



Effect of pore size distribution on tetracycline adsorption using magnetic hypercrosslinked resins



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ABSTRACT

Pore structures are very important factors that influence the adsorption and fouling-resistance properties of adsorbents. This study prepared three magnetic porous resins using different amounts of porogen. The pore volume, average pore size, and specific surface area of the resin improved with increased usage of the solvating porogen toluene. Q100-3, which was obtained at a porogen ratio of 3:1, showed the largest surface area (1322 m²/g) and pore volume (2.8 cm³/g). The increase in average pore diameter improved the adsorption equilibrium of the resins, and the increase in total pore volume and specific surface area enhanced the number of adsorption sites of the adsorbents. Q100-3 showed a larger adsorption capacity for tetracycline (TC) than Q100-1 and Q100-2. Two model compounds of natural organic matter, humic acid (HA) and tannic acid (TA), were chosen to evaluate the fouling-resistance of the resins during TC removal. The resins adsorbed very low amounts of HA (3–13 mg/g); thus, competition between HA and TC was weak. HA molecules, because of their large size, were prevented from transportation into the pores by size exclusion effects, leading to negligible pore blocking. By contrast, because of its small molecular size, TA could be well adsorbed by all three resins. The competitive adsorption experiment demonstrated that the presence of TA had a very important effect on both Q100-1 and Q100-2 in terms of TC adsorption. In particular, the amount of TC adsorbed onto Q100-1 with 200 mg/L TA dropped to only 7.88% of the adsorbed amount of TC on Q100-1 without TA because of serious pore blockage. Adsorbed TA could not cause pore blockage in the magnetic resin Q100-3, which featured an unobstructed internal pore structure. Thus, the decrease in adsorbed amount of TC was controlled to within 3% in this resin.

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1. Introduction

Organic micropollutants (OMPs), including pesticides, pharmaceutically active compounds, and endocrine-disrupting compounds, are ubiquitous in aquatic environments. Low concentrations of these organic contaminants (ng/L to mg/L levels) have been shown to exert significant effects on the health of vertebrates and the ecosystem [1]. However, most OMPs cannot be completely removed by conventional wastewater treatment processes [2]. Thus, the feasibility of many other treatment technologies to remove OMPs from the aquatic environment has been studied.

Among the advanced water treatment practices currently available, adsorption technology is commonly employed to remove OMPs from water because of its many advantages, which include efficiency and cost-effectiveness [3,4]. Activated carbons are the most widely used adsorbents in wastewater treatment and drinking water purification because of their high adsorption capacity [5–7], which renders the material very successful in removing

OMPs with significant ecotoxicity, such as antibiotics and pesticides, from the aquatic environment [8–11].

The pore size distribution of activated carbons plays an important role in the adsorption process. The effective removal capacity of adsorbents is based on their micro- and mesopore structures. Activated carbons preferentially adsorb target compounds when the molecular size of the OMPs is similar to the pore diameter of the adsorbent. When the average pore diameter is smaller than 1.7 times the molecule's second-widest dimension, the target compounds cannot be effectively adsorbed because of size exclusion effects [12]. Thus, microporous activated carbons are more suitable for small molecular substances like phenol, whereas mesoporous materials exhibit better adsorption capacities for compounds with a much larger molecular size.

Natural organic matter (NOM) in aquatic environments is considered to be the main competitor of OMPs during water treatment. In natural water, NOM is usually present at concentrations (mg/L) much higher than those of OMPs (μg/L), resulting in significant competition between the two compounds. This competition could be summed up via two major mechanisms: direct site competition and pore blockage [13,14], both of which may be related to the pore size distribution of activated carbons.

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Increased attention has recently been paid to the use of magnetic resins in water treatment because of their advantages of easy separation and effective regeneration [15–18]. Magnetic resin is used in a completely mixed contactor similar to powder activated carbons (PACs). However, unlike PACs, magnetic resin may be collected by a magnet after adsorption and regenerated for reuse. In our previous work [19], we synthesized several magnetic resins for different uses. Among these adsorbents, the hypercrosslinked magnetic resin Q100 was proven to be effective in removing OMPs from water samples. To fully understand the adsorption characteristics of Q100, the effects of the pore structure and NOM on the adsorption process require further study.

In this contribution, three hypercrosslinked magnetic resins were prepared through suspension polymerization with different porogen contents. Tetracycline (TC), a commonly used antibiotic, was used as a representative OMP in batch adsorption experiments. Humic acid (HA) and tannic acid (TA), two model compounds of NOM with different molecular sizes, were chosen to investigate the effects of NOM on the removal of OMPs by the resins.

2. Experimental

2.1. Chemical

Divinylbenzene (DVB, 80%, wt.%, J&K Scientific Ltd., China) was washed with 20% (wt.%) sodium hydroxide solution and dried with anhydrous sodium sulfate prior to its use. Oleic acid (OA), ferrous chloride (FeCl_2), ferric chloride (FeCl_3), benzoyl peroxide (BPO), toluene, polyvinyl alcohol (PVA), sodium sulfate (Na_2SO_4), 1,2-dichloroethane (DCE), and TA were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). TC (Alfa), fluorescein isothiocyanate isomer I (FITC) and HA (Alfa) were provided by J&K Scientific Ltd. (China).

2.2. Preparation of porous hypercrosslinked resins

The preparation procedures of the porous hypercrosslinked resins have been reported in our previous paper [19]. Briefly, the magnetic nanoparticles were prepared through a coprecipitation reaction in the presence of FeCl_2 and FeCl_3 in alkaline solution and then modified by OA in situ. The oil phase, which contained DVB, BPO, toluene, and OA-coated nanoparticles, was dispersed in the aqueous phase, which consisted of PVA, Na_2SO_4 , and distilled water. The magnetic beads were obtained through suspension polymerization after heating at 358 K for 8 h under stirring in a nitrogen atmosphere. After rinsing and drying, the magnetic beads were swelled in DCE. Finally, the post-crosslinking reaction was carried out at 353 K for 12 h in the presence of anhydrous FeCl_3 as the catalyst. The resultant magnetic hypercrosslinked resin was obtained after washing with ethanol and drying at 60 °C.

2.3. Characterization of the resins

The surface properties of the resins were determined by nitrogen adsorption and desorption experiments at 77 K. The standard Brunauer–Emmett–Teller equation was employed to calculate the surface area of the resins. The pore size distribution was obtained from the desorption isotherms using the BJH (Barrett, Joyner, and Halenda) method. All calculations were automatically performed by an accelerated surface area and porosimeter system (Auto-sorb-iQ2, Quantachrome, USA).

2.4. Adsorption assay

All of the resins were revived in methanol for 4 h before use. To obtain adsorption kinetic data and evaluate the adsorption rates of the samples, 500 mL of 100 mg/L TC solution was poured into a series of 150 mL conical flasks. The solution was shaken with 0.1 g of resin at 293 K and sampled at different time intervals. To investigate the maximum adsorption capacity of the adsorbents, 0.1 g of resin was transferred into a series of 150 mL conical flasks containing a series of TC concentrations. The flasks were then placed in an incubator shaker at 293 K. The concentrations of the residual TC were determined after equilibrium had been achieved. The competitive adsorption experiment was performed using binary systems of TC (200 mg/L) and HA/TA (ranging from 0 to 200 mg/L).

For regeneration, excess solution was removed from the flasks and the resin was washed with distilled water. NaOH solution (pH = 12, 40 mL) as the desorption agent was mixed with the resin for 1 h, after which the separation was performed by an external magnet. The resin was then rinsed with distilled water to restore it to a neutral state.

2.5. Analytical methods

The concentrations of TC in the solutions were determined by HPLC (Agilent 1200, USA) with an ultraviolet detector at 360 nm. The chromatographic column was an Agilent Eclipse C18 (4.6×250 mm, $5 \mu\text{m}$). The mobile phase consisted of 0.02 M ammonium oxalate–acetonitrile mixture (80:20, v:v), and the flow rate was 0.5 mL/min. The amounts of HA/TA in the solutions were obtained by measuring the total organic carbon (TOC).

2.6. Distribution of FITC in resin pores

A confocal laser scanning fluorescence microscope (CLSM, TCS-SP5, Leica, Germany) was used to observe the distribution of fluorescent dye (FITC) adsorbed on resins. FITC was excited at 488 nm, and the fluorescent images were taken at 420–450 nm.

3. Results and discussion

3.1. Characterization of the employed resins

The porous structure of resins is mainly formed by phase separation, which depends on the amount of porogen used and its solvating power [20]. In this work, a solvating porogen, toluene, was used during polymerization to produce a large specific surface area. A series of magnetic hypercrosslinked resins with diverse pore structures was prepared using different amounts of toluene. The physicochemical properties of the resultant resins, as determined by the nitrogen adsorption/desorption method, are listed in Table 1. The pore size and pore volume of the resins significantly improved as the ratio of porogen increased. Large amounts of porogen also led to much wider pore size distributions (Fig. 1),

Table 1
Physicochemical properties of the employed resins.

Resin	Q100-1	Q100-2	Q100-3
Porogen	Toluene	Toluene	Toluene
Porogen ratio ^a	1:1	2:1	3:1
Specific surface area/m ² g ⁻¹	1150	1154	1322
Average pore size/nm	3.3	6.8	8.4
Pore volume/cm ³ g ⁻¹	1.0	2.0	2.8
Micropore volume ratio(%)	18.8	5.6	3.6

^a Porogen ratio means porogen volume/monomer volume.

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