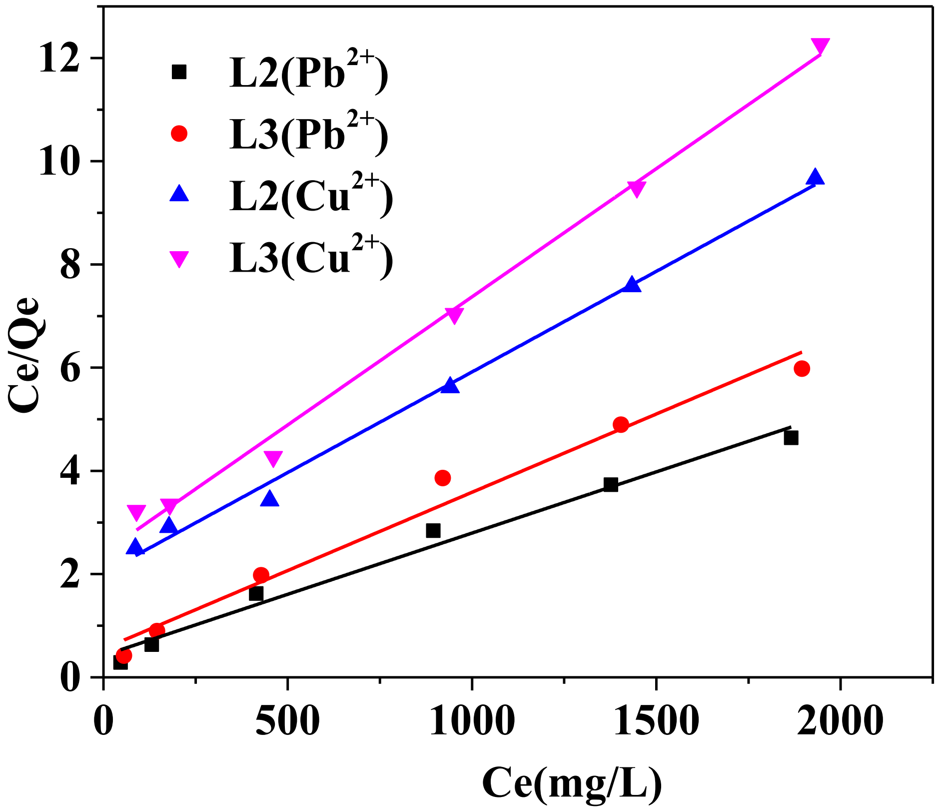


Fig. 3-9 The correlation of experimental data to langmiur isotherms models

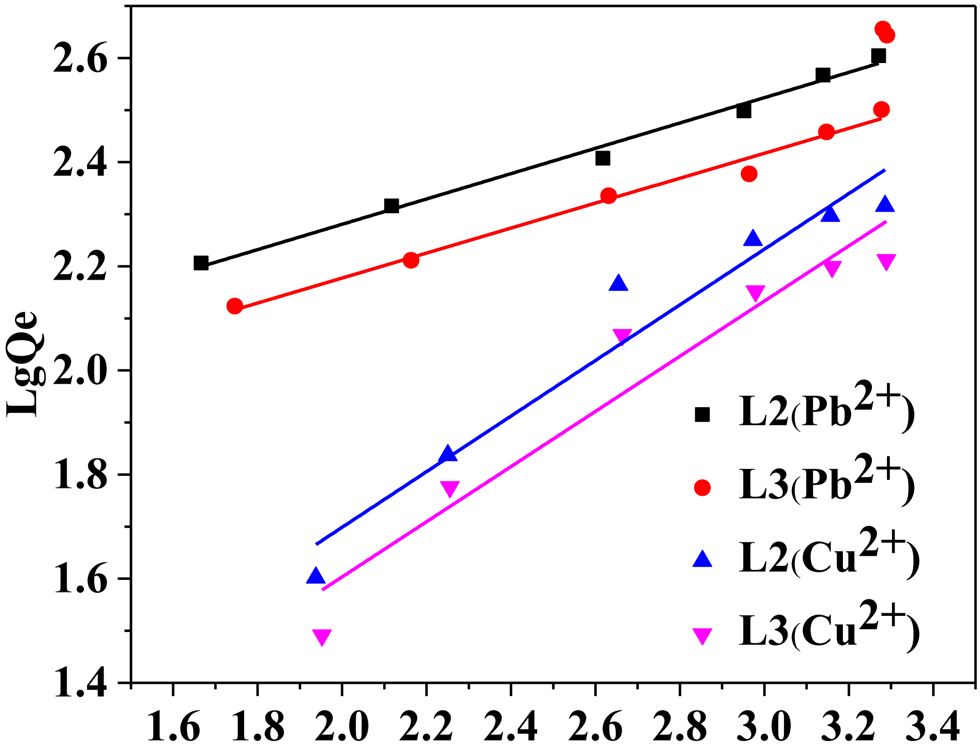


Fig. 3-10 The correlation of experimental data to Freundlich isotherms models

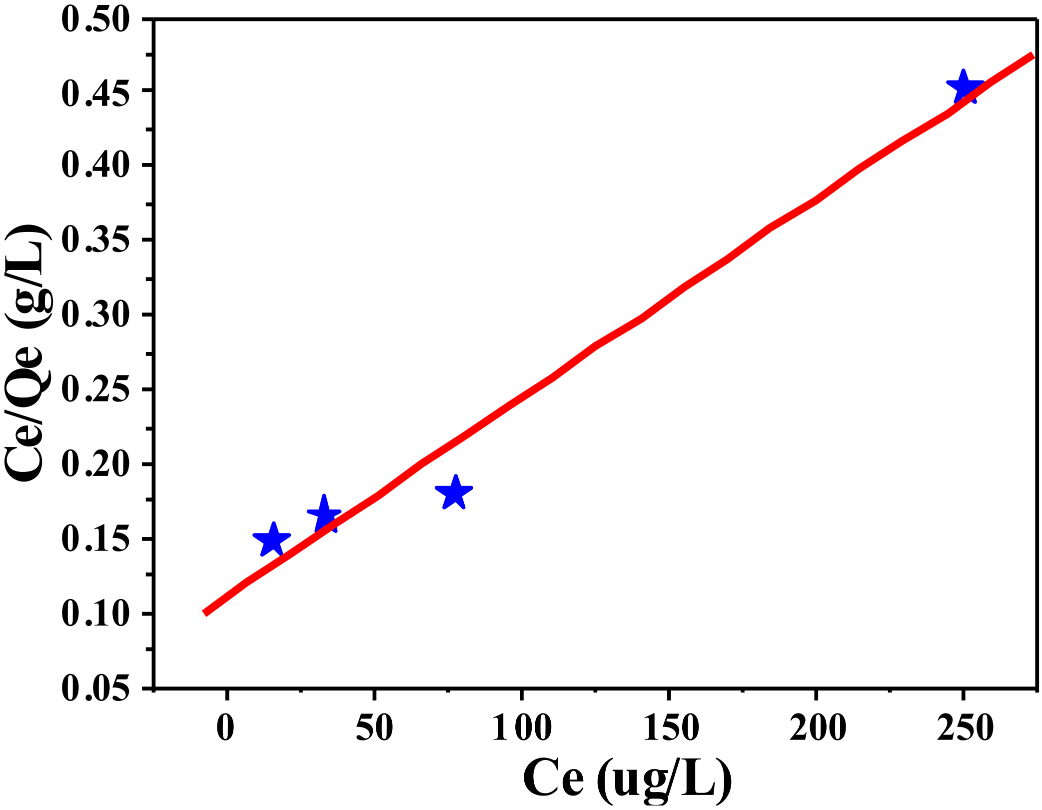


Fig. 3-11 Langmuir isotherm fitting for Cd(II) adsorption onto L5

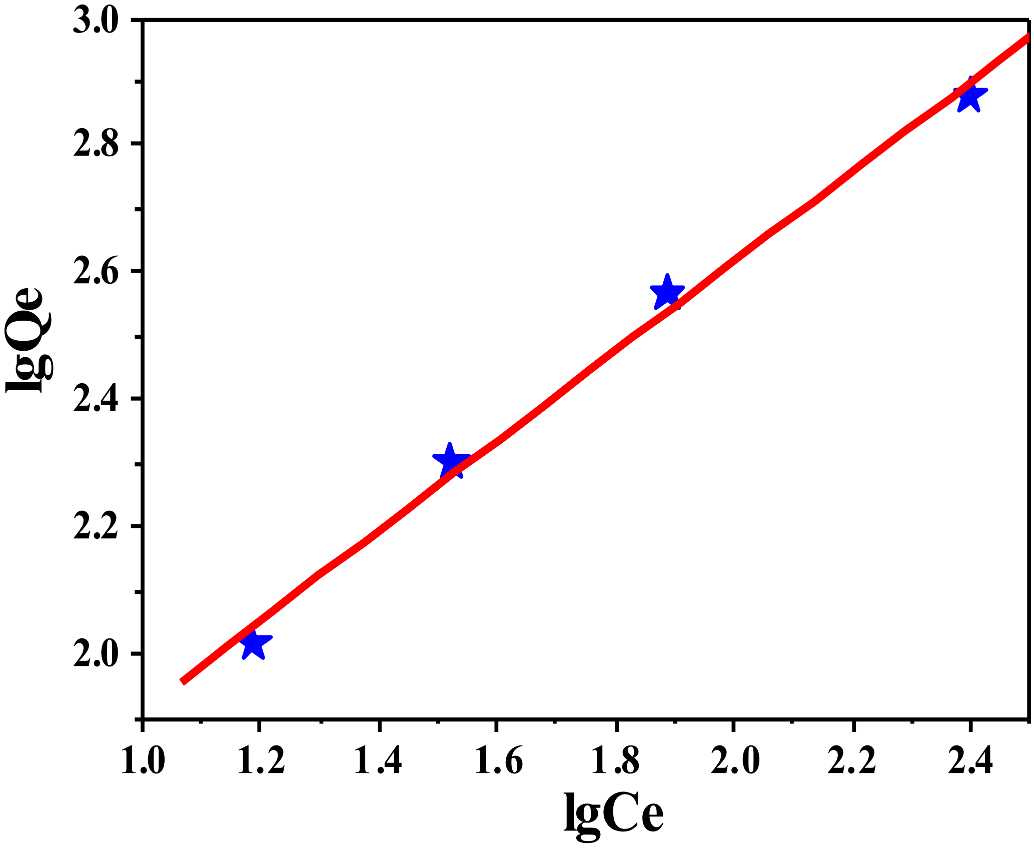


Fig. 3-12 Frendlich isotherm for Cd(II) adsorption onto L5

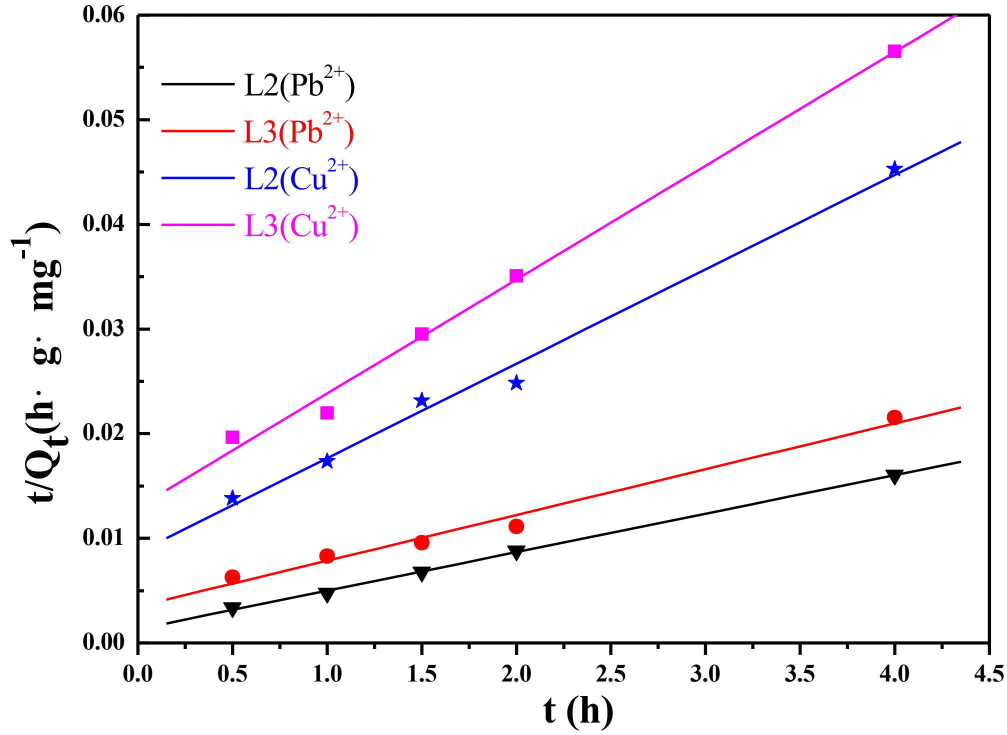


Fig. 3-13 The correlation of experimental data to pseudo second-order models

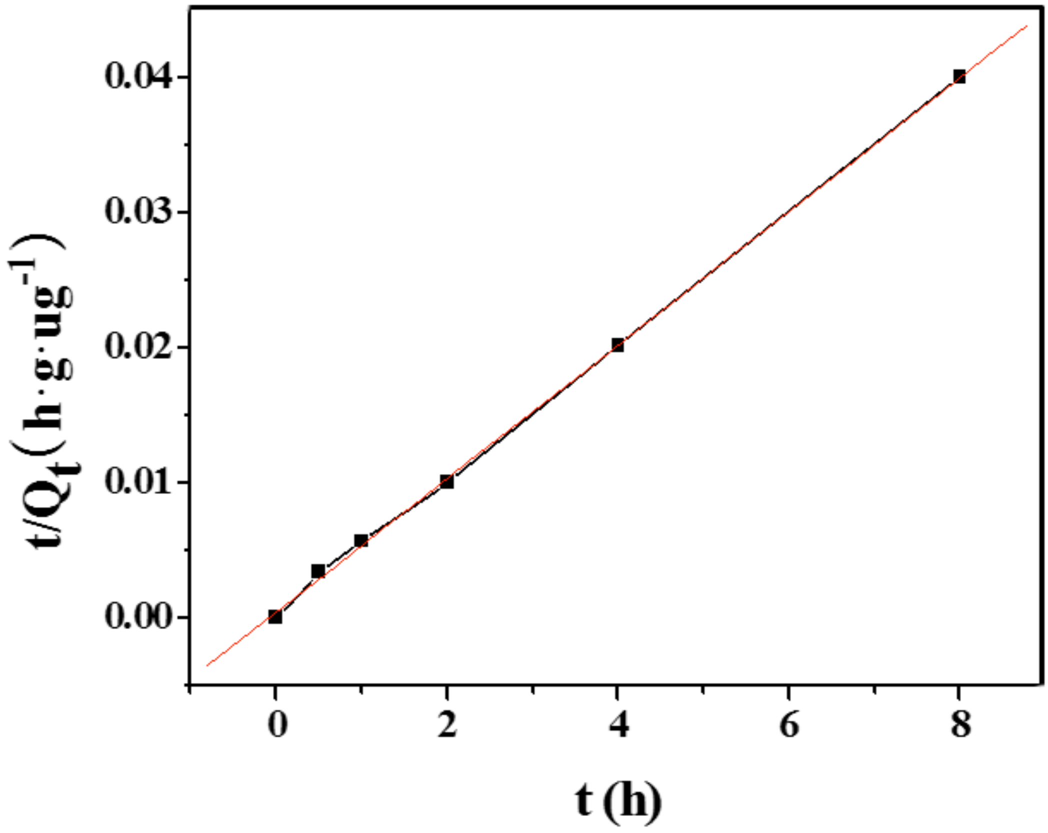


Fig. 3-14 The pseudo-second-order kinetic model for Cd(II) adsorption onto L5

Table 3-1 Properties of DHT-4A (Taken from the Examination Report by Kyowa Chem. Ind. Co. Ltd)

Examination item	
Appearance	White powder
Molar ratio (MgO/Al_2O_3)	4.24
Loss on drying (105℃, 1h) [％]	0.2
Specific surface area (BET) [$m^2 \cdot g^{-1}$]	9
Average particle diameter [μm]	0.46

Table 3-2 Operating conditions of the ICP-AES

Parameters	Conditions
Rf frequency	27.12 MHz
Incident power	1.3 kW
Outer gas	17 dm^3Ar min^{-1}
Intermediate gas	0.55 dm^3Ar min^{-1}
Carrier gas	0.58 dm^3Ar min^{-1}
Observation height/mm	10.3 mm above work coil
	3 s
	213.86 (Zn)
Integration time	226.50 (Cd)
Detection wavelength/nm	237.312 (Al)
	379.48(La)
	381.97 (Eu)

Table 3-3 Coefficient of Langmuir and Freundlich isotherms for Cu(II) and Pb(II) adsorption onto L2 or L3

Sample/T (298 K)	Langmuir			Freundilich		
	R^2	K_L ($L^{-1} \cdot mg^{-1}$)	q_{max} (mg/g)	R^2	K_F ($mg^{1-1/n} \cdot g^{-1} \cdot L^{-1}$)	n
L2(Pb^{2+})	0.979	5.60×10^{-3}	422	0.988	346	4.11
L3(Pb^{2+})	0.976	5.40×10^{-3}	330	0.983	199	4.17
L2(Cu^{2+})	0.994	1.90×10^{-3}	256	0.930	9.90×10^{-3}	1.87
L3(Cu^{2+})	0.993	2.10×10^{-3}	201	0.914	2.20×10^{-3}	1.89

Table 3-4 Coefficient of Langmuir and Freundlich isotherms for Cd(II) adsorption onto L5

Sample/T (298 K)	Langmuir				Freundilich		
	R^2	K_L ($L^{-1} \cdot \mu g^{-1}$)	q_{max} ($\mu g \cdot g^{-1}$)	R_L	R^2	K_F ($\mu g^{1-1/n} \cdot g^{-1} \cdot L^{-1}$)	n
L5(Cd^{2+})	0.982	0.016	730	0.465	0.992	16.1	1.41

Table 3-5 The Kinetic fit parameters for Cu(II) and Pb(II) adsorbed on L2 or L3

Sample/T (298 K)		Pseudo-first order			Pseudo-second order		
	$q_{e\,EXP}$ (mg·g^{-1})	R^2	q_e (mg·g^{-1})	K_1 (h^{-1})	R^2	q_e (mg·g^{-1})	K_2 (g·mg^{-1}·h^{-1})
L2(Pb^{2+})	228	0.990	217	5.48	0.997	276	2.75
L3(Pb^{2+})	169	0.940	169	5.27	0.993	229	1.25
L2(Cu^{2+})	71	0.983	78.5	4.35	0.991	111	0.104
L3(Cu^{2+})	59	0.983	54.8	4.09	0.995	91.9	0.910

Table 3-6 The Kinetic fit parameters for Cd(II) adsorbed on L5

Sample/T (298 K)		Pseudo-first order			Pseudo-second order		
	$q_{e\,EXP}$ (ug·g^{-1})	R^2	q_e (ug·g^{-1})	K_1 (h^{-1})	R^2	q_e (ug·g^{-1})	K_2 (g·μg^{-1}·h^{-1})
L5(Cd^{2+})	200	0.406	8.80	-0.434	0.998	202	0.057

Chapter 4 Adsorption of REEs onto LDHs with EDTA

4.1 Introduction

Experimental pollution has become more and more serious in the world with the rapid development of modern industry and agriculture. In particular, water pollution due to heavy metal has become one of the largest problems in recent years [38, 39]. On the other hand, the demand of rare earth elements (REEs) in modern technology has increased remarkably over the past years. However, the shortage of trace metals including REEs (and the necessity of stable supply for these metals) has been concerned in recent years. Therefore, the development of the removal (or recovery) method for the trace metals is important from the viewpoint of resources recovery as well as environmental protection [40, 104].

Layered double hydroxide (LDH) is a class of two-dimensional anionic clays which is composed of an ionic lamellar solid that contains positively charged brucite-type layers and exchangeable hydrate gallery anions. The ability of LDHs to intercalate anions makes them useful as catalysts, catalyst supports, anion exchangers, adsorbents, electrochemical reactions and bioactive nanocomposites. The general formula of LDH is $[\mathrm{M}^{\mathrm{II}}_{1-\mathrm{x}}\mathrm{M}^{\mathrm{III}}_{\mathrm{x}}(\mathrm{OH})_2]\,(\mathrm{A}^{\mathrm{n}-})_{\mathrm{x}/\mathrm{n}}\cdot\mathrm{mH_2O}$, where cationic M^{II} and $\mathrm{M}^{\mathrm{III}}$ are divalent and trivalent metals and occupy the octahedral holes in the brucite-like layer. A^{n-} is the interlayer anion of charge n that leads to the electro-neutrality of the LDH; and the coefficient x is the molar ratio of $\mathrm{M}^{\mathrm{II}}/(\mathrm{M}^{\mathrm{II}} + \mathrm{M}^{\mathrm{III}})$. They are structurally similar to the mineral brucite [$\mathrm{Mg(OH)_2}$] with a fraction of M^{II} ions replaced by $\mathrm{M}^{\mathrm{III}}$ ions. Due to uniform distribution of cations in the brucite layer, the LDH is an excellent precursor for preparing spinels or mixed oxides [50-52, 105]. The structure of LDHs suggested that these materials can be intercalated easily with with other anions. Moveover LDHs modified with chelating agents has been also studied as the potential adsorbents of heavy metals from aqueous solution [2, 11, 12].

Considering the above-mentioned, uptake experiments for the adsorption of REEs (La, Eu) from aqueous solutions by LDHs modified with EDTA both in single and multiple solution were carried out in this work. Firstly, the effects of pH, contact time and dosage of adsorbents on the removal of La(III) and Eu(III) from the aqueous solution were investigated. After obtaining the optimum conditions regarding the adsorption of metallic ions, the adsorption capacity of La(III) and Eu(III) onto L5 was discussed. In order to apply the adsorbent on various field, various equilibrium, kinetic, and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorption process [75, 80, 81].

4.2 Experimental Section

4.2.1 Materials

REEs nitrate salt including $Eu(NO_3)_3·6H_2O$ (99%, 446.07), $La(NO_3)_3·6H_2O$ (97%, 433.01) were purchased from Kishida Chemical Co. Inc., and prepared as single La(III) or Eu(III) ion stock solution. In addition to the REEs standard solutions were also prepared by diluting the standard solutions (XSTC-1 for REEs; $10mg·dm^{-3}$ 5% HNO_3 solution) purchased from SPEX Certi. Prep., Inc. (USA). For all experiments, each stock solution was suitably diluted with deionized water for use. All reagents used were of analytical grade, and water (> 18.2 MΩ) which was treated by an ultrapure water system (Advantec aquarius: RFU 424TA) was employed throughout the work.

4.2.2 Apparatus

The concentration of REEs in the filtrate was determined with an inductively coupled plasma-atomic emission spectrometry (ICP-AES). The operating condition of ICP-AES is shown in **Table 3-2**. The adsorbent was characterized both before and after adsorption using Fourier transform infrared (FT-IR) spectroscopy (FTIR-4200, Jasco, Japan) in pressed KBr pellets. The measurement of pH in solution was carried out using a pH meter (HORIBA, F-21, Japan).

4.2.3 Adsorption experiments

For obtaining the optimum conditions regarding the adsorption of La(III) and Eu(III), the batch experiments were studied by varying pH, contact time, adsorbent dose, and initial concentration on the adsorption of REEs. The adsorption of metals or REEs is usually studied in single- component systems. However, several metals could co-exist in natural waters or in wastewaters [47]. To investigate the effect of competitive conditions on REEs adsorption, adsorption experiments were carried out in multi-component systems.

The adsorption experiments of La(III) and Eu(III) using L4 and L5 were carried out. 20mg of L4 or L5 were contacted with 30 mL of an aqueous solution containing La(III) or Eu(III) ion (nitrate salts) with known initial concentration. the adsorption capacity of L4 and L5 by using multiple La(III) (REEs standard solutions) were also discussed. Sorption experiments were conducted in the pH range of 4–6 (optimum pH), contact time from 10 min to 8 h, temperature from 20 to 40°C, and adsorbent dosage 5–40 mg. The pH of each solution was adjusted using 0.1 $mol \cdot L^{-1}$ NH_4OH and 0.1 $mol \cdot L^{-1}$ HNO_3.

4.2.4 Data Analysis

Adsorption isotherms of adsorption data were studied at varying initial concentration of metallic ions under optimized conditions of contact time and the dosage of adsorbents in this work. Based on other previous study, two common adsorption models, Langmuir (eq. (4)) and Freundlich isotherm (eq. (7))models were applied to evaluate the adsorption data obtained for La(III) and Eu(III).

Furthermore, in order to describe the adsorbate-adsorbent interaction, the kinetic isotherms were analyzed by fitting experiments data into pseudo-first-order (eq. (9)), pseudo-second-order (eq. (10)), intra particle diffusion (eq. (11)), and Elovich equation (eq. (12)) to find out the suitable model that may be used for design consideration.

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change(ΔG^{O}), standard enthalpy (ΔH^{O}) and standard entropy (ΔS^{O}) were also discussed in this work by using equation 13-15.

4.2.5 Regeneration studies

For the potential application of LDHs intercalated chelating agents in the future, the regeneration studies are necessary to investigate. For the regeneration study, 20mg of L5 was first contacted with 30 mL of aqueous solution which containing 100 $\mu g \cdot L^{-1}$ La(III) and Eu(III) ions. After adsorption equilibrium, the exhausted adsorbent was separated and regenerated by 30mL HCl or HNO_3 solution with different concentrations. Then the suspension was filtered and finally Eu(III) and La(III) content in the filtrate was determined. Subsequently, the adsorbent was neutralized by deionized water and reconditioned for adsorption in succeeding cycles. The cycles adsorption experiments were carried out by using regeneration adsorbent under the optimum condition.

4.3 Results and Discussion

4.3.1 Adsorption of La(III) and Eu(III) using L5

Fig. 4-1 shows the comparison experiment of single La(III) (nitrate salts) and multiple La(III) (REEs standard solutions) by using L4 or L5. The REEs standard solution including both the sixteen kinds of REEs, the content of REEs standard solution which we used in this work as shown in **Table 4-1**. From **Fig. 4-1**, the rapid increase of the adsorption capacity in the initial stage might be associated to the abundance of the surface reactive sites that occupied by the metallic ions, with further increasing time, the accessibility of the metallic ions to unoccupied active sites on the adsorbent surface decrease, and these sites ultimately become saturated when the process reaches its equilibrium state. The adsorption capacity of single La(III) ions are higher than that diluted from REEs standard solution. From the experiment for comparison, the adsorption capacity is L4 less than L5 which is same as the case of the adsorption of heavy metallic ions.

Fig. 4-2 shows the comparison experiment of single Eu(III) (nitrate salts) and multiple Eu(III) (REEs standard solutions) by using L4 or L5. The adsorption capacity of single Eu(III) ions are higher than that of REEs standard solution in the same condition, and the adsorption capacity is also L4 < L5 both in the nitrate salt solution and in the REEs multiple solution. It indicates that the intercalation of EDTA make the adsorption capacity of LDHs higher. By comparing the adsorption of La(III), the adsorption capacity of Eu(III) is higher than that of La(III) under the same condition no matter in single or multiple solution. It may be attributed to their stability constant. The stability constant of La-EDTA and Eu(III) was 15.5 and 17.4 respectively. Especially in the adsorption by using L4, compared with lower adsorption capacity of La(III), adsorption of Eu(III) has a higher adsorption capacity.

In this study, all the obtained q_{mul}/q_{sin} values were less than 1, suggesting that all the REEs were inhibited by the presence of other lanthanides. The values of La(III) (0.65) were much less than that of Eu(III) (0.80), indicating that La(III) was more effected by a ternary mixture. The adsorption capacity could be explained by Pearson law: La(III) and Eu(III) are classified as hard metals and the most significant degree of ionic competition happens among the metals from the same class Thus, our results have shown that lanthanide elements such as La(III) and Eu(III) probably compete for same binding sites on the adsorbent [107-109].

4.3.2 Adsorption isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. To quantify the sorption capacity of the adsorbents studied for the REEs removal, the most commonly used isotherms, namely Langmuir, Freundlich isotherms have been adopted. The Langmuir adsorption isotherm and Freundlich adsorption isotherm were applied to the data obtained in this work. A plot of C_e/q_e versus C_e and $\lg q_e$ versus $\lg C_e$ based on the Langmuir model and Freundlich model are shown in **Fig 4-3**, **Fig 4-4**, **Fig 4-5** **Fig 4-6**, respectively. **Fig 4-3** and **Fig 4-4** are the adsorption isotherm of La(III) using L5. **Fig 4-5** and **Fig 4-6** are the adsorption isotherm of Eu(III) under the same condition. The linear correlation coefficients (R^2) and other parameter are shown in **Table 4-2** and **Table 4-3**, respectively. The adsorption experimental data of La(III) and Eu(III) onto L5 were well fitted by the Freundlich isothermal adsorption equation, and the correlation coefficients were all bigger than 0.9. As shown in **Table 4-2** and **Table 4-3**, the parameters K_F and $1/n$ are constants of the Freundlich isotherm, which denote the adsorption capacity and intensity. The Langmuir and Freundlich isotherms describe the homogeneous (single-layer) and heterogeneous (multi-layer) adsorption of the adsorbate onto the adsorbent, respectively. However, the $1/n$ ($0<1/n<1$) observed from Table 4-2 also can suggest whether the adsorption is single-layer [79, 81, 82].

4.3.3 Kinetic model

The first-order kinetic and Pseudo second order, intra particle diffusion, and Elovich models were applied to test the experimental data and explain the kinetics of the layered double hydroxide adsorption process [74-76]. **Table 4-4** shown the linear constant (R^2) and other parameter of the four kinetic model for La(III) and Eu(III) adsorption onto L5 which were calculated from in **Fig. 4-7** and **Fig. 4-8**, respectively. The value of R^2 indicated that the adsorption of La(III) and Eu(III) onto L5 was better fit with the pseudo-second-order kinetic model than the others. The confirmation of this model implies that the rate-limiting step in this adsorption system may be controlled by chemical process. Also, it suggests that the concentrations of both adsorbent and adsorbate are associated with the rate determining step of the adsorption process.

In adsorption process, the study of intra-particle kinetic model suggested for understand whether the intra- particle diffusion model is the main step in controlling the adsorption process. It also employed for determination of the diffusion mechanisms and discern the plausible rate controlling step which has significant influence on adsorption kinetics. As shown in **Fig. 4-7** and **Fig. 4-8**, the plots of q_t vs.

$t^{0.5}$ for La(III) and Eu(III) are shown in two stages. The first straight portion depicts macrospore diffusion, and the second one represents microspore diffusion. Based on this model, the rate of adsorption would be in charge of intra-particle diffusion when the line pass through the origin (C_{ip}=0). According to **Table 4-5**, the values of the C_{ip} was > 0, indicating that the intra-particle diffusion is part of the adsorption but not the only rate-controlling step in this process. Hence, it can be stated clearly that other mechanisms including complexes or ion-exchange had significant effect in controlling the adsorptive removal of La(III) and Eu(III) on L5.

The Elovich equation interprets the predominantly chemical adsorption on highly heterogeneous adsorbents [74,76]. As described in **Fig. 4-7(c)**, the plots of q_t vs. ln (t) display relative good linear relationship before reaching the adsorption equilibrium. This result shows that the heterogeneous distribution of adsorption energy was dominant in adsorption process.

4.3.4 Adsorption Thermodynamics

The Thermodynamic parameters for the adsorption of La(III) and Eu(III) onto L5 are shown in **Table 4-6** and **Table 4-7**. From these data plot of $\ln K_d$ versus $1/T$ is shown in **Fig. 4-9** and **Fig. 4-10**. The slope and intercept of **Fig.4-9** and **Fig. 4-10** gives the values of ΔH^0 and ΔS^0. The values of ΔG^0 were obtained from the application of equation (13), and the value of $\ln K_d$ can be obtained by plotting $\ln(q_e/C_e)$ vs. q_e by extrapolating q_e to zero as shown in **Fig.4-11** and **Fig 4-12**. The negative value of ΔG^0 indicated that the adsorption process is highly favorable and spontaneous, and that it is more negative at higher temperature. It shows that the adsorption process increases with the rise in temperature [78, 79, 81]. The value of ΔH^0 (47.19KJ/mol) indicates that the adsorption force perhaps is hydrogen-bonding force. The positive value of entropy change (ΔS^0) implies some structural changes in adsorbate and adsorbent during the adsorption process, which reflects the affinity of the adsorbent towards the adsorbate species. In addition, the positive value of ΔS^0 (20.1J/molK) suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed ions, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system.

4.3.5 Regeneration studies

In order to investigate the potential application of this adsorbent, it is desirable to recover the adsorbed material along with the adsorbent in wastewater treatment processes. Effective reuse of adsorbent material directly affects the cost factor and hence its utility in continuous batch adsorption processes [79]. In this work, the regeneration of the used EDTA-LDHs adsorbent was investigated. The desorption efficiency of exhausted adsorbent is shown in **Fig.4-13**, and the removal efficiency on regenerated L5 adsorbent are shown in **Fig.4-14**. From **Fig.4-13**, the desorption by HNO_3 shows a well desorption efficiency for both of La(III) and Eu(III). The optimum concentration is 200mmol/L. The desorption efficiency of La(III) were found to be 95.67%, however the efficiency of Eu(III) is slightly lower, which may be based on the stability consistent of Eu-EDTA is higher than that of La ions. **Fig.4-14** shows the better reuse performance of L5 after 3 cycles. The hydrogen ions may destruct the structure during the desorption process, which results in the decrease of removal efficiency after 4th or 5th cycle.

4.3.6 Adsorption mechanism

$La^{3+} + Hedta^{3-} \leftrightarrow La(edta)^{-} + H^{+}$ eq. (16)

$Eu^{3+} + Hedta^{3-} \leftrightarrow Eu(edta)^{-} + H^{+}$ eq. (17)

Eq. (16) and (17) show the chelation between the Ln ions and EDTA. Based on the desorption experiments by alkaline solution, they make the adsorbent become carbonate LDHs [79]. Desorbing the adsorbent by acid solution indicates that chelation and complexation play a significant role in the adsorption. To further validate the adsorption mechanism, the FT-IR spectra of L5 before and after the adsorption of Eu(III) were compared in **Fig. 4-15**. Moreover, in order to confirm the effect of EDTA firstly reacting with metallic ions before intercalating with LDHs, the FT-IR spectra of the solid by filtered after the above process was also shown in **Fig. 4-15 (d)**. The FT-IR spectra of the absorption bands around at 1,600 and 1,400 cm^{-1} are characteristics of the symmetrical and asymmetrical vibration of COO- groups. The peak around wavenumber 2950 cm^{-1} (-CH) and 1136 cm^{-1} (-CN) are also the typical peak of EDTA [79,111-112]. A relatively sharp band at 776 cm^{-1} is assigned to C-H out-of-plane bending, and a broad band at about 620 cm^{-1} is due either to a vibrational mode of hydroxyl groups and water or to a metal-oxygen vibration ν(M-O) (M) Zn, Al).Two peaks at about 560 and 426 cm^{-1} are attributed to ν(M-O) and δ(M-O-M), respectively. No significant changes were observed in this region upon incorporation of the lanthanide ions. However, after Eu(III) adsorption, the band at 1645 cm^{-1} shifted to 1600 cm^{-1} cm was observed both in **Fig. 4-15** (b), (c) and (d). it suggests that metallic ions have chelated with EDTA and that the adsorption process did not destroy the layer structure [89,113-115].

The peak around 1365 cm^{-1} in **Fig.4-15** (d) indicated that the intercalated by Eu-EDTA make other anions compete with EDTA. The chelation reaction is based on the covalent bond of the metallic ion and EDTA, and the connection of the interlayer anions with layer by the H-bond, both of them are stable [116, 117]. from the EPMA elemental mapping of LDHs after the simultaneous adsorption of metallic ions (which was carried out in chapter 2). The adsorption also distributes on the surface of the adsorbent.

4.4 Conclusion

The adsorption of REEs on LDHs modified with EDTA was investigated, and some influence factors such as contact time, initial ions concentration, adsorbent dosage, solution pH, and adsorption temperature were also discussed. It was shown that both La(III) and Eu(III) could be rapidly adsorbed. The sorption process was completed within 60 min, followed by slow attainment of equilibrium in around 2 h. The removal efficiency increased, but the amount of La(III) and Eu(III) adsorbed on unit weight adsorbent decreased. The adsorption capacity of single Eu(III) ions are higher than that in REEs standard solution under the same condition, and the adsorption capacity of L5 larger than that of L4 both in the nitrate salt solution and in the REEs multiple solution. The comparison result indicating that La(III) was more effected in a ternary mixture. The adsorption isotherms data were fitted by Freundlich isotherms. The adsorption kinetics data were well described by a pseudo-second order kinetic model, showing that the adsorption process was controlled by chemical process. The results of adsorption thermodynamic suggested that the reaction of REEs adsorbed by LDHs was spontaneous and endothermic. Moreover, desorption of Eu(III) and La (III) from the adsorbent has been found to depend upon the stability constant of M-EDTA. And LDHs still present the high adsorption capacity towards heavy metals through 3 cycles of adsorption/desorption behavior. LDHs could be an efficient adsorbent for heavy metals and REEs, although the structure may be reconstructed by the hydrogen ion after 4 or 5 cycles.

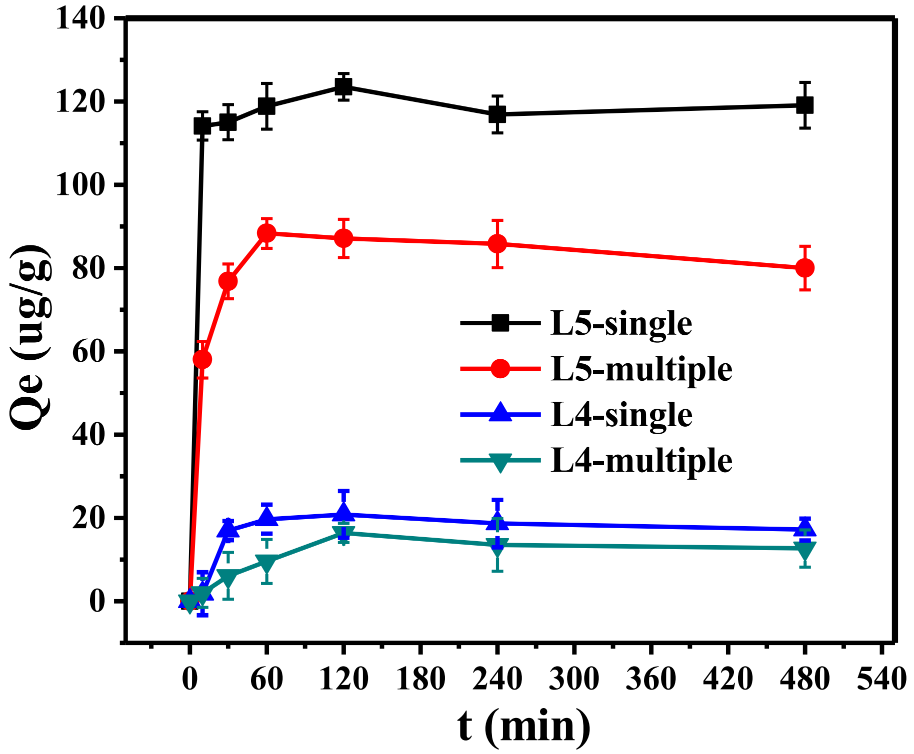


Fig. 4-1 Adsorption capacity of La(III) both in single and multiple solution by using L4 or L5

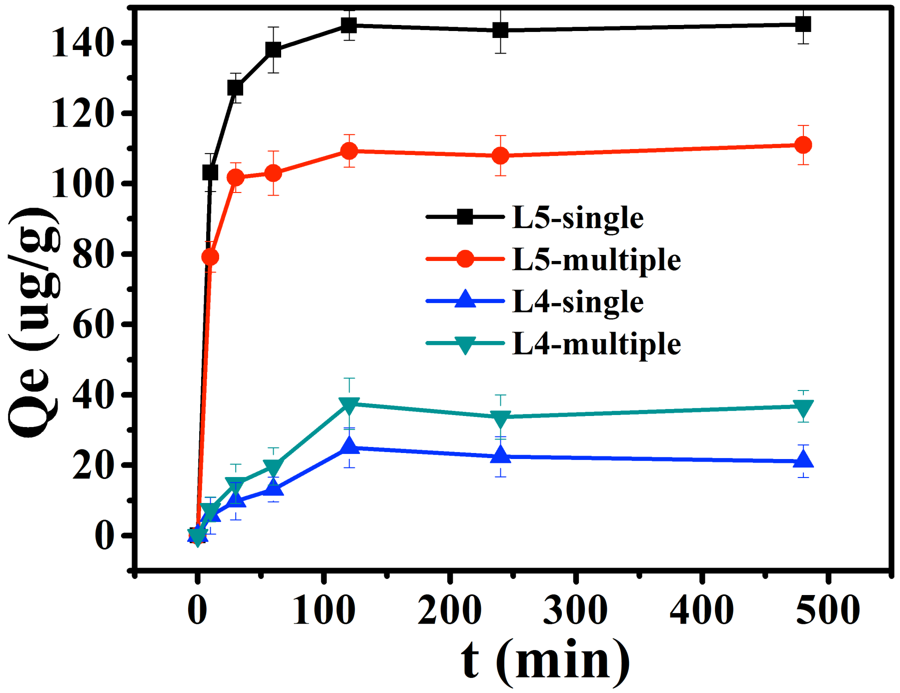


Fig. 4-2 Adsorption capacity of Eu(III) both in single and multiple solution by using L4 or L5

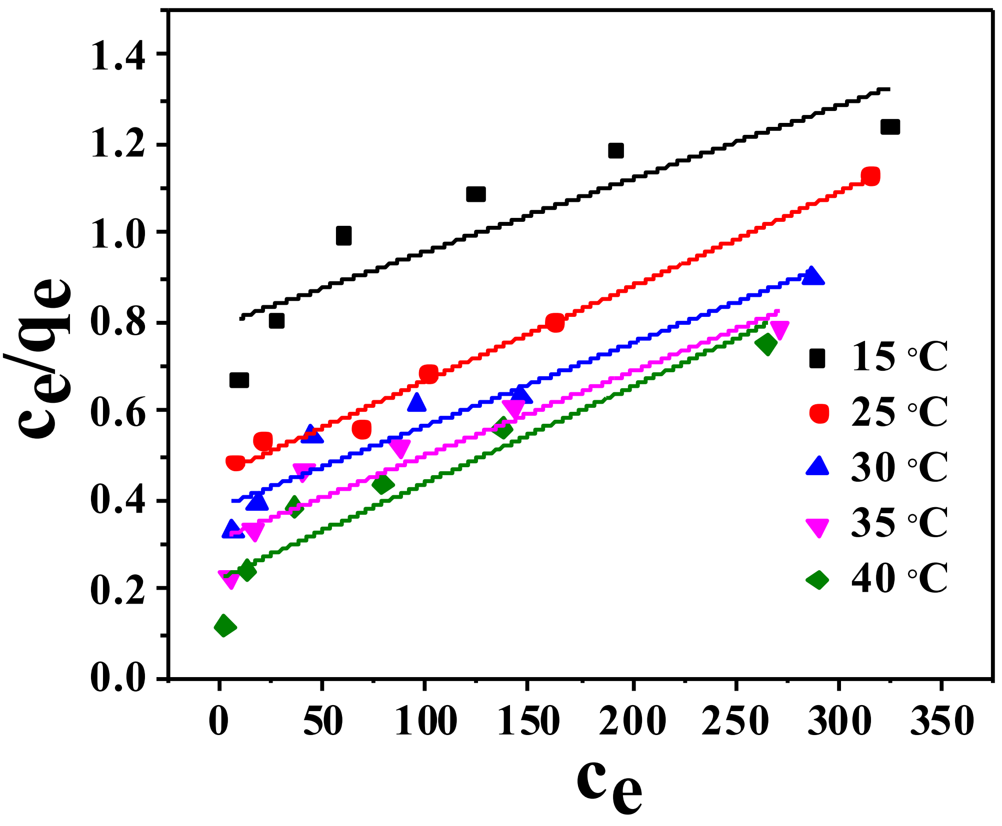


Fig. 4-3 Langmiur isotherm for La(III) adsorption onto L5

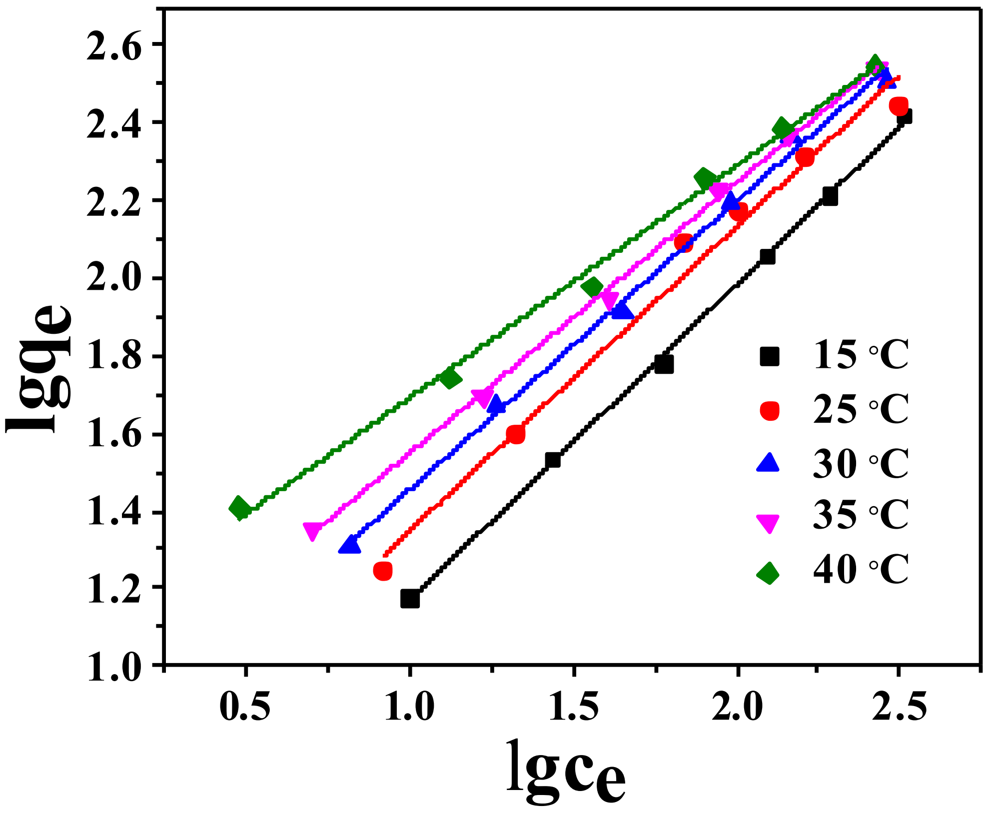


Fig.4-4 Frendlich isotherm for La(III) adsorption onto L5

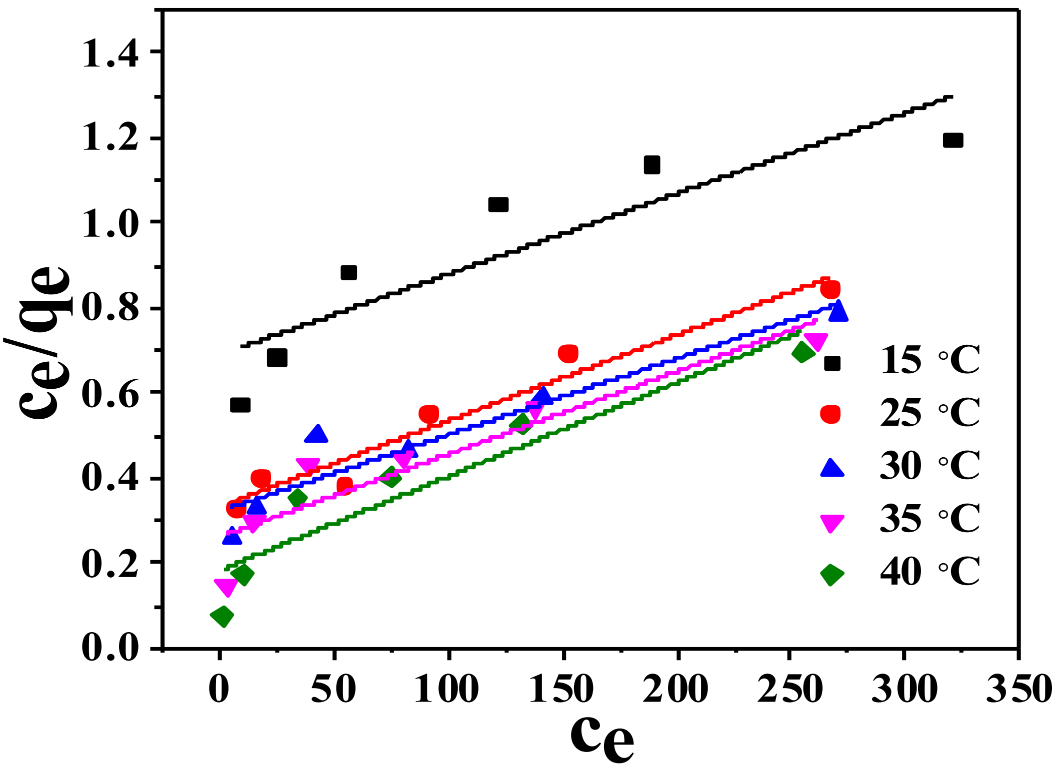


Fig.4-5 Langmiur isotherm fitting for Eu(II) adsorption onto L5

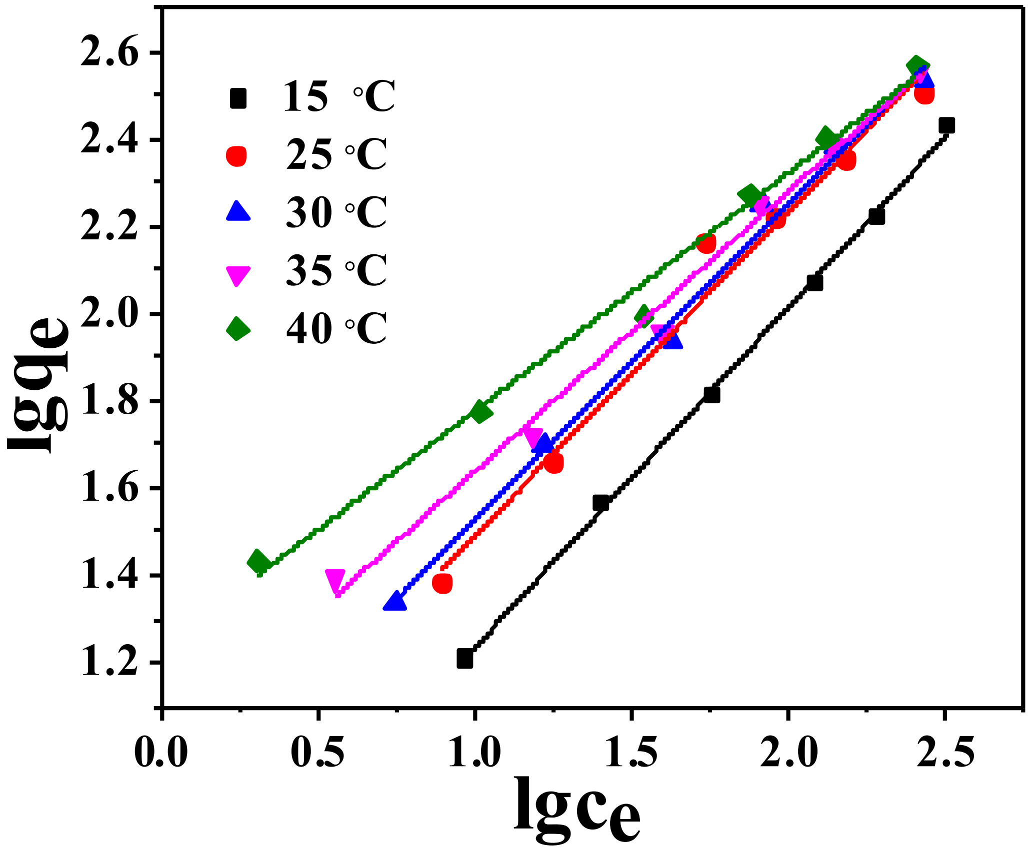


Fig.4-6 Frendlich isotherm fitting for Eu(III) adsorption onto L5

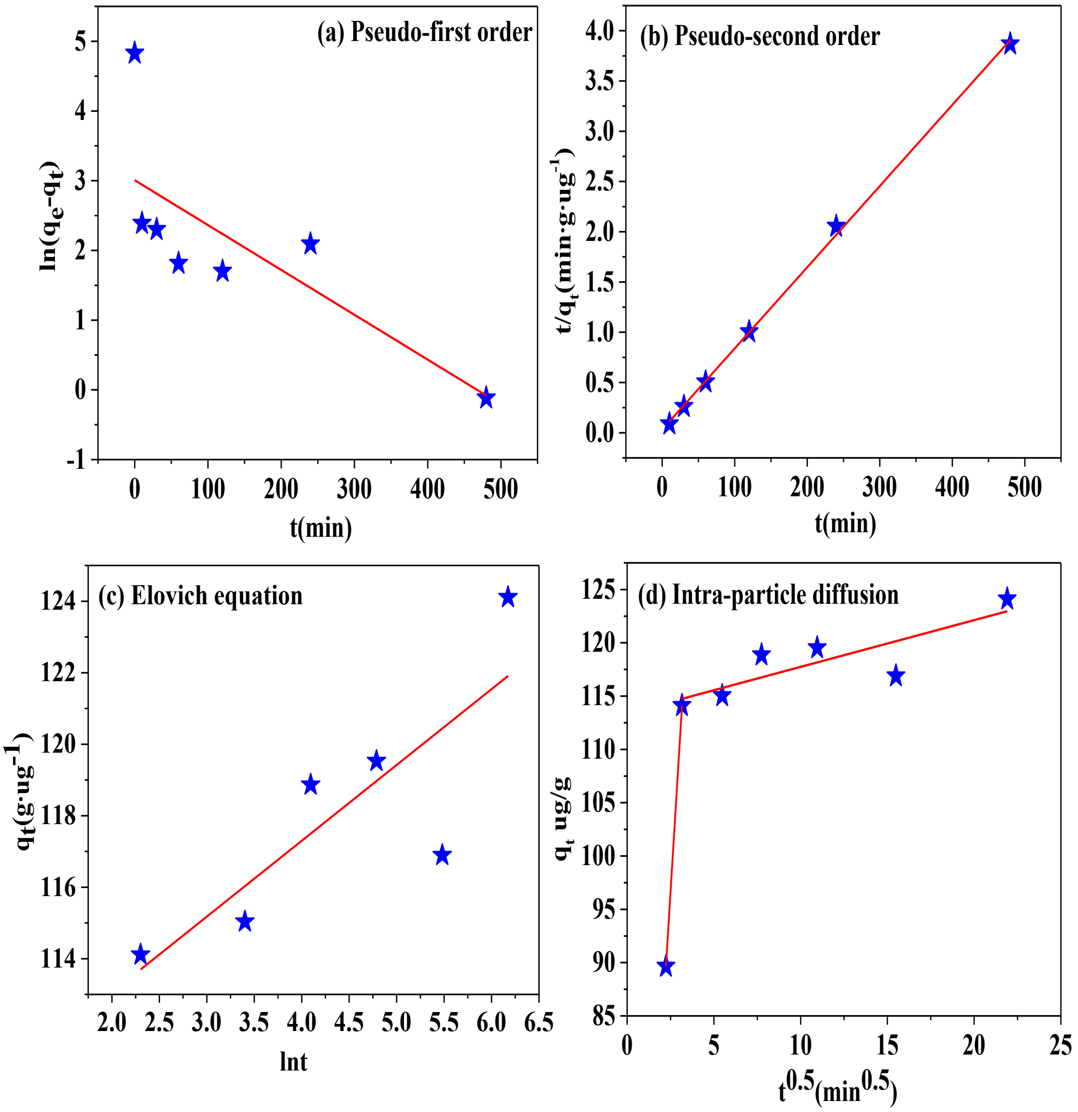


Fig. 4-7 The kinetic model for La(III) adsorption onto L5

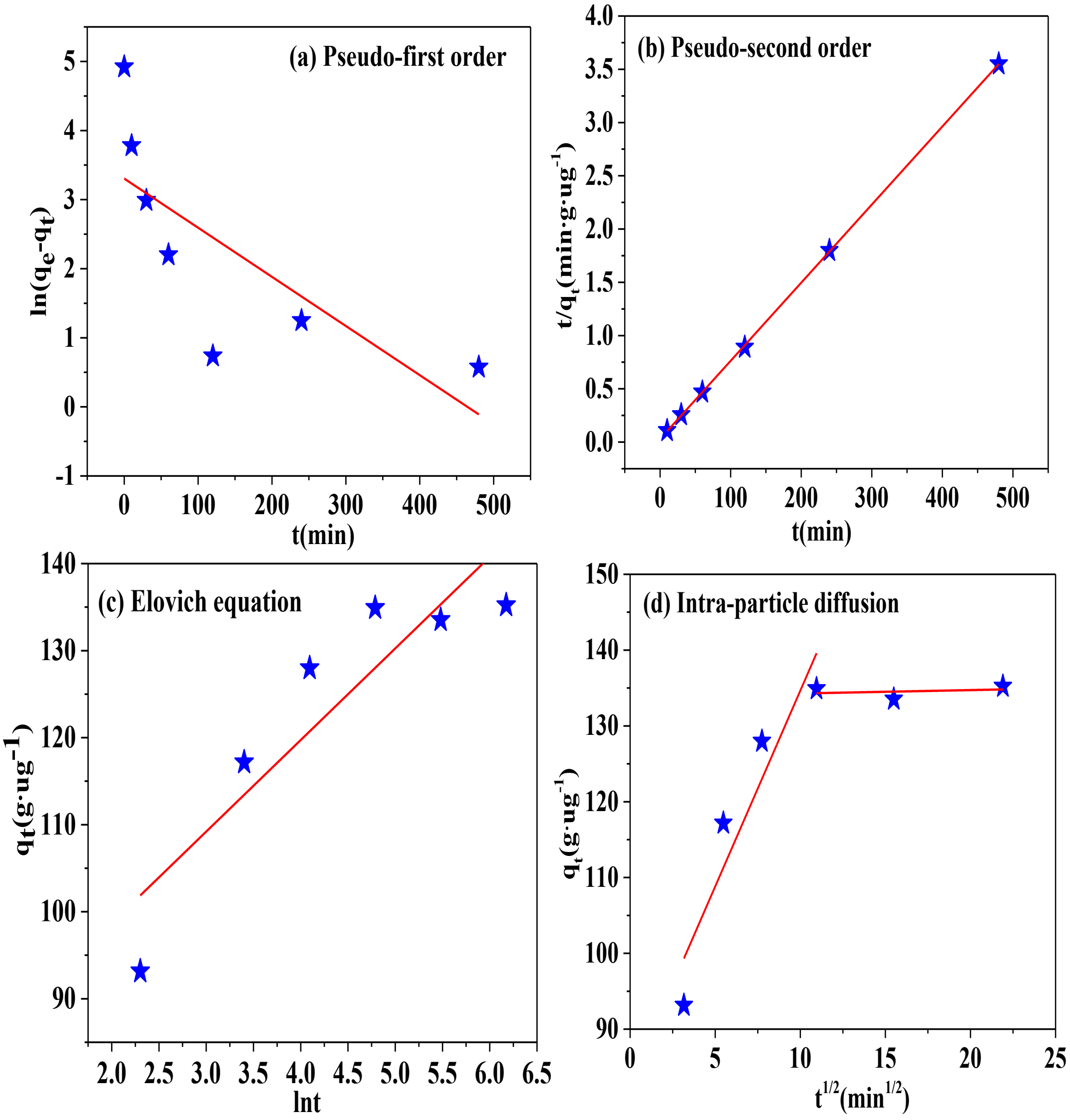


Fig. 4-8 The kinetic model for Eu(III) adsorption onto L5

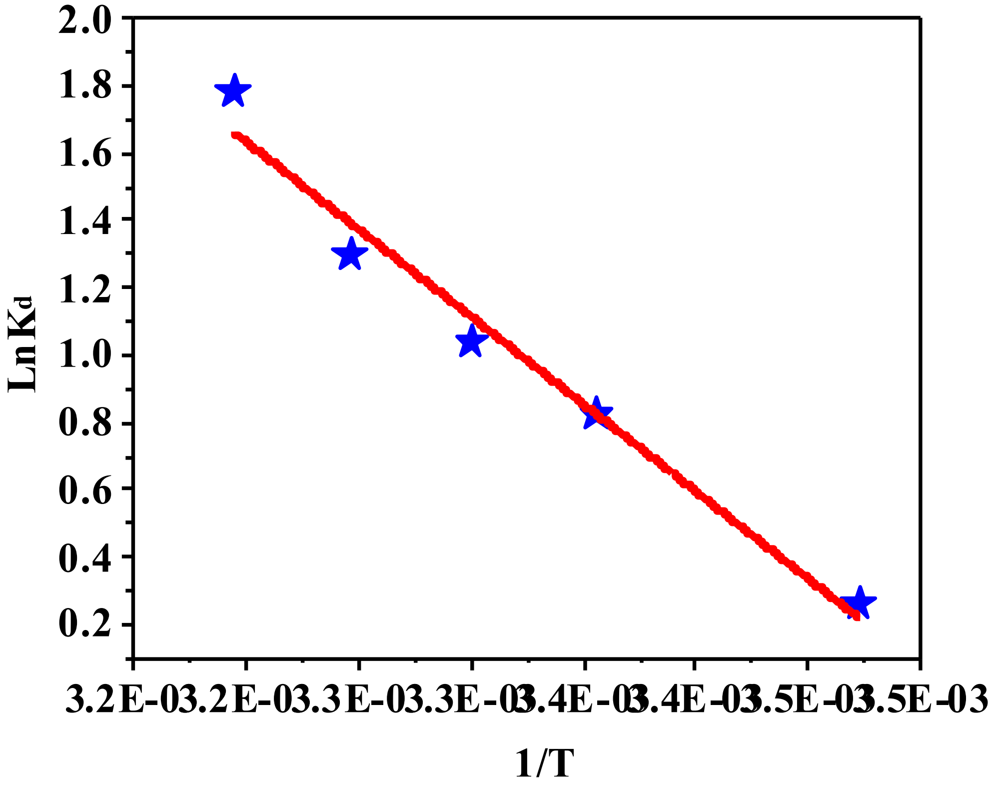


Fig.4-9 Plot of lnK_0 vs 1/T for the estimation of thermodynamic parameters obtained for the adsorption of La(III) on L5

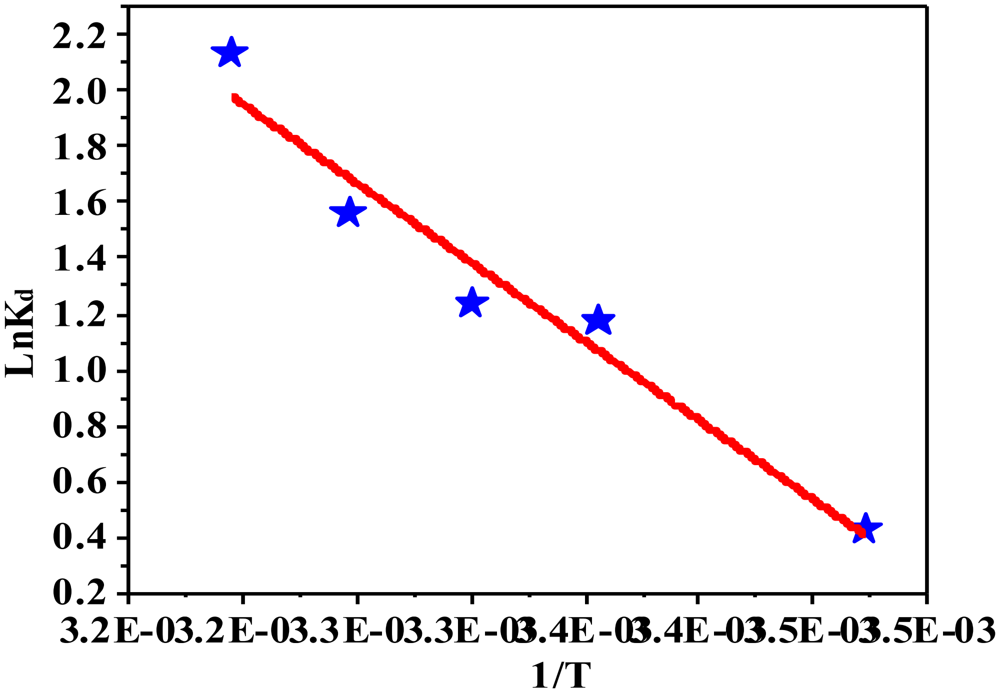


Fig.4-10 Plot of lnK_0 vs 1/T for the estimation of thermodynamic parameters obtained for the adsorption of Eu(III) on L5

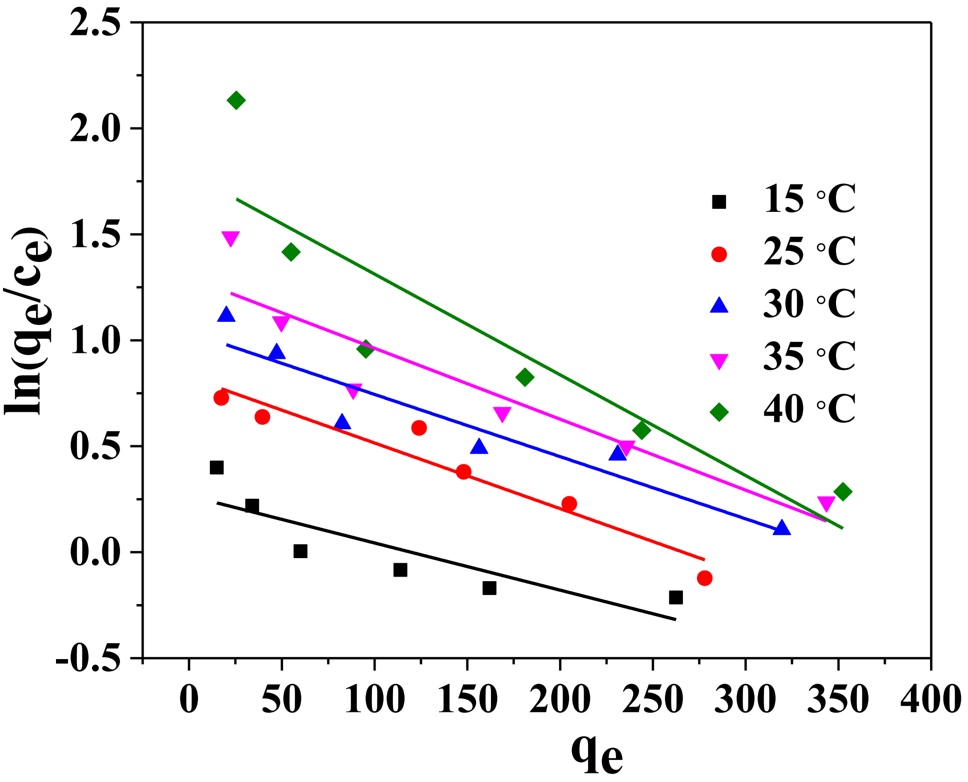


Fig. 4-11 A plot of q_e vs. ln (q_e/c_e) of La(III) on L5

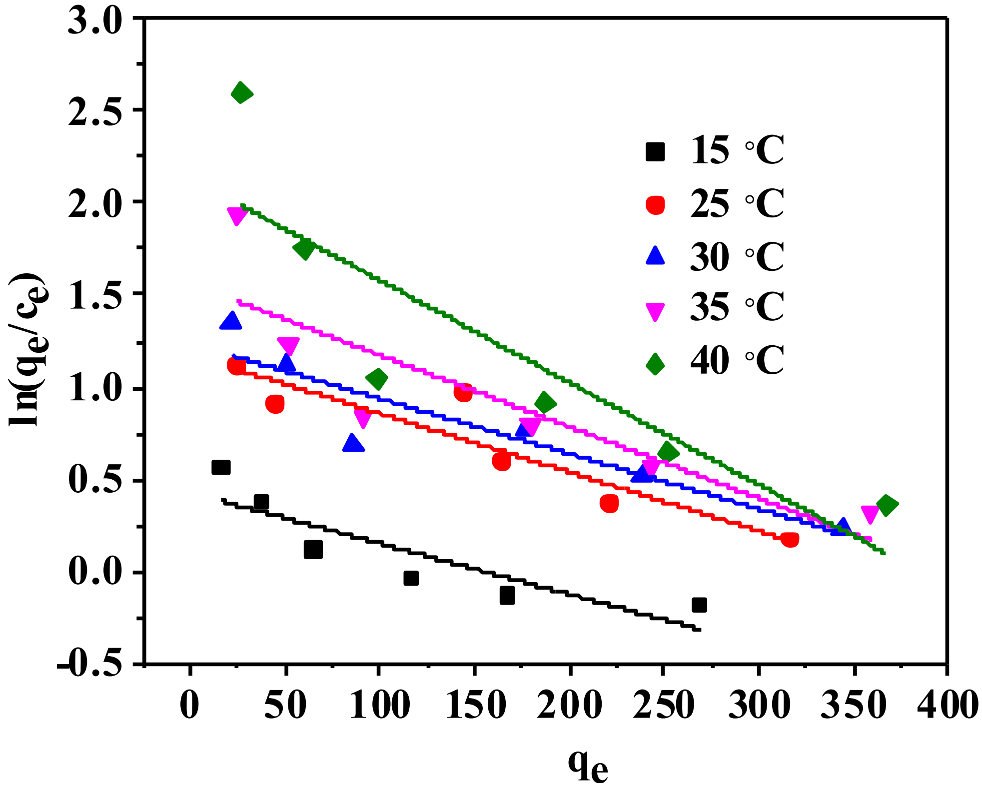


Fig. 4-12 A plot of q_e vs. ln (q_e/c_e) of Eu(III) on L5

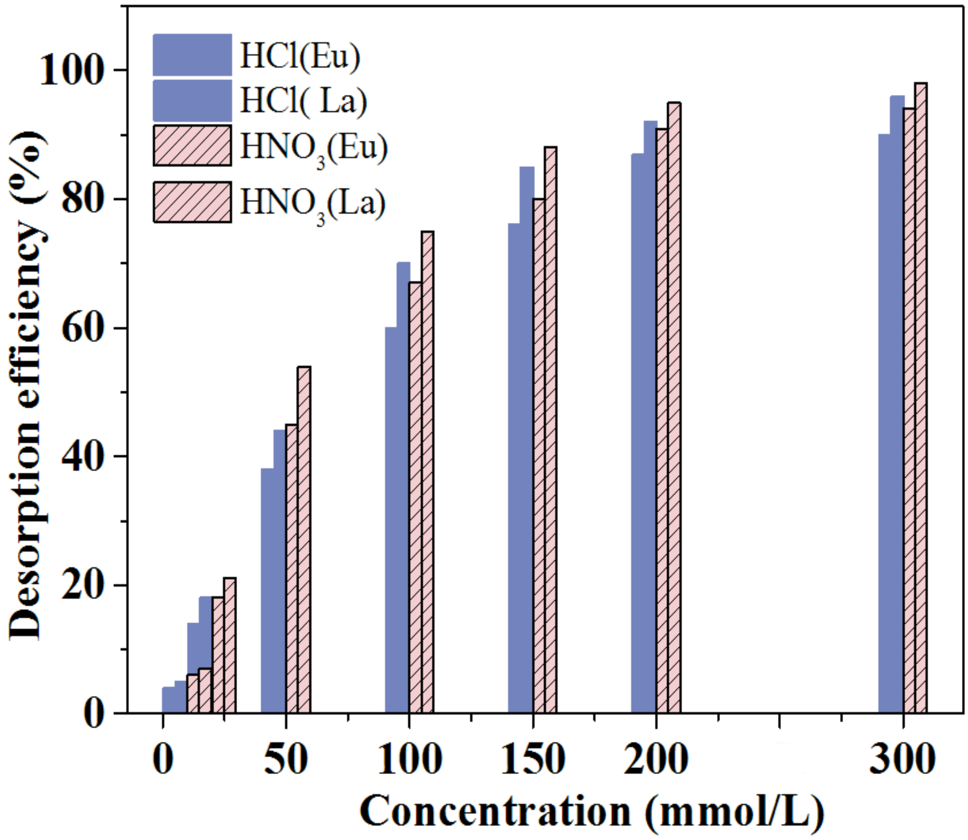


Fig. 4-13 Desorption efficiency of Eu(III) and La(III) ions using HCl or HNO_3.

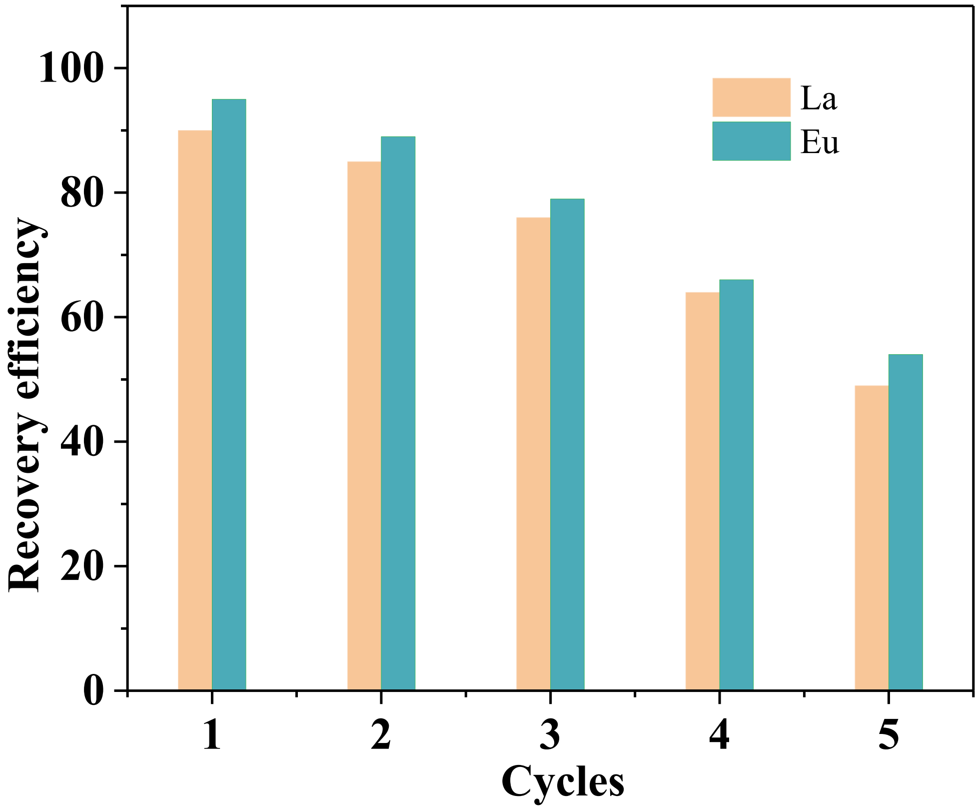


Fig. 4-14 Recovery efficiency of La(III) and Eu(III) ions using L5.

Table 4-1 The Content of Rees Standard solution

Content of Rees Standard solution (10ppm, 5% HNO_3)			
Ce	Dy	Er	Eu
Gd	Ho	La	Lu
Nd	Pr	Sm	Sc
Tb	Tm	Yb	Y

Table 4-2 Coefficient of Langmuir and Freundlich isotherms for La(III) adsorption onto L5

Sample	Langmuir			Freundilich		
T (K)	R^2	K_L(L·ug^{-1})	q_{max}(ug·g^{-1})	R^2	K_F	n
288	0.728	2.10×10^{-3}	610	0.999	2.24	1.22
298	0.986	4.60×10^{-3}	472	0.980	3.64	1.27
303	0.909	4.80×10^{-3}	541	0.995	5.09	1.34
308	0.885	6.00×10^{-3}	529	0.998	7.05	1.43
313	0.878	9.60×10^{-3}	463	0.994	12.3	1.67

Table 4-3 Coefficient of Langmuir and Freundlich isotherms for Eu(III) adsorption onto L5

Sample	Langmuir			Freundilich		
T (K)	R^2	K_L(L·ug^{-1})	q_{max}(ug·g^{-1})	R^2	K_F	n
288	0.755	2.70×10^{-3}	526	0.998	2.23	1.28
298	0.940	6.10×10^{-3}	495	0.975	5.62	1.35
303	0.883	5.60×10^{-3}	556	0.991	6.28	1.38
308	0.830	7.10×10^{-3}	513	0.989	9.93	1.56
313	0.852	12.1×10^{-3}	452	0.988	16.9	1.84

Table 4-4 parameters for four kinetic models of adsorption of La(III) or Eu(III) on L5

Sample/T (298 K)		Pseudo-first order			Pseudo-second order		
	$q_{\exp}$ (ug·g^{-1})	R^2	q_e (ug·g^{-1})	K_1 (min^{-1})	R^2	$q_{\max}$ (ug·g^{-1})	K_2 (g·ug^{-1}min^{-1})
La(III)	124	0.011	20.1	0.044	0.997	125	2.06×10^{-3}
Eu(III)	144	0.480	27.1	0.003	0.992	142	1.69×10^{-3}

Sample/T (298 K)		Elovich model			Intra-particle diffusion		
	$q_{\exp}$ (ug·g^{-1})	R^2	β (ug·g^{-1}min^{-1})	α (ug·g^{-1}min^{-1})	K_{p1}(ug·g^{-1}min$^{-1/2}$)	K_{p2}	C_{ip}(ug·g^{-1})
La(III)	124	0.604	1.39	1.96	26.4	113	30.6
Eu(III)	144	0.770	0.095	0.264	5.15	0.044	82.9

Table 4-5 Thermodynamic parameters for the adsorption of La(III) on L5

T(K)	ΔH(kJ/mol)	ΔS(J/mol K)	ΔG(kJ/mol)
288	43.3	0.152	-0.637
298	-	-	-2.04
303	-	-	-2.61
308	-	-	-3.32
313	-	-	-4.63

Table 4-6 Thermodynamic parameters for the adsorption of Eu(III) on L5

T(K)	ΔH(kJ/mol)	ΔS(J/mol K)	ΔG(kJ/mol)
288	47.2	20.1	-1.02
298	-	-	-2.91
303	-	-	-3.11
308	-	-	-3.99
313	-	-	-5.55

Chapter 5 Conclusions

In the work of the thesis, LDHs intercalated with chelating agents have been extensively examined and applied for adsorption of aqueous containing heavy metals and REEs. The following five kinds of compounds were synthesized (MgAl-NO_3 (L1), MgAl-EDTA (L2) and MgAl-EDDS (L3), ZnAl-NO_3 (L4), ZnAl-EDTA (L5)). These five kinds of synthesized samples are characterized by some instruments and the adsorption capaciteis of LDHs intercalated with chelating agents for Cu(III), Pb(III), Cd(III) and REEs ions were investigated by batch experiments. Influence of various condition including pH, adsorbents dose, concentration of metallic ions, adsorption time and temperature on the removal of metallic ions was evaluated. The Langmuir and Freundlich models were used for the mathematical description of the adsorption isotherms. The suitability of the kinetic model for the adsorption processes are also discussed. In addition, thermodynamic considerations of an adsorption process are necessary to determine whether the process is spontaneous or not. The Gibb's free energy change(ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were also calculated in this work.

The following matters were suggested from the experimental results:

1. In present study, the precursor LDHs (ZnAl-NO_3 and MgAl-NO_3) were intercalated with the chelating agent EDTA (Ethylenediaminetetraacetic Acid) and EDDS (N, N'-1, 2-Ethanediylbis-1-Aspartic Acid) by anion exchange. The obtained material was characterized and used for the removal of heavy metallic ions and REEs removal from aqueous solutions. The result from FT-IR etc. suggests that the intercalation into LDHs is performed successfully.

2. LDHs synthesized in this work were very effective for removing both heavy metallic ions and REEs ions from water solutions. Higher adsorption efficiency is obtained by intercalating chelating agent (i.e. EDTA or EDDS) into LDHs. It is

considered that adsorption capacity of metallic ions onto LDHs is based on the stability constant of metal-chelating agents. For example, the adsorption efficiency of Cu(III) was higher than that of Pb(III) for the same absorbent. Moreover, the adsorption capacity of single Eu(III) ions are higher than that of REEs standard solution in the same condition, and the adsorption capacity is also according the order L4 < L5 both in the nitrate salt solution and the REEs multiple solution. The comparison result indicates that La(III) was more suffered from other REEs interfere in a ternary mixture.

3. Adsorption isotherms of adsorption data were studied at varying initial concentration of metallic ions under optimized conditions of contact time and the dosage of adsorbents in this work. The adsorption experimental data of heavy metallic ions onto LDHs were well fitted by the Freundlich adsorption isotherms model. The results suggest that LDHs synthesized in this work could be suitable as sorbent materials for the adsorption and removal of heavy metal ions from aqueous solutions.

4. The pseudo first order kinetic and pseudo second order, intra particle diffusion, and Elovich models were applied to test the experimental data and explain the kinetics of the LDHs adsorption process. The comparison of evaluated correlation coefficients suggested that the pseudo second order model is most suitable for describing the adsorption processes. The confirmation of this model implies that the rate-limiting step in this adsorption system may be controlled by chemical process. Also, the concentrations of both adsorbent and adsorbate are associated with the rate determining step of the adsorption process.

5. The adsorption thermodynamic suggested that the reaction of REEs adsorbed by LDHs adsorbents was spontaneous and endothermic. In addition, the desorption of Eu(III) and La (III) from the adsorbent has been found to depend

upon the stability consistent of M-EDTA. And LDHs still present the high adsorption capacity towards heavy metals through 3 cycles of adsorption/desorption behavior. LDHs could be an efficient adsorbent for heavy metals and REEs, although the structure may be reconstructed by the hydrogen ion after 4 or 5 cycles.

From this work, it was quantitatively clarified to that LDHs could be an efficient adsorbent for heavy metal and REEs. It is very significant information from the viewpoint of environmental protection, and can be used for treating industrial waste waters including pollutants, and thus a promising option for the treatment of contaminated waters.

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