Chemical Engineering Journal xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Immobilization of aqueous and sediment-sorbed ciprofloxacin by stabilized Fe-Mn binary oxide nanoparticles: Influencing factors and reaction mechanisms

Zhi-li Yan [a,b], Yun-guo Liu [a,b,*], Xiao-fei Tan [a,b], Shao-bo Liu [c,*], Guang-ming Zeng [a,b], Lu-hua Jiang [a,b], Mei-fang Li [a,b], Zan Zhou [a,b], Su Liu [a,b], Xiao-xi Cai [a,b,d]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] School of Metallurgy and Environment, Central South University, Changsha 410083, PR China
[d] College of Art and Design, Hunan First Normal University, Changsha 410205, PR China

HIGHLIGHTS

- A class of carboxymethyl cellulose stabilized Fe-Mn nanoparticles was synthesized.
- The maximum adsorption capacity of CIP onto CMC-FMBO was 1172.25 mg/g.
- Pseudo-second order kinetic model adequately simulated the adsorption kinetics.
- CMC-FMBO could potentially be delivered and distributed in contaminated sediment.
- Electrostatic interaction, hydroxyl complexation were the main mechanisms.

ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form 3 December 2016
Accepted 3 December 2016
Available online xxxx

Keywords:
Fe-Mn binary oxide
Stabilized nanoparticles
Ciprofloxacin
Water treatment
Sediment contamination
Reaction mechanisms

ABSTRACT

Fe-Mn binary oxide nanoparticles were reported to be effective for removal of aqueous pharmaceutical chemicals. However, little is known about its potential application in removing the sediment-sorbed contaminants. To bridge this knowledge gap, we synthesized stabilized Fe-Mn binary oxide nanoparticles using water-soluble carboxymethyl celluloses (CMC) as a stabilizer and tested their effectiveness for removal of aqueous and sediment-sorbed ciprofloxacin (CIP). Fully stabilized Fe-Mn binary oxide nanoparticles (0.05 g/L as Fe) were obtained in the presence of 0.5 g/L of CMC. When compared with non-stabilized Fe-Mn nanoparticles (FMBO), CMC-stabilized Fe-Mn nanoparticles (CMC-FMBO) showed relatively more favorable removal performance and particles stabilization facilitated delivering nanoparticles into sediment for in situ removal of CIP. The CIP removal by CMC-FMBO was highly pH dependent and the optimum pH was 6.0. A pseudo-second-order kinetic model was able to interpret the removal kinetics. When CIP-spiked sediment was treated with the CMC-FMBO, CMC-FMBO exhibited more excellent resistance to the sediment inhibitive effects and higher removal efficiency of CIP, compared to FMBO. This primary research suggests that CMC-FMBO hold the potential for facilitating removal of emerging contaminants in wastewater and sediment.

1. Introduction

Growing awareness of the long term impacts of pharmaceuticals on the environment has increased over the last decades [1,2]. The fluoroquinolone group is one of the most important pharmaceuticals used worldwide in a variety of human and veterinary applications. As a third generation of fluoroquinolones (FQs) antibiotic, ciprofloxacin (CIP, Fig. 1) similar to many other pharmaceuticals, is not readily biodegradable [3]. Of the administered dosage of CIP in humans, about 30–90% eventually was released into the environment as the parent compound [4]. CIP released to the environment might pose serious threats to the ecological systems as well as human beings albeit at small concentrations

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China (Y.-g. Liu). School of Metallurgy and Environment, Central South University, Changsha 410083, PR China (S.-b. Liu).
E-mail addresses: liuyunguo_hnu@163.com (Y.-g. Liu), liushaobo23@aliyun.com (S.-b. Liu).

http://dx.doi.org/10.1016/j.cej.2016.12.019
1385-8947/

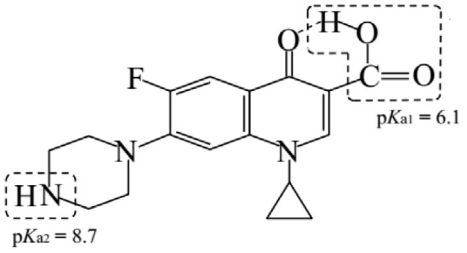

Fig. 1. Molecular structure of CIP.

or with low residues. Currently, it has been widely detected in the environment such as surface waters [5,6], groundwater [7], sediments [8,9] and soil [10]. Higher concentrations were even reported 50 mg/L near drug manufacturing plants [11]. Thus, the removal of CIP from the environment has already become a mandatory issue. Even so, there are not so many studies dealing with the elimination of CIP, when compared with other antibiotics.

Several recent studies in literature have investigated the removal of CIP by various methods: adsorption [12,13], photodegradation [14,15], photo-Fenton oxidation processes [16], oxidation [17,18] and biodegradation [19]. Among these available treatment processes, the adsorption technique was envisioned to be an efficient and cost-effective treatment technology for removing CIP from water, because of its low cost, easy operation, high efficiency and relatively simple regeneration.

Various manganese oxides/hydroxides such as birnessite [20], manganese oxide (MnO_2) [21] and Fe-Mn binary oxide [22], have been found effective for removal of emerging contaminants from water. Xu et al. [21] elucidated that the steroid estrogens from water were rapidly removed within 220 min by manganese oxide (MnO_2). By combination of the oxidation and sorption effect, Liu et al. [22] synthesized Fe-Mn binary oxides (FMBO) and results showed that removal efficiency of tetracycline onto FMBO was much higher than that of hydrous iron oxide and hydrous manganese oxide. However, conventional nanoscale adsorbents tend to aggregate rapidly into larger scale particles, losing their unique characteristics such as high specific surface area and reactivity. To overcome the above difficulties, organic polymers were exploited as a stabilizer to hinder the particles from aggregating through steric and/or electrostatic stabilization mechanisms [23,24]. Xie et al. [25] discovered that the selenite sorption capacity of CMC stabilized Fe-Mn binary oxide nanoparticles (CMC-FMBO) were much greater (>3 times) than other sorbents reported. Moreover, particles stabilization allowing the nanoparticles to be transmitted into the contaminated subsurface areas, promoting in situ remediation of contaminated soil and groundwater [26]. For example, stabilized iron sulfide (FeS) and magnetite (Fe_3O_4) nanoparticles have been gauged at several contaminated zones and exhibited to be deliverable into the contaminated source sites [27].

CMC-FMBO has elicited great interests for immobilization of trace contaminants in soil and groundwater, since it shows low cost, excellent adsorption capacity, affinity toward target contaminants stabilization and decent soil deliverability. However, information on removal or in situ immobilization of CIP in water and sediment has been rare. The overall goal of this research was to investigate the effectiveness of CMC-FMBO for removing CIP from water and sediment. The specific objectives of this study were to: (1) synthesize and characterize a new class of Fe-Mn binary oxide nanoparticles using CMC as a stabilizer; (2) probe the effects of the stabilizer concentration and particles dosage on CIP removal by CMC-FMBO; (3) examine the effects of different solution properties, including solution pH, adsorption time, temperature, ionic strengths and background electrolytes; (4) acquire further insights into the underlying CIP removal mechanisms; and (5) investigate the effectiveness of the stabilized nanoparticles for immobilizing CIP in a contaminated sediment.

2. Materials and methods

2.1. Materials

Ciprofloxacin ($C_{17}H_{18}FN_3O_3$, molecular weight 331.35, 98% in purity) was purchased from Bomei Biotechnology Co., Ltd., Hefei, China. CMC (sodium salt, MW = 90,000) was provided by Shan Pu Chemical Co., Ltd., Shanghai, China. The other chemicals including $FeCl_2{\cdot}4H_2O$, $KMnO_4$, NaOH, HCl, NaCl, $NaNO_3$, Na_2SO_4, Na_3PO_4, KCl, $CaCl_2$, $MgCl_2$, phosphoric acid were purchased from Municipality Kemi'ou Chemical Reagent Co., Ltd., Tianjin. All the chemicals were of analytical grade or higher, and the water used in all experiments was ultrapure water (18.25 Ω/cm) generated by Millipore Milli-Q water purification system.

The sediment was obtained from Xiangjiang river of Hunan province Changsha, in China. Before use, the sample was air-dried, smashed, screened through 200 mesh sieves, and then stored at room temperature (20 ± 1 °C) for further use. The key sediment properties include: OM (organic matter) = 6.02%, CEC = 2.16 - meq/100 g, TOC = 3.49% and Fe = 5.06% (see Table S1 in Supplementary Material for details).

2.2. Synthesis of CMC-FMBO

CMC-FMBO was prepared by modifying the method by An et al. [26].

First, the following solutions were prepared: 10 g/L stock solution of CMC, 1.785 mM $FeCl_2$, 0.85 mM $KMnO_4$. Then, a desired volume (0–20 mL) of CMC solution was mixed with 100 mL $FeCl_2$ solution in a 250 mL glass beaker for 20 min. The redox reaction was then initiated by adding 70 mL of the $KMnO_4$ solution into the mixture of CMC-$FeCl_2$ under vigorous magnetic stirring.

The pH of the mixture was immediately increased to ~7.5 using 1 M NaOH and the total volume of the mixture was maintained at 200 mL by adding water (0–20 mL). After continuous mixing and reacting for 20 min, CMC-FMBO was then acquired as either fully stabilized suspension or precipitates depending on the content of the stabilizer present. The resultant particle suspensions contained 0.05 g/L Fe and 0.017 g/L Mn with a CMC concentration of 0–0.6 g/L. The nanoparticles were allowed to grow for 1 h at room temperature and then stored in refrigerator before subsequent tests or analysis.

2.3. Analysis methods

The structural properties of CMC-FMBO were obtained on a X-ray diffractometer (Rigaku D/max-2500, Japan), with Cu Kα radiation (λ = 1.541 Å) at 40 kV and 30 mA in a 2θ range of 10–90°. For the zeta potentials analysis, the samples were prepared by ultrasonification of 1 mL suspensions with 20 mL ultrapure water and the solution pH was adjusted to different values (3.0–10.0) by adding negligible volumes 0.1 M NaOH or HCl. Then, the zeta potential of CMC-FMBO was measured with a zeta potential meter (Zetasizer nano-ZS90 Malvern) at 25 °C. The mesoporous pore structure of the CMC-FMBO was gained using a transmission electron microscopy (TEM) (JEM-3010, Japan) operating at 200 kV. Fourier transform infrared (FTIR) spectrum was collected on a spectrophotometer (Nicolet 6700 spectrometer, USA) over the wave number ranging from 400 to 4000 cm^{-1} at room temperature.

Please cite this article in press as: Z.-l. Yan et al., Immobilization of aqueous and sediment-sorbed ciprofloxacin by stabilized Fe-Mn binary oxide nanoparticles: Influencing factors and reaction mechanisms, Chem. Eng. J. (2016), http://dx.doi.org/10.1016/j.cej.2016.12.019