



Reusable magnetic microspheres for efficient removal of atrazine in aqueous media



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HIGHLIGHTS

- Q150 exhibited higher adsorption capacity and better reusability than 1240AC.
- A small dose of Q150 was needed to reach a high atrazine removal efficiency.
- Q150 prevented fouling more than 1240AC due to its weak direct site competition.
- The micromolecular DOM accumulated inside Q150 and cause pore blockage.
- NDMP pretreatment improved the performance of Q150 for atrazine adsorption.

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ABSTRACT

In this study, a magnetic hypercrosslinked microsphere (Q150) was prepared and used for organic micropollutants (OMPs) removal. Q150 has a high surface area (1103.6 m²/g) with a narrow particle size distribution (10–30 μm). The high saturation magnetization (9.6 emu/g) of Q150 demonstrates its excellent separation ability. The adsorption behaviors of a typical OMPs, atrazine, were studied and a commercial powdered activated carbon, 1240AC, was selected as comparison. Q150 and 1240AC both displayed fast adsorption kinetics, and the adsorption followed a pseudo-second-order equation ($R^2 > 0.99$). Q150 exhibited a slightly larger adsorption capacity (107.1 mg/g) for atrazine than 1240AC (101.8 mg/g). The most cost-effective adsorbent dose was 0.06 g/L at an initial atrazine concentration of 20 μg/L, resulting in an atrazine removal efficiency that was higher than 99.5%. Q150 could treat 600 ml more of the atrazine solution than 1240AC in a single batch before reaching a breakthrough point (3 μg/L). In the presence of dissolved organic matter (DOM), the water treatment volume of Q150 decreased by 29.2%, which is less than that observed for 1240AC (47.6%). 1240AC completely lost its adsorption capability after 3 adsorption–desorption cycles, whereas Q150 maintained approximately 50% of the initial adsorption capacity after 6 repeated uses. NDMP (magnetic anion exchange resin) pretreatment removed 45.2% of DOM, which improved the atrazine treatment capability of Q150 by 20.8% and enhanced the reusability.

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1. Introduction

Organic micropollutants (OMPs) primarily include pesticides, endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs) [1,2]. OMPs typically have low water solubility and high lipid solubility, which renders them bioaccumulative in organisms where lipids are an indispensable component. Therefore, although OMPs are present at trace concentrations in the environment, bio-enrichment through the food chain will eventually pose a threat to human health. According to previous studies [3–5], OMPs can induce drug resistance in

microorganisms. In addition, OMPs can disrupt the development of the reproductive, nervous and immune systems of humans and animals [6–8]. Some OMPs are considered carcinogenic [9,10].

Conventional water treatment processes are not sufficient for the elimination of OMPs [11–13]. Therefore, advanced treatment technologies are needed to enhance their removal [14,15]. Adsorption technology has been extensively used for the removal of OMPs due to its simplicity of operation and low cost [16,17]. As the most common adsorbent, activated carbon exhibits high removal efficiency for organic contaminants, such as colored compounds, odorous substances and pesticides [18,19]. Nevertheless, its practical applications are largely restricted due to numerous drawbacks including weak mechanical strength, difficulty of desorption, low reusability and high operational costs [20,21]. More importantly,

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the high concentrations of dissolved organic matter (DOM) (mg/L level) that are present in nearly all natural water bodies will compete with OMPs (ng/L– μ g/L level) and block the pores of activated carbon decreasing the adsorption efficiency of OMPs [22–24].

In comparison to activated carbon, synthetic resins have distinct advantages, such as high adsorption selectivity, great adsorption capacity, adjustable structures, high mechanical strength and high reusability. Therefore, resins have been widely utilized in the field of water treatment. In addition, adsorption resins exhibit an excellent removal rate for OMPs due to their high specific area and abundant functional groups [25–27]. The hydrophobic backbone of resins weakly interacts with hydrophilic DOM in natural waters leading to anti-fouling [27]. However, traditional adsorption resins are typically 0.3–1.2 mm in diameter resulting in slow adsorption kinetics. The large investment in the fixed-bed or moving-bed reactor, the operational complexity and the high operation cost render it barely acceptable for practical use. Therefore, to develop a new resin, researchers have focused on diminishing the particle size, enhancing the adsorption capacity, improving the efficiency and reinforcing the antifouling property. However, smaller particles are more difficult to recycle during practical application. To prevent the loss of powdered resins during use, magnetic nanoparticles incorporated into adsorbents have been developed to achieve facile separation [28]. MIEX[®] resin developed by Orica is a typical magnetic resin, and its particle size is 150 μ m in diameter, which is 2–5 times smaller than traditional resins. MIEX[®] exhibits fast kinetics, a larger adsorption capacity and easy regeneration, which increases the treatment capacity and reduces the cost. MIEX[®] resin has been applied in drinking water treatment, which displays high efficiency for the removal of both hydrophilic and hydrophobic organic pollutants [29,30].

MIEX[®] resin essentially removes negatively charged DOM by anion exchange. However, most of typical OMPs are non-ionic under natural conditions, which are theoretically difficult to remove by anion exchange resins. Humbert et al. studied the removal of atrazine and isoproturon by MIEX[®] and observed a poor elimination rate (<12%) even after 24 h [28,31]. According to Schaffer et al., MIEX[®] resin exhibits a high removal efficiency (70%) for oestrone at pH > 11 when oestrone is present in an anionic form, and only 30% of the oestrone is removed under neutral conditions [32]. Therefore, the commercially available MIEX[®] cannot effectively eliminate OMPs. Hence, it is necessary to develop a magnetic adsorption resin with a high specific area and large adsorption capacity for OMPs.

The main objective of the current work was to prepare the magnetic adsorption resin with a high surface area and develop a new technology for efficient removal of OMPs based on this resin. For comparison of the adsorption and reuse performance, 1240AC was selected because it is a commercial powdered activated carbon with a similar surface area to the resin. Atrazine, a typical OMPs, was used as an adsorbate in the adsorption experiments.

2. Experimental section

2.1. Chemicals and materials

Divinylbenzene (DVB, 80 wt%), atrazine (97 wt%), and 4',6-diamidino-2-phenylindole (DAPI) were purchased from J&K Chemical Co. Ltd. (China). Alfa HA (J&K Chemical, Ltd) was produced by Alfa Aesar company from the decomposition of dead plants. DVB was extracted with a sodium hydroxide solution to remove inhibitors prior to use. Analytical reagent grade ferric chloride (FeCl_3), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), aqueous ammonia (25 wt%), oleic acid (OA), polyvinyl alcohol, sodium sulfate, p-dihydroxybenzene, toluene,

benzoperoxide (BPO), methanol, 1,2-dichloroethane (DCE), and sodium hydroxide were purchased from Shanghai Chemical Reagent Corp. (China). Ethyl acetate (HPLC grade, JT Baker, Phillipsburg, USA) and methanol (HPLC grade, Tedia, USA) were purchased from Nanjing Jukang (China). Deionized water was used in the study. The commercial powdered activated carbon 1240AC (Noris, Germany) was purchased from the Shanghai Chemical Reagent Corp. (China).

2.2. Preparation of the magnetic microspheres

The Q150 magnetic microspheres were synthesized following a sequence of membrane emulsification, suspension polymerization and post-crosslinking reactions [33]. For the membrane emulsification procedure, the oil phase contained DVB (80.0 g), toluene (240.0 g), BPO (1.0 g) and OA-coated Fe_3O_4 nanoparticles (20.0 g). Polyvinyl alcohol (2.0 g), p-dihydroxybenzene (0.15 g) and sodium sulfate (0.10 g) were dissolved in 500 ml of deionized water to prepare the dispersed phase. The oil phase was passed through a Shirasu porous glass (SPG, SPG Technology Co., Japan) membrane with a pore diameter of 5 μ m and then mixed with the dispersed phase to form the homogeneous emulsion. The homogeneous emulsion was subsequently heated to 358 K for 10 h with stirring. This suspension polymerization process resulted in polydivinylbenzene microspheres. Next, post-crosslinking was performed by adding 50 g of the polydivinylbenzene microspheres to 250 ml of DCE under a nitrogen atmosphere. Then, 4.0 g of FeCl_3 was added and dissolved by stirring for 2 h. The mixture was subsequently heated to 353 K for 12 h. The obtained magnetic microsphere Q150 was isolated using a permanent magnet, washed with methanol and dried at 383 K for 12 h.

2.3. Characterization

A scanning electron microscope (SEM, S-3400N II, Hitachi, Japan) and a transmission electron microscope (TEM, JEM-200CX, JEOL, Japan) were employed to characterize the morphology of the microspheres and the distribution of magnetic nanoparticles in the polymer matrix, respectively. The sample magnetization curves were determined using a vibrating sample magnetometer (Quantum Design MPMS-5S, USA). The surface properties of the adsorbents were measured using nitrogen adsorption–desorption experiments at 77 K. The surface area was calculated using the standard Brunauer–Emmett–Teller (BET) equation. The Barrett–Joyner–Halenda method was used to identify the pore size distribution from the desorption isotherms. All of the calculations were automatically performed using an accelerated surface area and porosimeter system (ASAP 2010, Micromeritics, USA). The pore blockage of the resin was determined using confocal laser scanning microscopy (CLSM, Leica TCS-SP5, Germany).

2.4. Adsorption assay

For the kinetic experiments, 500 ml of the atrazine solution was introduced to two 1000 ml conical flasks. The initial concentration of atrazine was 10 mg/L. The solution was shaken with 0.050 g of adsorbent at 130 rpm and 293 K and sampled at different time intervals. To determine the effect of the adsorbent dose, 500 ml of the atrazine solution with an initial atrazine concentration of 20 μ g/L was shaken with different amounts of adsorbent (i.e., 0.010 g, 0.015 g, 0.020 g, 0.025 g, 0.030 g, 0.035 g) for 2 h. For the breakthrough tests, 100 ml of the atrazine solution with an initial concentration of 20 μ g/L was introduced to two 250 ml conical flasks. The atrazine solution was shaken with 0.100 g of adsorbent for 2 h, decanted and sampled. Next, a new batch of the atrazine solution at the same concentration was added to the conical flasks.

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