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Research paper

Adsorption behavior and mechanism of core–shell magnetic rhamnolipid–layered double hydroxide nanohybrid for phenolic compounds from heavy metal–phenolic pollutants

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ABSTRACT

A core–shell magnetic rhamnolipid (RL)–layered double hydroxide (LDH) nanohybrid (Fe_3O_4@(RL–LDH)) was synthesized by the delamination of magnetic LDH (Fe_3O_4@LDH) initially and then assembling with RL/NaOH water solution to remove p-cresol/hydroquinone from heavy metal–phenolic pollutants in aqueous solution. The characteristics of the obtained Fe_3O_4@(RL–LDH) nanohybrid was analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, inductively coupled plasma atomic emission spectrometry, CHN elemental analysis, transmission electron microscopy, vibrating sample magnetometer, thermogravimetry and differential scanning calorimetry, specific surface area, and zeta potential. Results confirmed that the Fe_3O_4@(RL–LDH) particles possessed core (Fe_3O_4)–shell (RL–LDH) structures and magnetic properties, and RL^- anions were successfully introduced into interlayers of Fe_3O_4@LDH. The adsorption of p-cresol/hydroquinone by Fe_3O_4@(RL–LDH) from Cu^{2+}–phenolic pollutants in aqueous solution was studied with magnetic separation in detail. The effect of factors, including the initial solution pH, contact time, initial p-cresol/hydroquinone concentration, and temperature, on the adsorption were investigated. Findings revealed that (1) the adsorption capacities of Fe_3O_4@(RL–LDH) for p-cresol and hydroquinone were much greater than those of Fe_3O_4@LDH in the presence/absence of Cu^{2+} and (2) the adsorption amount of p-cresol by Fe_3O_4@(RL–LDH) was higher than that of hydroquinones with (or without) Cu^{2+} ions. The efficient p-cresol/hydroquinone adsorption was mainly due to the dissolution of p-cresol/hydroquinone in the hydrophobic interlayer region formed by RL^- anions, and the adsorption mechanism was confirmed by the difference between the adsorption capacities of Fe_3O_4@(RL–LDH) for p-cresol and hydroquinone.

1. Introduction

Phenols and heavy metal cations present high toxicity and are generally considered to be the important pollutants discharged into the environment, as they have high toxicity and/or poor biodegradability (Unlu and Ersoz, 2006; Liu et al., 2010). An effective means to solve water pollution is to treat and regenerate wastewater by using layered double hydroxides (LDH) (Galindo et al., 2014). LDH, a positively charged inorganic material, possesses a layered structure, high porosity, high surface area, and interlayer anion mobility (Miyata, 1980; Cavani et al., 1991). Because both the surface and interlayer of LDH exhibit strong hydrophilicity, LDH is highly adsorptive for hydrophilic anionic contaminants from wastewater (Goswamee et al., 1998; Klumpp et al., 2004). Additionally, the adsorption selectivity and performance can be improved by changing the surface properties and interlayer spacing. Therefore, on the one hand, LDH modified with anionic surfactants is an ideal adsorbent for organic phenolic pollutants (Chuang et al., 2008). On the other hand LDH containing chelating agents manifests good adsorption properties for heavy metals (Pérez et al., 2006). In the actual wastewater, heavy metal ions often coexist with organic pollutants; thus, the effects of heavy metal ions cannot be ignored in the treatment of organic pollutants in sewage. Therefore, developing LDH materials that can remove both organic and heavy metal pollutants simultaneously would represent a significant advance in wastewater treatment.

Our previous studies (Li et al., 2017) demonstrated that LDH modified with rhamnolipid (RL), a biosurfactant produced by *Pseudomonas bacteria*, can achieve a good adsorptive ability for p-cresol and Cu^{2+} ions. However, RL–LDH adsorbed with the pollutants is difficult to separate, recover, and reuse; as such, RL–LDH will be limited in its

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practical application to some extent. Therefore, the water environment protection field must develop magnetic LDH materials that can be recovered easily and quickly by an external magnetic field.

Conventional methods, such as ion exchange and reconstruction, have been used to synthesize RL–LDH nanohybrid (Chuang et al., 2010). However, these methods hold the following drawbacks: complex processes, time-consuming, high reaction temperature, and relatively low RL loading amount. Therefore, the water environment protection field must focus on developing magnetic LDH materials that can be easily synthesized and recovered quickly by an external magnetic field.

In this work, we describe a delamination/reassembling process for the facile fabrication of Fe_3O_4@(RL–LDH) nanohybrid. The Fe_3O_4@LDH nanohybrid was initially prepared by coprecipitation followed by delamination with formamide to form a suspension containing Fe_3O_4 particles and LDH nanosheets. Lastly, the magnetic core-shell Fe_3O_4@(RL–LDH) nanohybrid was facilely prepared by coassembling of the suspension (Fe_3O_4 + LDH nanosheets) and RL/NaOH water solution. The adsorption behaviors of Fe_3O_4@(RL–LDH) nanohybrid for phenolic pollutants (p-cresol or hydroquinone) from heavy metal-–phenolic pollutant systems (p-cresol + Cu^{2+} or hydroquinone + Cu^{2+}) with magnetic separation assistance were investigated and the possible adsorption mechanism involved was confirmed by the difference between the adsorption capacities of the nanohybrid for p-cresol and hydroquinone.

2. Experimental

2.1. Materials

Monorhamnosyl RL (> 90%) was purchased from Zijin Biological Technology Co., Ltd. (Huzhou, China), and its structure is shown in Scheme 1a. All other reagents were supplied by Tianjin Chemical Reagent Co. Ltd., China and were of analytical grade. Deionized water was decarbonated by boiling and bubbling N_2 before use in all synthesis steps.

2.2. Preparation of Fe_3O_4@LDH

Magnetic Fe_3O_4 microspheres were prepared by a modified solvothermal route (Deng et al., 2005). Initially, 3.2438 g of $FeCl_3 \cdot 6H_2O$ and 8.6383 g of $CH_3COONa \cdot 3H_2O$ were dissolved in 80 mL ethylene glycol at 313 K to form a clear brown solution under vigorously stirring. The solution was sealed in a stainless steel reactor with polytetrafluoroethylene liner. The reactor was then heated for 8 h at 473 K. After cooling down, the resultant suspension was attracted by a magnet and then washed three times at intervals between the deionized water and ethanol solution. The precipitate was dried at 333 K overnight to yield the black powder of Fe_3O_4.

Magnetic core–shell Fe_3O_4@Mg_3Al LDH nanohybrid (abbreviated as Fe_3O_4@LDH) was synthesized by a coprecipitation method (as shown in Scheme 1b). Typically, the appropriate amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (the molar ratio Mg^{2+}/Al^{3+} was 3) were dissolved in deionized water to obtain a solution with a total metal ion concentration of 0.5 $mol \cdot L^{-1}$. Then, a moderate amount of Fe_3O_4 powder (3 $g \cdot L^{-1}$) was ultrasonically dispersed into the mixed salt solution for 5 min. An ammonia-water solution (volume ratio of 1:4) was slowly poured into the suspension under stirring until precipitation at pH 9–10, and then a precipitate was produced. After standing at room temperature for 1 h, the suspension was filtered and then washed four times with deionized water. The filter cake was sealed and peptised at 353 K in an oven for about 24 h, and Fe_3O_4@LDH sol was obtained. Finally, the sol was dried at 353 K to yield a product of Fe_3O_4@LDH powder.

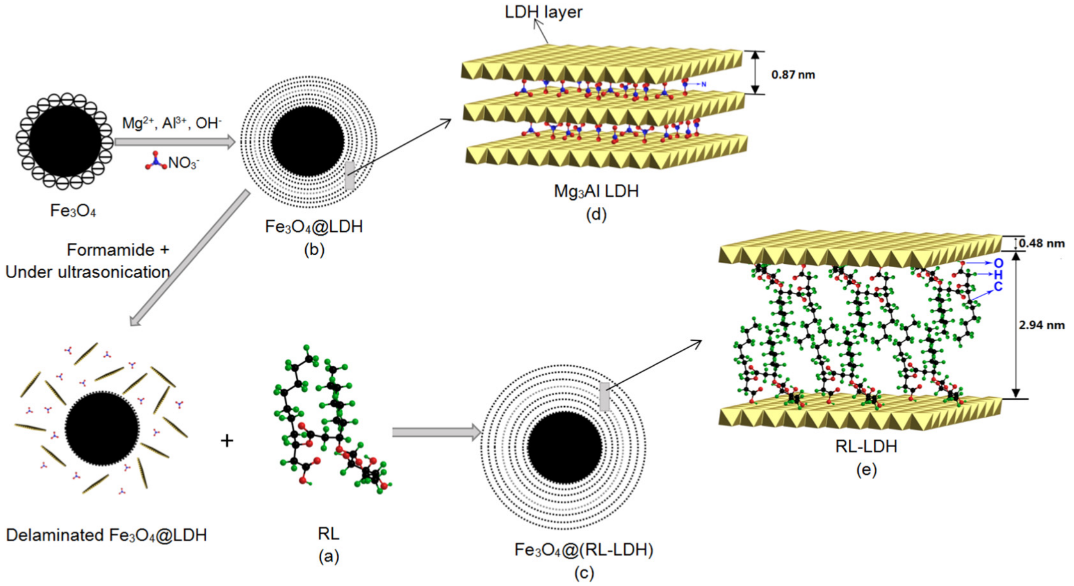
For comparison, Mg_3Al LDH was synthesized in accordance with the above method when no Fe_3O_4 was added.

2.3. Preparation of Fe_3O_4@(RL–LDH)

Fe_3O_4@(RL–LDH) nanohybrid (abbreviated as Fe_3O_4@(RL–LDH)) was synthesized by a delamination–reassembling method (as shown in Scheme 1c). First, 0.4 g of Fe_3O_4@LDH was added to 20 mL of formamide under vigorous stirring, and then the suspension was sonicated for 20 min. Subsequently, 20 mL of the suspension was dropped into 20 mL of RL/NaOH water solution containing 1 g of RL under slow stirring for 30 min. The suspension was centrifuged at 12,000 rpm for 15 min, and then washed twice with deionized water and once with ethanol in a redispersion/centrifugation cycle. The precipitate was finally collected and dried in an oven at 353 K to obtain the Fe_3O_4@(RL–LDH) powder.

2.4. Characterization

Transmission electron microscopy (TEM) images of the samples were obtained using a Tecnai G^2 F20 instrument (FEI Company, USA).



Scheme 1. Schematic diagrams of (a) RL, (b) Fe_3O_4@LDH, (c) Fe_3O_4@(RL–LDH), (d) Mg_3Al LDH and (e) RL–LDH.