Applied Surface Science 442 (2018) 45–53

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Enhanced removal of natural organic matters by calcined Mg/Al layered double hydroxide nanocrystalline particles: Adsorption, reusability and mechanism studies

Liping Fang [a,*], Jingwei Hou [a], Cuihong Xu [a], Yaru Wang [a], Ji Li [a,*], Feng Xiao [b], Dongsheng Wang [b]

[a] Department of Chemistry, Faculty of Material Sciences and Chemistry, China University of Geosciences, Wuhan 430074, China
[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:
Received 23 October 2017
Revised 11 January 2018
Accepted 12 February 2018
Available online 14 February 2018

Keywords:
Anionic clays
Adsorption process
Molecular weight distribution
Natural organic matters (NOMs)

ABSTRACT

Natural organic matters (NOMs) can generate disinfection by-products during water treatment process, threatening to human health. However, the removal of NOM is still unsatisfactory in water treatment. Hence, this work investigated the removal efficiency of humic and fulvic acids (HA and FA) by layered double hydroxide (LDH) and its calcined forms under different conditions. Our results show that calcination of LDH at 500 °C can effectively enhance the NOM removal with adsorption capacities of 98.8 mg/g for HA and 97.6 mg/g for FA at pH 9.5. The removal efficiency of HA and FA notably increases by decreasing pH. The presence of SO_4^{2-} and CO_3^{2-} significantly suppresses the removal of HA or FA by CLDHs. The release of Al from LDH and CLDH is negligible and safe to aquatic organisms at pH > 6.5. Moreover, CLDH shows a good reusability for NOM removal in water treatment. The removal of HA and FA by CLDH is governed through electrostatic interactions and intercalation into the interlayers of LDH was not observed. Fluorescence and molecular weight analyses show that the microbial by-products with mid-molecular weight are more difficult to be removed than HA and FA. This study provides a new insight into the NOM removal using LDH and CLDH.

1. Introduction

Natural organic matters (NOMs) including humic and fulvic acids (HA and FA) are products of biodegradation of dead vegetation and animals. HA and FA are widespread in soils and various water bodies, the contents of which differ from regions and climates. Recent investigations declare that a considerable increase of humic substances in various water bodies occurs during the past 20 years, due to the changes of environmental factors such as temperature raising and the increase in acid deposition [1,2]. The increase of HA and FA concentration above 5 mg/L will cause water color and taste issues, though they do not show direct toxicity to aquatic organisms and humans. As complex polyelectrolyte colloids, HAs and FAs consist of many functional groups such as carboxyl acid, phenolic, ketone and quinone groups [2]. This allows HAs and FAs to bind with different metal ions and organic pollutants, affecting their fates in the environment [3,4]. Meanwhile, the presence of high concentration of HAs and FAs in groundwater can also decrease redox potential, causing the release of toxic metal ions into overlaying water and affect water quality [5]. Moreover, the increased content of HAs and FAs in drinking water sources could lead to the occurrence of carcinogenic disinfection by-products (DBPs) such as trihalomethane and haloacetic acid in the chlorination process of drinking water treatments [6,7].

Considering the aforementioned problems attributed to the presence of HAs and FAs in aqueous systems, removal of HAs and FAs from water resources is of great importance in providing safe drinking water. Many approaches have been applied to remove HAs and FAs from natural water bodies, including coagulation [8], membrane separation [9], advanced oxidation processes [2], and adsorption [10,11]. In comparison to other methods, adsorption is commonly regarded as simple, cost-effective and versatile technology for water purification now days [12]. Even though a variety of adsorbents have been used for HA and FA removal, e.g. iron oxides [13], ammonia modified activated carbons [10], chitosan beads [14] and montmorillonites [15], the key challenge of developing suitable adsorbents is to reach a compromise between high efficiency of HA and FA removal and treatment cost.

Layered double hydroxides (LDHs) such as hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$; HT) belong to a class of anionic clays with a “sandwich”-like structure [16–18]. Various studies have

---

[*] Corresponding authors.
E-mail addresses: fang@plen.ku.dk (L. Fang), ljyu191@sohu.com (J. Li).

https://doi.org/10.1016/j.apsusc.2018.02.131
0169-4332/

demonstrated that LDHs have strong capability of adsorbing/intercalating various anionic pollutants (e.g. As, Se and organic molecules) [19–21]. It is well known that LDHs are facile to synthesize by means of simply coprecipitation of cations such as Mg and Al, which is considered as a low cost solution for further application. To date, there are only a few studies on HAs and FAs removal using LDHs [22,23]. The drawback for LDHs is that accessibility of a number of inner binding sites is restricted as a result of geometric hindrance and therefore causing less anion exchange capability [19]. To release sufficient valid adsorption sites within LDHs, many efforts have been made, one of which is to calcine LDHs to active metal oxides. Their studies demonstrate that the adsorption of LDHs to anionic pollutants such as arsenate and selenite is notably enhanced after calcination treatment, and the layered structure of LDH is reformed after hydration as a result of the structural 'memory effect' [19,24]. HAs and FAs present as complex macromolecules containing a variety of functional groups and molecular weights, whose structure is more complicate than those inorganic anions. However, knowledge on the removal of such complex organic matters by calcined LDHs is scarce; specifically it is unknown which chemical fraction and molecular weight distribution are preferentially adsorbed by CLDHs. A systematic elucidation for NOM removal mechanisms (e.g. HA and FA) by calcined LDHs is of great importance for future LDH application in water treatment. In addition, the reusability of LDH for HA or FA removal is also an important matter for practical application, while little progress has been made by far.

Hence, the objectives of this study aim to (i) explore the effect of calcination temperature ranging from 200 to 800 °C for LDH on the HA and FA removal from water; (ii) investigate the effects of different environmental factors including pH and the presence of background anions on the removal of HA and FA, (iii) study the reusability and removal mechanism of HA and FA by calcined LDHs; and finally (iv) characterize the chemical property of NOM after its removal by CLDH in terms of molecular weight and chemical fraction.

2. Materials and methods

2.1. Chemicals

$Al(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals used in this study were of analytic grade. MilliQ water was used throughout the whole experiment. HA stock solution was prepared by dissolving 5 g of solid HA obtained from Sigma Aldrich, in 400 mL of 0.01 M NaOH, and mildly stirring over a magnetic stirrer over 24 h. Then, the HA solution was filtered through 0.45 μm membrane to remove any solid particles. FA was purchased from Nanjing Chemlin Chemical Industrial Co. Ltd, and its stock solution was prepared by adding 5 g FA powders into 400 mL Milli-Q water. The concentration of the prepared HA and FA stock solutions is 3567 and 3550 mg-C/L (measured as TOC) over a TOC analyzer (Tekmar, USA), respectively.

2.2. Synthesis of Mg/Al LDH and its calcined forms

Nanocrystalline Mg/Al LDH was prepared via rapid coprecipitation followed with hydrothermal treatment method [25]. Briefly, 15.5 g of $Mg(NO_3)_2{\cdot}6H_2O$ and 7.5 g $Al(NO_3)_3{\cdot}9H_2O$ were dissolved into 80 mL of MilliQ water (Mg: Al = 3: 1). Then the solution was added into 120 mL mixed solution of 1 M NaOH and 3.5 M Na_2CO_3, under vigorously stirring for 0.5 h at room temperature (25 °C ± 1). After repeatedly washing and centrifugation for 5 times, the obtained LDH slurry was transferred into a stainless steel autoclave, and placed in an oven at 100 °C aging for 16 h. The calcined LDHs were prepared by calcination of the freshly synthesized Mg/Al LDH at 200 °C, 500 °C and 800 °C in a muffle furnace for 5 h, respectively. The respective calcined product was denoted as CLDH-200, CLDH-500 and CLDH-800. The resulting products were then stored in a desiccator for further use.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the synthesized Mg/Al LDH and its calcined products were recorded on a X'Pert PRO MRD diffractometer (PANalytical, Netherlands) coupled with monochromatic Cu Kα radiation (λ = 0.15405 nm) at 40 keV and 40 mA. Fourier transformation infrared spectroscopy (FT-IR) spectra of the products were analyzed by using a Nicolet 8700 (Thermo scientific, USA), over a range from 400 to 4000 cm^{-1}. The morphologies of the samples were explored on Hitachi SU8000 ultra high resolution field emission scanning electron microscope (FE-SEM; Hitachi, Japan) at beam energy of 15 kV. Transmission electronic microscopy (TEM) images were obtained on a Hitachi H-7500 microscope (Hitachi, Japan). The BET surface area and porosity characteristics were determined over a Micromeritics ASAP 2010 system at 77 K.

2.4. HA and FA adsorption experiments

Kinetic experiments of HA and FA were conducted by dosing 15 mg LDH or its calcined products to 50 mL of HA or FA aqueous solution with an initial concentration of 50 mg-C/L at pH 9.5 ± 0.1, resulting in a solid/solution ratio of 0.3 g/L. The suspension solutions were equilibrated in a thermostatic shaker at 200 rpm for different time intervals (5 min to 24 h) at 25 ± 1 °C. Adsorption isotherm experiments were performed at HA initial concentrations of 5–150 mg-C/L in the presence of 0.3 g/L of LDH or CLDH. The pH of the suspensions was at 9.5 during the 24 h equilibrium time. The pH edge experiment was carried out by reacting 50 mg-C/L of HA with 0.3 g/L of HA or CLDH-500, respectively. The pH of the suspensions was adjusted by using HCl and NaOH to cover a pH range of 5–10. The effects of different background anions on the removal of HA and FA was also investigated at pH 9.5, by adding different concentration of anions (i.e. Cl^-, SO_4^{2-} and CO_3^{2-}) respectively. The reusability of CLDH was studied by adopting a process of adsorption/calcination at 500 °C. All experiments were in triplicate, and the ionic strength of the solutions was remained by 0.01 M $NaNO_3$.

After reaction, the suspension solutions were centrifugated at 9000 rpm for 10 min. The final concentrations of HA or FA in aqueous phase after reaction were obtained by analyzing the respective supernatant.

2.5. Analytical methods

The concentrations of HAs and FAs of the samples were analyzed at a wavelength of 254 nm by using a UV-2600 spectrophotometer (Shimadzu, Japan). The standard curve was plot according to corresponding UV absorbance values of HA or FA standards that were prepared by dilution proper amounts of the HA or FA stock solution. The molecular weight distribution of HA and FA was measured using a high performance size exclusion chromatography (HPSEC) method, including a high performance liquid chromatography (HPLC, waters, USA) installed with a gel-chromatography column (Shodex Protein KW-802.5, Sholo, Japan). The mobile phase comprised 0.02 M orthophosphate and 0.1 M NaCl mixed solution (pH 6.8), and the flow rate of the mobile phase was kept at 0.8 mL/min. The standards were prepared using polystyrene sulfonate solution with molecular weight (MW) of 1800–35,000 Da in acetone (MW = 48 Da).

The chemical compositions of the NOM were characterized using three-dimensional excitation emission matrix (3D-EEM)