



Rattle-type magnetic mesoporous hollow carbon as a high-performance and reusable adsorbent for water treatment



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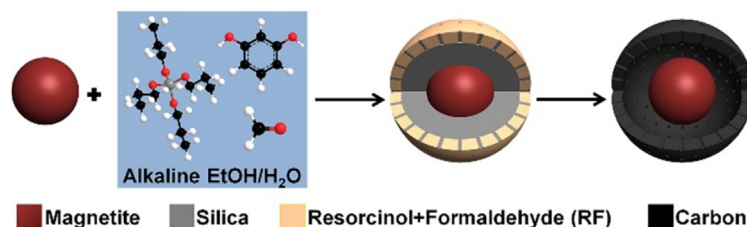
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HIGHLIGHTS

- Synthesis of large pore size rattle-type magnetic mesoporous hollow carbon nanoparticles (RMMHC NPs).
- A new understanding of the influence of carbonization temperature on the properties of RMMHC NPs.
- A superior performance for water treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Rattle-type magnetic mesoporous hollow carbon (RMMHC) materials have shown great promise as adsorbents for water treatment. In this work, we report a surfactant-free synthesis of RMMHC nanoparticles (NPs) using magnetite NPs as the core, tetrapropyl orthosilicate, resorcinol and formaldehyde to form the shell followed by carbonization and selective silica etching. The pore size, specific surface area and pore volume of RMMHC NPs can be tuned by varying the carbonization temperature (500, 700 and 900 °C). At the optimized temperature of 700 °C, the RMMHC NPs possess the highest specific surface area of 579 m² g⁻¹, the largest pore volume of 0.795 cm³ g⁻¹, and the largest pore size of 7.6 nm among all three samples. The adsorption capacity of optimized RMMHC NPs towards di (2-ethylhexyl) phthalate (a model organic pollutant) reaches as high as 783.1 mg g⁻¹. Taking advantage of the magnetic property, the adsorbents retain more than 87% of their initial adsorption capacity over five times' reuse.

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1. Introduction

Water pollution is a challenging issue gathering global attention (Shannon et al., 2008). One major class of water contaminants is organic compounds, such as phthalates, posing serious health risks to mankind (Ali, 2012). Di-(2-ethylhexyl) phthalate (DEHP) is a

widely used chemical in plastic production (de Moura Carrara et al., 2011; Horn et al., 2004). Prolonged exposure to DEHP can lead to a range of adverse effects on the liver, lungs, kidneys and the reproductive system, mainly in males (Huang et al., 2011; Matamoros et al., 2012; Yuan et al., 2010; Yuwatini et al., 2006). Due to the persistent nature of DEHP, conventional treatment methods such as biological degradation, membrane filtration and photo-catalytic degradation are not feasible to remove DEHP from water (Zolfaghari et al., 2014). Adsorption approach has been proved as a simple, effective and time-saving technology for the

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removal of DEHP (Qu et al., 2013; Zolfaghari et al., 2014). Several studies revealed the potential of porous carbon materials with the pore sizes similar to the size of DEHP molecule for the removal of DEHP (Adhoum and Monser, 2004; Tripathi et al., 2014). While adsorption capacities reached as high as 364 mg g^{-1} , reusability remained a concern (Adhoum and Monser, 2004; Tripathi et al., 2014). Thus, developing an effective adsorbent with improved adsorption capacity and recyclability is in urgent need.

Mesoporous hollow carbon (MHC) materials have attracted increasing attention in diverse applications, such as catalysis (Song et al., 2015), adsorption (Xu et al., 2015), and energy storage (Boettger-Hiller et al., 2013). Their wide-spread use results from the unique properties of MHCs including adjustable nanostructures, high specific surface area and large pore volume, chemical and thermal stability, electrical conductivity, and intrinsic hydrophobicity (Liang et al., 2008). In addition, the interior cavity of MHCs could serve as reservoirs and enhance guest molecule loading and the mesoporous carbon shell endows the easy diffusion of guest molecules (Liu et al., 2011; White et al., 2010). Benefiting from these unique features, Guo et al. reported that MHC with a pore size of 3.4 nm showed an adsorption capacity of 304 mg g^{-1} towards bilirubin (Guo et al., 2009). Chen et al. also demonstrated that the adsorption capacity of MHCs towards phenol can reach 207.8 mg g^{-1} (Chen et al., 2016). In a recent breakthrough, Noonan and co-workers attributed the ultra-high adsorption capacity of 5084 mg g^{-1} of DEHP to large mesopore size (8 nm) and total pore volume ($4.88 \text{ cm}^3 \text{ g}^{-1}$) (Noonan et al., 2016). Despite of these achievements, separation of MHC from the treated solution involves disadvantageous procedures such as filtration and centrifugation, which restricted their application as adsorbents for water treatment. Both centrifugation and filtration methods cause a loss of time. The blockage of filters and the loss of adsorbents may occur in the filtration method. The centrifugation method requires very high speeds and energy. The use of magnetic separation method offers an alternative way to solve these problems (Duman et al., 2016a, 2016b; Gholami et al., 2016; Mahdavinia et al., 2014).

To tackle the separation issue, rattle-type magnetic mesoporous hollow carbon (RMMHC) materials have entered into sight as advanced adsorbents for water treatment (Liang et al., 2014; Liu et al., 2014; Shao et al., 2015; Wan et al., 2013; You et al., 2014; Zeng et al., 2013; Zhang et al., 2011). The magnetic property of RMMHC materials facilitates their separation and recovery from complex systems under an external magnetic field, which is promising for adsorbent regeneration and safe disposal of the waste (Hao et al., 2010; Lu et al., 2007). In a pioneering work, Zhang et al. utilized a hard-templating approach to prepare RMMHCs, which involves encapsulation of phenol-formaldehyde resin in the mesopores of preformed hard template of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{meso-SiO}_2$, followed by carbonization and silica removal (Zhang et al., 2011). The preparation process is tedious and time-consuming. Later, Wan and co-workers reported an *in situ* strategy to fabricate RMMHC with a pore size of 3.46 nm, a relatively small pore volume of $0.31 \text{ cm}^3 \text{ g}^{-1}$ and low adsorption capacity (191.64 mg g^{-1}) towards a model pollutant of Rhodamine B, in which octadecyltrimethoxysilane was used as both structure-directing agents and carbon precursors in the presence of magnetic microspheres (Wan et al., 2013). Lately, Liu et al. (2014) developed a one-pot, surfactant-free approach to fabricate RMMHC with a pore size of 4.5 nm through the co-condensation of tetraethyl orthosilicate (TEOS) and resorcinol-formaldehyde resin (RF). However, the lack of open mesopores and low mesopore volume ($<0.3 \text{ cm}^3/\text{g}$) restricted the adsorption capacity of RMMHCs to only 77 mg g^{-1} to adsorb pyrene. Beside the low adsorption capacity, the slow diffusion rate of pollutants is another concern of current adsorbents with relatively small pore sizes (Gibson, 2014). To date, it is still a challenge to

develop a facile approach to prepare RMMHC with large pore sizes ($>4.5 \text{ nm}$) and high pore volume for fast and enhanced adsorption performance of organic pollutants in water.

In the present work, we report a facile and surfactant-free approach to synthesize RMMHC nanoparticles (NPs) using tetrapropyl orthosilicate (TPOS), resorcinol and formaldehyde (RF) as precursors in the presence of magnetic particles (Zhang et al., 2016). The typical procedure is schematically illustrated in Fig. 1. In step I, silica primary nanoparticles are formed owing to the relatively faster polymerization and condensation rate of silica precursors compared to RF precursors, then coat on the surface of magnetite NPs forming magnetite@ SiO_2 core-shell structures (Zhang et al., 2016; Zhang et al. 2015). When RF starts to polymerize, there are still a large amount of silica primary nanoparticles that co-condense with RF oligomers onto magnetite@ SiO_2 , forming magnetite@ $\text{SiO}_2@ \text{SiO}_2/\text{RF}$ core-shell structures (step II). The silica primary nanoparticles and their aggregates in the composite SiO_2/RF shell contribute to the formation of large mesopores (Zhang et al., 2016; Zhang et al. 2015). After carbonization under an optimized temperature of $700 \text{ }^\circ\text{C}$ (step III) and selective removal of SiO_2 component (step IV), RMMHC NPs are obtained with a particle size of 945 nm, a large pore size of 7.6 nm and high mesopore volume of $0.53 \text{ cm}^3 \text{ g}^{-1}$. The novel RMMHC NPs show a high DEHP adsorption capacity of 783.1 mg g^{-1} . Moreover, RMMHC NPs can be reused, retaining 87% of the initial adsorption capacity after 5 cycles.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), tri-sodium citrate dihydrate, urea, ethylene glycol, ammonium hydroxide (28 wt%), TPOS, TEOS, resorcinol, formalin (37 wt%), ethanol, sodium hydroxide, DEHP and acetone were of analytical grade and purchased from Aldrich and used as received. Doubly distilled water obtained from a laboratory purification system was used throughout the experiments.

2.2. Synthesis of magnetite particles

The magnetite particles were prepared through a solvothermal reaction (Cheng et al., 2009). Briefly, 0.811 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.044 g of sodium citrate dihydrate and 1.802 g of urea were completely dissolved in 30 mL of ethylene glycol by ultrasonication and vigorous magnetic stirring. The obtained homogeneous yellow solution was transferred to a Teflon lined stainless-steel autoclave (50 mL capacity) and sealed to heat at $200 \text{ }^\circ\text{C}$. After reaction for 6 h, the autoclave was cooled to room temperature. The obtained black magnetite particles were separated magnetically and washed with ethanol and deionized water three times to eliminate organic and inorganic impurities, and then dried in vacuum at $60 \text{ }^\circ\text{C}$ for 6 h.

2.3. Synthesis of RMMHC NPs

RMMHC NPs were synthesized according to a reported approach with some modifications (Zhang et al., 2016). In a typical synthesis, a mixture consisting of 50 mg of magnetite spheres, 10 mL of water and 70 mL of ethanol was ultrasonicated for 1 h and then injected into a 200 mL three-necked round-bottom flask. Next, 3 mL of ammonia aqueous solution and 2.6 mL of TPOS were added, and the solution was mechanically stirred for 15 min followed by the addition of 0.3 g of resorcinol and 0.42 mL of formalin water solution. After stirring at room temperature for 24 h, the product was separated using a magnet and washed repeatedly with ethanol and water to remove non-magnetic by-products, and subsequently

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