JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Adsorptive removal of antibiotics from water using magnetic ion exchange resin

Tianyue Wang[1,2], Xun Pan[3], Weiwei Ben[1,*], Jianbing Wang[2], Pin Hou[2], Zhimin Qiang[1]

1. Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
2. School of Chemical and Environmental Engineering, Beijing Campus, China University of Mining and Technology, Beijing 100083, China
3. Foreign Economic Cooperation Office, Ministry of Environmental Protection, Beijing 100035, China

ARTICLE INFO

Article history:
Received 31 December 2015
Revised 22 March 2016
Accepted 24 March 2016
Available online xxxx

Keywords:
Sulfamethoxazole
Tetracycline
Amoxicillin
Antibiotics
MIEX resin
Adsorption

ABSTRACT

The occurrence of antibiotics in the environment has recently raised serious concern regarding their potential threat to aquatic ecosystem and human health. In this study, the magnetic ion exchange (MIEX) resin was applied for removing three commonly-used antibiotics, sulfamethoxazole (SMX), tetracycline (TCN) and amoxicillin (AMX), from water. The results of batch experiments show that the maximum adsorption capacities on the MIEX resin for SMX, TCN and AMX were 789.32, 443.18 and 155.15 μg/mL at 25°C, respectively, which were 2–7 times that for the powdered activated carbon. The adsorption kinetics of antibiotics on the MIEX resin could be simulated by the pseudo-second-order model (R^2 = 0.99), and the adsorption isotherm data were well described by the Langmuir model (R^2 = 0.97). Solution pH exhibited a remarkable impact on the adsorption process and the absorbed concentrations of the tested antibiotics were obtained around the neutral pH. The MIEX resin could be easily regenerated by 2 mol/L NaCl solution and maintained high adsorption removal for the tested antibiotics after regeneration. Anion exchange mechanism mainly controlled the adsorption of antibiotic and the formation of hydrogen binding between the antibiotic and resin can also result in the increase of adsorption capacity. The high adsorption capacity, fast adsorption rate and prominent reusability make the MIEX resin a potential adsorbent in the application for removing antibiotics from water.

Introduction

Antibiotics have been widely used in veterinary and human medicine, but these compounds pose potential risks to human health and aquatic ecology when released into the environment (Watkinson et al., 2009). Now their residues have been detected worldwide in aquatic environment including surface, ground, and even drinking water (Nikolaou et al., 2007; Kim et al., 2010). Although the concentrations were generally reported to be in the range of ng/L to μg/L levels, long-term exposure even to the low level of antibiotics could induce chronic allergic reactions, toxic effects and potential development of antibiotic resistant bacteria (Boxall et al., 2003; Baquero et al., 2008).

* *Corresponding author*. E-mail: wwben@rcees.ac.cn (W. Ben).

http://dx.doi.org/10.1016/j.jes.2016.03.017
1001-0742 © 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

As conventional water treatment processes, such as coagulation, flocculation, sedimentation and ultraviolet irradiation, were relatively ineffective in eliminating antibiotics from water (Adams et al., 2002; Huerta-Fontela et al., 2011), some novel technologies including nanofiltration, reverse osmosis, advanced oxidation and adsorption have been developed in recent years. However, the use of membrane separation technologies is hampered by the problem of membrane fouling, and advanced oxidation processes may cause the formation of undesirable oxidation by-products, which hinder their popularization in water treatment plants. Adsorption is considered as an effective method to remove antibiotics from water. Activated carbon is the most widely used adsorbent in water treatment for the removal of organic micro-pollutants. Nevertheless, it is also known as a broad-spectrum adsorbent presenting lower selectivity for antibiotics (Choi et al., 2008), and high cost is needed to regenerate the activated carbon. Thus, more highly-selective and easily-regenerative adsorbents need to be explored for effectively removing antibiotics from water.

Magnetic ion exchange resin (MIEX) is a strong base anion exchange resin with iron oxide integrated into a macroporous, polyacrylic matrix, and is typically used with chloride as the exchangeable ion. In contrast to traditional anion exchange resins, the MIEX resin has a larger surface area due to the very small resin bead size. The average size in diameter of MIEX resin is 150–180 μm (2–5 times smaller than traditional resins), which may lead to fast adsorption of pollutants on the MIEX resin surface (Fearing et al., 2004; Hsu and Singer, 2010). Furthermore, the saturated resin can be easily regenerated using brine (Kitis et al., 2007). It was reported that the MIEX resin was effective in removing NOM from drinking water sources at relatively low dose (*i.e.*, 5 mL/L), while bromide can be removed to different levels from water depending on the alkalinity and initial bromide ion concentration (Boyer and Singer, 2005). The adsorption efficiencies of MIEX resin for micro-pollutants from water were also studied. Humbert et al. (2008) evaluated the removal of two pesticides (*i.e.*, atrazine and isoproturon) from surface water using a series of strong anion exchange resins. The results showed that the MIEX resin dosage of 8 mL/L only brought about the removal of 7% and 5% for atrazine and isoproturon, respectively. As for 2, 4-dichlorophenoxyacetic acid, a widely used herbicide on crops, the removal efficiency was greater than 80% at MIEX resin dosage of 1 mL/L (Ding et al., 2012). These results suggest that the removal efficiencies of micro-pollutants with MIEX resin are closely related to the characteristics of the target objects. To the best of our knowledge, the research about the removal of antibiotics by MIEX resin adsorption is still very limited.

This study aimed to investigate the adsorptive removal of three representative antibiotics from water using MIEX resin. The selected antibiotics were sulfamethoxazole (SMX), tetracycline (TCN) and amoxicillin (AMX), which were detected with high frequency in the aquatic environment (Heberer, 2002). The adsorption kinetics and isotherms of antibiotic on the MIEX resin were determined through batch experiments, and the removal mechanism was explored. In addition, the adsorption isotherms of these antibiotics on powdered activated carbon (PAC) were studied for comparison.

1. Materials and methods

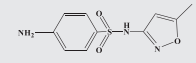
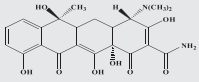
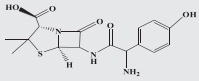
1.1. Chemicals and materials

Three antibiotics (SMX, TCN and AMX) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The organic solvents, methanol and acetonitrile, were of high performance liquid chromatography grade. Other chemicals were purchased from Beijing Chemical Reagents Company (Beijing, China) with analytical grade. The MIEX resin was virgin resin provided by Orica Watercare (Melbourne, Australia). The stock solution of antibiotics was prepared individually at a concentration of 100 mg/L in ultrapure water, which was produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA) with a resistivity of >18.2 MΩ. The major physicochemical properties of the selected antibiotics are provided in Table 1.

1.2. Experimental setup

To determine the adsorption kinetics of antibiotics on MIEX resin, batch experiments were conducted in magnetically stirred 100 mL glass conical flasks at room temperature of 25 ± 0.5°C. Each flask was added with 250 μL MIEX resin and 50 mL of an aqueous antibiotic solution at an initial concentration of 20, 100 and 500 μg/L, respectively. The solution pH was not controlled, which changed by less than 0.2 units after adsorption. A series of 1 mL of samples were taken out at pre-selected reaction times and were filtered through 0.22 μm PES syringe filters (Pall, USA). The residual antibiotic concentration was determined. Control experiments with 50 mL of aqueous antibiotic solution were conducted simultaneously in the absence of MIEX resin for comparison purposes. The adsorption isotherms were performed with a series of different initial antibiotic concentrations ranging from 100 to 5000 μg/L, the dose of MIEX resin and PAC were set as 5 mL/L and 20 mg/L, respectively. The adsorption experiment lasted for 30 min, which was sufficient to reach equilibrium. The effect of pH on the adsorption of antibiotics was evaluated with varying initial pH of solution from 3 to 11 by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solution. All experiments were performed in duplicate.

Table 1 – Major physicochemical properties of the selected antibiotics.

Antibiotics	Chemical formula	Molecular weight	Molecular structure	p*Ka*[a]	logK_{ow}[b]
SMX	$C_{10}H_{11}N_3O_3S$	253.28		1.85 ± 0.30 5.60 ± 0.04	0.89
TCN	$C_{22}H_{24}N_2O_8$	444.43		3.32 ± 0.10 7.78 ± 0.15 9.58 ± 0.15	-1.37
AMX	$C_{16}H_{19}N_3O_5S$	365.40		2.68 ± 0.10 7.49 ± 0.10 9.63 ± 0.10	0.87

[a]Goddard et al., 1996; Qiang and Adams, 2004.
[b]Machatha and Yalkowsky, 2005.
SMX: sulfamethoxazole; TCN: tetracycline; AMX: amoxicillin.

Please cite this article as: Wang, T., et al., Adsorptive removal of antibiotics from water using magnetic ion exchange resin, J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.03.017