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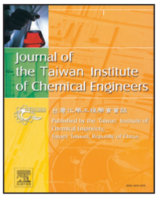

Remediation of waste water by Co–Fe layered double hydroxide and its catalytic activity

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ABSTRACT

Layered double hydroxide (LDH) nanoparticles have tremendous anion-intercalating property. Co–Fe LDH has been synthesized using the ball milling method. Characterization of Co–Fe LDH was done by XRD, SEM, TEM and FT-IR. The prepared LDH was used, for the first time, as a catalyst for multi-walled carbon nanotubes (MWCNTs) via chemical vapor deposition (CVD) of acetylene at different temperatures (400–700 °C). Also, the ability of Co–Fe LDH as an adsorbent was investigated for the removal of Cd^{2+} ions from aqueous solutions. Various physicoechemical parameters such as pH, initial metal ion concentration, and time were studied. To get the adsorption isotherms, the concentrations of the metal ions ranging from 6 to 18 mg/l were used. The adsorption process follows pseudo-second-order reaction kinetics, as well as Langmuir adsorption isotherms. Interestingly, Co–Fe LDH demonstrated 95% Cd^{2+} removal at pH 9 and 6 h which could be applied in wastewater treatment characterized by a high efficiency and low cost.

1. Introduction

Layered materials have been extensively studied in recent years due to the wide range of properties that could be tailored by intercalation and functionalization (surface chemical modification) reactions, allowing them to be used in different fields of science and technology. Therefore, the preparation of the layered materials to investigate their properties and applications has been the focus of our research group [1]. Layered double hydroxide (LDH) is a layered inorganic compound that is composed of an ionic lamellar solid that contains infinite layers of brucite-type, positively charged and exchangeable hydrate gallery anions. The ability of LDHs to intercalate anions makes them useful as catalysts, tailor made adsorbents or precursor materials for oxides. The general formula of LDH is $[M^{II}_{1-x}\,M^{III}_{x}(OH)]^{x+}.[(A^{n-}_{\frac{x}{n}}).mH_2O]^{x-}$, where M^{II} and M^{III} are the divalent and trivalent cations, respectively, and A^{n-} is the interlayer anion of charge n that leads to the electro-neutrality of the LDH. The coefficient x is equal to the molar ratio $[M^{III}/(M^{II}+M^{III})]$, and m is the number of water molecules located in the interlayer region with the anions [2,3].

Layered double hydroxides (LDHs) are the antitypes of clay minerals. Clay minerals found increasing interest as adsorbents by virtue of their properties, which make them attractive materials for adsorbing heavy metal ions. Adsorption reactions at solid–water interfaces decrease solute mobility and often control the fate, bioavailability, and transport of heavy metal ions such as Zn^{2+},Cu^{2+},Pb^{2+} and Ni^{2+} in the environment [4,5] The adsorption mechanisms of metal ions on the surfaces of clay minerals and others are significant for understanding their fate in the environment. LDHs could adsorb metal cations from aqueous solution in spite of positive layer charge. A major reaction could be surface-induced precipitation that occurs due to localized high pH values and the released carbonate ions available to metal cations. Positive layer charge attracts hydroxide ions around the surfaces of LDH crystals in aqueous solution to induce formation of metal hydroxides. Meanwhile, charge-compensating carbonate ion attached on the surface and edge could also contact with metal cations to form insoluble metal carbonates. There is also another possibility to adsorb metal cations via diodachy, as suggested by Komarneni et al. [6]. These imply that LDHs could be utilized as an adsorbent for heavy metal cations. However, there are only a few studies on the interaction between LDH and heavy metal cations in solution.

The layered structure of layered double hydroxides is destroyed and transformed into mixed oxides with large surface area and good dispersion of metal cations after a controlled thermal treatment. This makes them capable of acting as an excellent precursor

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Table 1
Reported CNT for some layered double hydroxide structures.

Catalyst	Type of the tube	Diameters	Reference
Co/Fe/Al layered double hydroxides	Multiwalled carbon nanotubes	7–13.5 nm	[57]
Fe/Mg/Al LDH flake	Multiwalled carbon nanotubes	4–7 nm	[58]
Fe/Mg/Al LDH flake	Graphene/single-walled carbon nanotube		[59]
Zn–Al LDH	Zn–Al (LDH) and poly acrylic acid-functionalized multiwalled carbon nanotubes	20–30 nm	[60]
Co–Al LDH	Multiwalled carbon nanotubes	20–30 nm	[17]
$Fe_{0.1}Mg_2Al_{0.9}$ LDH	single-walled carbon nanotubes	1–3 nm	[41]
$Fe_{0.1}Zn_2Al_{0.9}$ LDH	Multi-walled carbon nanotubes and carbon nanofibers	15–50 nm	
$Fe_{0.1}Cu_2Al_{0.9}$ LDH		50–200 nm	
Co–Fe LDH	Multiwalled carbon nanotubes	3–17 nm	In present work

Table 2
Reported adsorption capacities of some adsorbents for Cd^{2+} metal ion.

Adsorbent	Adsorption capacity (mg/g)	Cd^{2+}concentration used mg/l^{-1}	Source
Vanadium mine tailing	3.52–8.83	20 mg/l	[29]
Carbon nanotubes	14.45	10–60 mg/l	[30]
Chelating sponge	90–100	1.0–5.0 mmol/l	[31]
$Mg–Al–CO_3–LDH$	61.40–70.20	100 mg/l	[28]
Magnetic $Fe_3O_4/Mg–Al–CO_3–LDH$	45.60–54.70	100 mg/l	[28]
Biogenic selenium Nanoparticles	18	30–210 mg/l	[27]
1*Co–Fe (LDH) nanoparticles	1* 65–94 at 6 h	12 mg/l	This study
2*Carbon nanotubes prepared on the Co–Fe LDH surface	2* 70–94 at 3 h		

to prepare catalyst-supported materials [7–11] for CNTs production as shown in Table 1. Catalyst mostly containing Fe, Co, Ni components supported over porous materials or high-surface-area oxide matrix in order to enhance the reactivity of catalyst clusters have great effort for the growth of CNTs [12–16], this due to catalytically active site in Co nanoparticles [17]. This may have a distinct effect on the dispersion of Co^{2+} ions in catalysts and thus the catalytic performance for CNTs production.

Carbon nanotubes have attracted worldwide attention because of not only their unique physicochemical properties but also their promising applications in transistors, field-emission tips, sensors, supercapacitors and bio-medical fields [18–22]. Electric-arc discharge and laser ablation synthesis techniques, catalytic pyrolysis of carbon-containing gases via catalytic chemical vapor deposition (CCVD) has been widely investigated in the production of various of carbon nanotubes (CNTs) [23–26]. Particle size and particle dispersion of the catalyst are the key factors for controlling the growth of nanotubes during the CCVD process. Good dispersion and size control of catalyst particles can be expected due to the ordered prearrangement of metal cations in the layers of the LDH precursor at an atomic level.

Although previous researchers allocated their attention on the adsorption of Cd^{2+} ion using different adsorbents, [27–31], our present study demonstrated 95% removal for Cd^{2+} ion by using Co–Fe LDH as illustrated in Table 2. Co–Fe LDH was prepared different methods as shown in Table 3, Co–Fe LDHs have been synthesized using coprecipitation methods. However, the conventional methods have the following serious drawbacks: the processes are very complicated, accurate pH control and subsequent heating are needed, and the reaction times are long. Another synthesis method such as topochemical technique and laser ablation technique have been developed. However, the above-mentioned drawbacks (complicated processes and long overall treatment times) remain in these methods. Therefore, a simple method for the rapid synthesis of Co–Fe LDHs is required. One-step synthesis method that requires neither pH control nor heating. In current study it was prepared by ball milling method with an advantage that it can easily be operated and produces large amounts of nanostructured powders for a short period of time [32] because the force of the ball impact is unusually great, and it is possible to produce a fine and homogeneous distribution of components in the final solids [33]. Then used as catalyst for MWCNTs synthesis by CVD. The effect of temperature on catalyst crystallite size, CNTs morphology change and yield percent were studied (see Scheme 1).

2. Experimental

2.1. Materials

Iron nitrate [Fe $(NO_3).9H_2O$] SDFCL, India, cobalt nitrate [Co $(NO_3)_2.4H_2O$] and cadmium nitrate [Cd $(NO_3)_2.4H_2O$], Oxford laboratory reagent, India, sodium hydroxide, NaOH, Piochem for laboratory chemicals, EGYPT and hydrochloric acid, HCl. All used chemicals were of analytical reagent grade and were not more purified and all solutions were prepared by using bi-distilled water.

2.2. Synthesis of Co–Fe layered double hydroxide

The Co–Fe nitrate LDH was prepared by blending a mixture of cobalt nitrate and the iron nitrate (3:1 molar ratio) (Fig. 1) with 8 M of sodium hydroxide solution, the resulting product was inserted into photon ball milling vessel, see Table 4, for 10 h with a continuous rotational speed of 200 rpm. After ball milling the dark brown precipitate was filtered and washed with bi-distilled water many times. Then, the obtained precipitate was dried at 80 ± 0.5 °C for 24 h.

2.3. Catalytic properties of Co–Fe layered double hydroxide for synthesizing MWCNTs

Catalytic reactions were carried out in a continuous-flow fixed bed. 0.5 g of Co–Fe LDH catalyst was packed in a cylindrical alumina cell. Co–Fe LDH catalyst preheated to 400–700 °C in a flow of nitrogen gas (70 ml/min) for 10 min. Then acetylene gas was allowed to pass over the catalyst bed with a rate of 10 ml/min for 30 min. The acetylene gas flow was stopped and the product on the alumina cell was cooled to room temperature in a flow of nitrogen gas. The weight of the carbon deposited along with the catalyst was noted. The percentage of carbon deposit (C%) obtained in each reaction was determined using the following relationship:

$$C(\%) = \left[\frac{W2 - W1}{W1}\right] \times 100 \quad (1)$$

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