JOURNAL OF ENVIRONMENTAL SCIENCES 31 (2015) 226–234

Available online at www.sciencedirect.com

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JOURNAL OF ENVIRONMENTAL SCIENCES

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Adsorption of three pharmaceuticals on two magnetic ion-exchange resins

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ARTICLE INFO

Article history:
Received 31 July 2014
Revised 16 September 2014
Accepted 19 September 2014
Available online 21 February 2015

Keywords:
Pharmaceuticals
Adsorption
Resins
Ion-exchange
Electrostatic interactions

ABSTRACT

The presence of pharmaceuticals in aquatic environments poses potential risks to the ecology and human health. This study investigated the removal of three widely detected and abundant pharmaceuticals, namely, ibuprofen (IBU), diclofenac (DC), and sulfadiazine (SDZ), by two magnetic ion-exchange resins. The adsorption kinetics of the three adsorbates onto both resins was relatively fast and followed pseudo-second-order kinetics. Despite the different pore structures of the two resins, similar adsorption patterns of DC and SDZ were observed, implying the existence of an ion-exchange mechanism. IBU demonstrated a combination of interactions during the adsorption process. These interactions were dependent on the specific surface area and functional groups of the resin. The adsorption isotherm fittings verified the differences in the behavior of the three pharmaceuticals on the two magnetic ion-exchange resins. The presence of Cl^- and SO_4^{2-} suppressed the adsorption amount, but with different inhibition levels for different adsorbates. This work facilitates the understanding of the adsorption behavior and mechanism of pharmaceuticals on magnetic ion-exchange resins. The results will expand the application of magnetic ion-exchange resins to the removal of pharmaceuticals in waters.

Introduction

Pharmaceuticals end up in natural waters after their excretion in unmetabolized form or as active metabolites, from the effluent of wastewater treatment plants (Ankley et al., 2007; Ternes et al., 2004). Continuous loading to aquatic systems causes pharmaceuticals to behave as pseudopersistent (Subedi et al., 2013; Rivera-Utrilla et al., 2013). It has been reported that sulfonamides were detected at concentrations of 24–385 ng/L in the Haihe River Basin, China (Luo et al., 2011). Diclofenac and ibuprofen, which are two of the most frequently detected pharmaceuticals present in wastewater, were found at levels up to μg/L in aqueous environments (Cho et al., 2011; Zhang et al., 2008). However, many pharmaceuticals possess toxicities similar to industrial chemicals, and exhibit the potential to induce adverse effects in humans even below 1 ng/L (Murray et al., 2010; Pomati et al., 2006). Thus, the treatment of pharmaceutical effluents has long been a major concern.

Several treatment technologies for pharmaceutical removal have been extensively investigated. These technologies include activated sludge systems (Carvalho et al., 2013), membrane bioreactors (Kovalova et al., 2012; Martinez et al., 2013), photocatalytic oxidation processes (Martinez et al., 2013), and adsorption processes (Domínguez et al., 2011). Regardless of the technology applied, adsorption is always involved (Landry and Boyer, 2013). Many researchers have investigated the adsorptive removal of pharmaceuticals by activated carbon (Guedidi et al., 2013; Mestre et al., 2009), carbon nanotubes (Ji et al., 2010; Cho et al., 2011), soils (Sukul et al., 2008), natural aquifer materials (Hari et al., 2005), and sediment (Stein et al., 2008; Kibbey et al., 2007). However, these natural or engineered adsorbents have a number of drawbacks in

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http://dx.doi.org/10.1016/j.jes.2014.09.035
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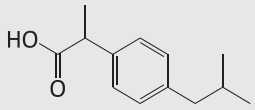
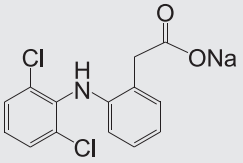
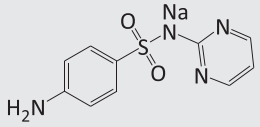
Table 1 – Molecular structure and physicochemical properties of ibuprofen (IBU), diclofenac sodium (DC), and sulfadiazine sodium (SDZ).

Compound	Structure	Molecular weight	pKa	$logK_{ow}$
IBU		206.3	4.9	3.97
DC		296.1	4.0–4.2	1.56
SDZ		250.28	1.57/6.50	−0.09

terms of economic feasibility, applicability, effectiveness, and regeneration problems.

Magnetic ion-exchange resin (MIER) is a strong base anionic resin with ammonia functional groups and a magnetized component within its structure that enables it to act as a weak individual magnet (Mergen et al., 2008). Compared with traditional ion-exchange resins, MIER has been designed for use in a suspended manner in a completely mixed flow reactor instead of a fixed bed. This condition increases its turbulence and decreases resistance to mass transfer, thus making the MIER particles hydraulically large and kinetically fast (Kitisa et al., 2007; Boyer et al., 2008; Bäuerlein et al., 2012b). Aside from the polyacrylic matrix and quaternary amine functional groups, the surface area and pore diameter of a resin are also important factors in its adsorption capacity. Considering the structures of MIER and pharmaceuticals, the removal of pharmaceuticals by MIER is expected to be an effective technique (Landry and Boyer, 2013). However, information on pharmaceutical removal by magnetic ion exchange resins remains limited. Whether pharmaceuticals interact only with the functional groups on the backbone of MIER or are adsorbed onto the pore surface by a weak physical attraction remains unclear. Insight into the relationship between pharmaceutical structure and adsorptive interaction enables the prediction of the fate of pharmaceuticals in purification processes with suitable resins or the development of new types of MIER corresponding to certain pharmaceuticals.

In this study, two widely used nonsteroidal anti-inflammatory drugs, ibuprofen (IBU) and diclofenac (DC), and an extensively consumed antibiotic, sulfadiazine (SDZ), were selected as model pharmaceuticals. MIER1 and MIER2, two kinds of magnetic ion-exchange resins, were used to remove the three selected pharmaceuticals. The most important factors controlling the adsorption of pharmaceuticals onto the MIERs include the type of active adsorption sites available, the nature of the pharmaceuticals, and the observed adsorption isotherms. This study aims to elucidate the affinity between the selected pharmaceuticals and resins. Adsorption kinetics and the effect of co-existing anions were also investigated.

1. Materials and methods

1.1. Adsorbates

IBU (99%), DC sodium (98%), methyl acrylate (MA), benzoyl peroxide (BPO), iron(III) chloride, iron(II) sulfate, ammonia solution (25 wt.%), methanol (Mt), sodium chloride and gelatin were purchased from Sinopharm Chemical Reagent Co., Ltd., China. SDZ sodium (99%) was purchased from Sigma-Aldrich Chemical Co. (Shanghai, China). Divinyl-benzene (DVB, 65%), g-meth-acryloxypropyl-trimethoxy-silane (g-MPS, 98%), N,N-dimethyl-1,3-propanediamine (DMPDA, >99%), and monochloro-methane (MCM, 98%) were all of industrial grade. Table 1 shows the physiochemical properties of IBU, DC, and SDZ.

1.2. Adsorbents

MIER1 was obtained from Orica Watercare of Victoria. MIER2 was synthesized through suspension polymerization of 40.0 g MA and 10.0 g DVB in a glass flask with 0.5 g of BPO as the initiator, in the presence of 10.0 g of Fe_3O_4 magnetic particles modified with g-MPS, 1 wt.% gelatin and 10 wt.% NaCl employed as the dispersion phase. The mixture was stirred at 70°C for 20 hr. The resin was washed with methanol and deionized water repeatedly to remove the unpolymerized monomer. After drying at 60°C, the microspheres underwent aminolysis with DMPDA and subsequently alkylated with MCM to form quaternary ammonium groups. After washing with distilled water three times, all of the aminolyzed microspheres were alkylated by reaction with MCM at 0.5 MPa in 500 mL of 10% NaOH solution. The resin MIER2 was rinsed repeatedly with distilled water until the effluent was neutral. The resins were repeatedly washed with ultra-pure water to remove the impurities and then vacuum desiccated at 40°C for 24 hr before use. Nitrogen adsorption and desorption experiments were carried out at 77 K to determine the surface properties of the resins. The BET surface area was calculated from the adsorption–desorption isotherms using the standard Brunauer–Emmett–Teller equation. All calculations were performed automatically by an Accelerated Surface Area and Porosimeter system (ASAP 2010, Micromeritics, USA). The infrared spectra of the two resins were obtained with a Nicolet 170 SX IR Spectrometer (Madison, WI, USA). Table 2 shows the characteristic properties of MIER1 and MIER2.

1.3. Adsorption assay

For the kinetics studies, a fixed dosage (0.05 g) of resin was added into a set of 150 mL conical flasks containing 100 mL of