Environmental Pollution 214 (2016) 524–531

Contents lists available at ScienceDirect

Environmental Pollution

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

Insight into the adsorption of PPCPs by porous adsorbents: Effect of the properties of adsorbents and adsorbates☆

Zengyin Zhu [a, b], Jiawen Xie [a], Mancheng Zhang [b], Qing Zhou [a, *], Fuqiang Liu [a]

[a] State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China
[b] Jiangsu Province Key Laboratory of Environmental Engineering, Jiangsu Provincial Academy of Environmental Science, Nanjing 210036, PR China

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
11 April 2016
Accepted 19 April 2016

Keywords:
Magnetic resin
Activated carbon
Hydrophobicity
Kinetics
Recyclability

ABSTRACT

Adsorption is an efficient method for removal of pharmaceuticals and personal care products (PPCPs). Magnetic resins are efficient adsorbents for water treatment and exhibit potential for PPCP removal. In this study, the magnetic hypercrosslinked resin Q100 was used for adsorption of PPCPs. The adsorption behavior of this resin was compared with those of two activated carbons, namely, Norit and F400D. Norit exhibited the fastest adsorption kinetics, followed by Q100. Norit featured a honeycomb shape and long-range ordered pore channels, which facilitated the diffusion of PPCPs. Moreover, the large average pore size of Q100 reduced diffusion resistance. The adsorbed amounts of 11 PPCPs on the three adsorbents increased with increasing adsorbate hydrophobicity. For Q100, a significant linear correlation was observed between the adsorption performance for PPCPs and hydrophobicity (logD value) of adsorbates ($R^2 = 0.8951$); as such, PPCPs with high logD values (>1.69) could be efficiently removed. Compared with those of Norit and F400D, the adsorption performance of Q100 was less affected by humic acid because of the dominant hydrophobic interaction. Furthermore, Q100 showed improved regeneration performance, which renders it promising for PPCP removal in practical applications.

1. Introduction

Several PPCPs have been in the waiting list of priority monitoring and control pollutants of USEPA and EU Water Framework Directive because of the significant influences of these compounds on human health and the environment. Most PPCPs exhibit persistence or false persistence, which results from continuous emissions from human activities. Various PPCPs have been detected from surface water, sediments, wastewater, and drinking water in the ng/L to μg/L concentration range (Bunzel et al., 2013; Carmona et al., 2014; Collado et al., 2014; Wang et al., 2015a, d), even as high as 20 mg/L in wastewater treatment plants with low flow and high populations equivalents under specific circumstances (Petrovic et al., 2009; Ratola et al., 2012). PPCPs in the environment show biological activity and chronic toxicity (Brausch and Rand, 2011; Symsaris et al., 2015), thereby conferring microbial resistance and affecting the growth and development of aquatic organisms (Boxall et al., 2012; Overturf et al., 2015). Therefore, efficient methods must be developed for the removal of PPCPs from the aquatic environment.

Various technologies, such as coagulation, membrane filtration, and ozonation, are used for PPCP removal, but several studies reported that these methods demonstrate poor efficiency or have high operational costs (Alexander et al., 2012; Chen et al., 2015; Nakada et al., 2007; Yoon et al., 2006). Adsorption technology exhibits potential for PPCP removal from the aquatic environment. Many adsorbents, such as activated carbon, polymer resins, zeolite, biochar, multi-walled carbon nanotubes, mesoporous silica, graphene, and composites, are applied for PPCP removal (Attia et al., 2013; Boxall et al., 2012; Chen et al., 2015; Escher et al., 2008; Liu et al., 2014; Zhou et al., 2012). In particular, activated carbon is extensively employed for PPCP removal because of its excellent adsorption performance and simplicity of operation (Kilduff et al., 1998). However, the practical applications of activated carbon are limited because of its poor regeneration and recyclability (Wang et al., 2015d). Moreover, the useful life of activated carbon

---

Abbreviations: PPCP, pharmaceuticals and personal care product; CBZ, carbamazepine; SMZ, sulfamethazine; CA, clofibric acid; PMD, primidone; BPA, bisphenol A; DMP, dimethyl phthalate; IBF, ibuprofen; TMP, trimethoprim; OTC, oxytetracycline; CP, chloramphenicol; AMC, amoxicillin; HA, humic acid; OA, oleic acid.

☆ This paper has been recommended for acceptance by Baoshan Xing.

* Corresponding author.
E-mail address: zhouqing@nju.edu.cn (Q. Zhou).

http://dx.doi.org/10.1016/j.envpol.2016.04.070

significantly decreases in the presence of natural organic matter in the aquatic environment because of competition for adsorption sites and pore blockage (Kilduff et al., 1998; Wang et al., 2015b). In this regard, the application of polymer resins, particularly magnetic resins, has gained increased attention (Ma et al., 2014a; Wang et al., 2015b). Magnetic resins feature high adsorption capacity, easy separation, and regeneration. These resins also require the use of a completely mixed contactor, instead of a fixed-bed column, for flux enhancement and cost reduction.

MIEX (Orica Pty Ltd., Australia) and NDMP (Nanjing University, China) are widely used magnetic resins; these ion exchange resins are employed for efficient removal of ionic compounds (Boyer et al., 2011; Shuang et al., 2013) but cannot adsorb neutral molecules (Humbert et al., 2005, 2008). In our previous work, a novel magnetic hypercrosslinked resin was prepared and applied for efficient adsorption of organic contaminants. However, previous studies only focused on removal of individual contaminants, such as tetracycline and atrazine (Wang et al., 2015c; Zhou et al., 2012). PPCPs in the environment contain various contaminants with different properties, including hydrophobicity, hydrophilicity, and amphotericity. As such, the adsorption mechanism of PPCPs with diverse properties must be investigated for practical applications. In particular, the antifouling performance of novel adsorbents must be evaluated.

This work primarily aims to compare the adsorption of 11 PPCPs on the magnetic hypercrosslinked resin and two activated carbons. The influence of adsorbate properties, such as hydrophobicity, on adsorption performance was studied. The underlying mechanism of PPCP removal by magnetic resin was also discussed. Furthermore, the effects of HA on the adsorption and reusability of the three adsorbents were evaluated.

2. Experimental

2.1. Chemicals

Coal-based activated carbon Norit and wood-based activated carbon F400D were provided by Sigma–Aldrich Co. LLC. (USA). CBZ, SMZ, CA, PMD, BPA, DMP, IBF, TMP, OTC, CP, AMC, and divinylbenzene were purchased from J&K Chemical Ltd. (Shanghai, China). Ferrous salts, OA, benzoyl peroxide, polyvinyl alcohol, toluene, sodium sulfate, and 1,2-dichloroethane were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). HA was purchased from J&K Chemical, Ltd and produced by Alfa Aeser company from the decomposition of dead plants. The molecular weight and elemental analysis of HA were listed in Table S1. HA is regarded as macromolecular substance as 76.9% of HA are the fraction with molecular weight larger than 10,000 Da. The surface charge of HA is negative at pH 2–11 (Fig. S1). The other detailed characterization has been conducted in our previous work (Shuang et al. 2014).

The activated carbons were ground to obtain fine particles with diameter of 100–150 μm, similar to that of Q100.

2.2. Preparation of magnetic hypercrosslinked resin Q100

Magnetic hypercrosslinked resin was prepared using our previously reported method (Zhang et al., 2014; Zhou et al., 2012). Briefly, Fe_3O_4 magnetic nanoparticles were synthesized through coprecipitation reaction and modification by OA in alkaline solution. OA-coated Fe_3O_4 nanoparticles, divinylbenzene, benzoyl peroxide, and toluene were mixed as the oil phase and dispersed in the aqueous phase containing PVA and sodium sulfate. The suspension was polymerized to obtain the magnetic beads. The beads were then swelled in 1,2-dichloroethane and post-crosslinked in the presence of the catalyst Fe_3O_4. The ethanol and DI water were used to wash away the porogen, unreacted monomer, and dispersing agent. After washing with ethanol and DI water for five times respectively, the resultant resin was dried at 333 K for 12 h and the obtained resin was denoted as Q100. The magnetic hypercrosslinked resin Q100 was revived in methanol prior to use.

2.3. Characterization

The surface morphology of adsorbents was observed through scanning electron microscopy (S-3400N, Hitachi, Japan). Specific surface area and pore size distribution were determined by N_2 adsorption–desorption experiment using Brunauer–Emmett–Teller equation and Barrett, Joyner, and Halenda method. All calculations were conducted automatically using the accelerated surface area and porosimeter system (ASAP 2010, Micromeritics, USA).

2.4. Adsorption assay

The performance of the three adsorbents on the adsorption of 11 PPCPs was conducted with the same procedure. Briefly, 0.01 g of the adsorbent was mixed with 100 mL of 10 mg/L PPCP solution ($pH = 7$) in a series of conical flasks, which were shaken at 293 K for 24 h. For the kinetics study, 0.1 g of the adsorbent was shaken with 1000 mL of 10 mg/L PPCP solution and sampled at different time intervals. Competitive adsorption experiment was conducted for each PPCP (10 mg/L) in the presence of HA (20 mg/L).

For the batch adsorption tests, 0.01 g of adsorbent was shaken with 200 ml of the PPCP solution with an initial concentration of 20 μg/L in the presence of 3.5 mg/L of HA for about 12 h. The effluent solution was decanted and sampled. Next, a new batch of the simulative solution was added to the conical flasks. The adsorption experiments were repeated until the PPCP concentration of the effluent exceeded 3 μg/L. The total volume of treated simulative water was recorded, and the adsorbents were regenerated. The above batch experiments were repeated until the adsorbents exhausted.

For regeneration evaluation, the adsorption was conducted with 10 mg/L PPCP solution in the absence of HA, and then the adsorbent was separated from the solution and washed with distilled water. Methanol (5 mL), as desorption agent, was mixed with the adsorbent for 10 min. The adsorbent was then rinsed with distilled water.

The experiments were all conducted with three batches of parallel, and the average values were used with errors less than 5%.

3. Results and discussion

3.1. Characterization

The adsorbents investigated in this work exhibited varied different physicochemical properties. Q100 featured a spherical shape and a relatively smooth surface (Fig. 1A). Norit was characterized by honeycomb shape and long-range ordered pore channel (Fig. 1B). F400D possessed irregular compact particles and a rough surface (Fig. 1C). Table 1 provides a list of the physicochemical properties of the three adsorbents. All adsorbents possessed large specific surface area, with Q100 having the largest value (1308 m^2/g). Q100 also possessed a mesoporous structure and exhibited the highest mesopore volume and the lowest micropore volume. F400D showed the smallest average pore diameter (2.16 nm) because of its high microporosity. Norit demonstrated a large average pore size (3.21 nm) with abundant micropores and mesopores. The surface of Q100 had no oxygenic or nitrogenous functional groups because this resin was synthesized from divinylbenzene (Ma et al., 2014b; Zhang et al., 2014; Zhou et al.,