Ordered mesoporous carbon immobilized nano zero-valent iron in bromate removal from aqueous solution

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A B S T R A C T

The present work aims to investigate bromate removal from water with the application of a material nano Fe^0/OMC (ordered mesoporous carbon) composite, under various experimental conditions. The effect of temperature, react time, bromate concentration, etc. on bromate removal efficiency was studied. Removal efficiency of bromate by nano Fe^0/OMC achieved 96.1% with a contact time of 10 min at 298 K. Reduction action dominates the whole process with a little adsorption accompanied, and approximately 90% bromate was restored to bromide. Kinetics models were used to correlate the kinetics experimental data and the kinetics parameters reveal that the kinetics data were well fitted to pseudo-second-order model. The maximum bromate uptake at 298 K was found to be 25.9 mg/g at the initial bromate concentration 10 mg/L, but it changed little with a decrease in temperature. Equilibrium isotherms were analyzed by the Freundlich and Langmuir isotherm models. The data fit favorable to the Langmuir isotherms with high-correlation coefficients (0.941–0.998). The present work shows that the nano Fe^0/OMC composite would be a promising material in the study of drinking water purification.

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1. Introduction

Bromate ion (BrO_3^-) has been classified as a Group 2B substance by the International Agency for Research on Cancer (IARC) and it is frequently formed after ozonation of water containing bromide ion (Br^-) [1–3]. Bromate is a possible carcinogen and a big threat to human health. An effective technique to remove bromate or prevent the formation from drinking water is urgent [4].

Many researchers have used the biological, photocatalytic/ photoelectrocatalytic or electrochemical techniques to remove bromate [5–7]; and also catalytic hydrogenation, reported recently, is applied in the use of bromate removal [8]. However, zero-valent iron (Fe^0) is a promising material for the purification of bromate containing water [9–11]. Nano zero-valent iron has significant reducivity for various pollutants, e.g. chlorinated methanes, decabrominated diphenyl ether, nitroaromatics and heavy metal ions [12–15]. The main advantages of using the iron particles are the mild reaction conditions; and the rapid reaction rate with water contaminants such as bromate, particularly when compared to the conventional physical or chemical methods [16–18]. Although zero-valent iron is widely applied in contaminant remediation, it still has some drawbacks in its utilization. In an aqueous environment, most Fe^0 particles tend to agglomerate due to inter-particle magnetic and Van der Waals interactions. Agglomeration increases the effective particle size, resulting in precipitation [19,20]. Therefore, the major problems of Fe^0 are aggregation and fast oxidation with air. To overcome the two technical challenges, offering a support for Fe^0 particles in/on one certain material might be a viable option. Activated carbon colloids, SBA-15 rods, polyethylene glycol (PEG)/nylon membranes and ordered mesoporous carbon have been used as supports to stablize Fe^0 particles [21–24].

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Researchers chose the porous carbon materials as supports for some nano-metals because they have unique physical characterization and have been used in many fields [25]. Porous carbon can immobilize nano-metal particles to keep them in certain shape. Also, the composite materials may have excellent adsorption capacity because of the large specific area of porous carbon materials. Mackenzie et al. used activated carbon colloids (ACC) and iron salts to synthesize Carbo-Iron® colloid (CIC) and investigated its suitability as a dehalogenation reagent [21]. However, the pore size of activated carbon materials is small and the porous structures may collapse in certain condition, which restrict the application of the materials [26]. Ordered mesoporous carbon can comparatively cover the shortage of AC materials, such as highly ordered porous structure, high specific surface area, controllable pore size, etc. [27,28]. Consequently, OMC has shown an excellent application potential in supporting nano-metals. Ling et al. have used Fe^0/OMC to uptake nitrobenzene [24].

In our previous papers, we reported BrO_3^- uptake from aqueous solution on OMC [29] and nano Fe^0/AC. Considering of the merits of OMC materials, we immobilize nano Fe^0 onto OMC to synthesize a composite material and use the material in the application of bromate ion removal. Batch experiments were conducted to investigate the effects of various parameters (e.g. temperature, time and initial bromate concentration, etc.) on the removal efficiency of BrO_3^-. Additionally, the particle structure, morphology, and surface area were characterized using X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis.

2. Experimental

2.1. Materials and chemicals

The chemical reagents used, such as GR $FeCl_2 \cdot 4H_2O$, C_2H_6O, $NaBrO_3$, NaBr, NaCl, Na_2CO_3, NaOH and HCl, were obtained from Kermel Chemical Reagent. KBH_4 was obtained from Sinopharm Chemical Reagent. Ordered mesoporous carbon (OMC) was synthesized in our laboratory [29]. All chemical reagents were used directly without any pre-treatment. Ultrapure water used for preparing chemical solutions was produced from an ultra-purification system (UPW-I-90T, Chengdu Ultrapure Technology, China).

2.2. Preparation and characterization

The Fe^0/OMC was synthesized using the impregnation method by excess of solution. In a typical procedure, 1.279 g of $FeCl_2 \cdot 4H_2O$ was mixed with 1.799 g OMC (Fe/C mass ratio 1/5) in 90 mL 80% ethanol solution for 30 min to obtain a slurry. Then 0.3 g PEG-4000 was slowly added into the slurry as dispersant and the pH value was regulated to 6.0 with 0.1 mol/L NaOH solution. Next, 0.5 mol/L KBH_4 solution (1.735 g KBH_4 dissolved in 64 mL deionized water) was added drop wise (1 drop/s) into the above mixture while stirring vigorously and the solution was stirred for another 30 min after addition of all KBH_4. The resulting black solid was collected by magnetic separation and washed with deoxygenated water and deoxygenated absolute ethanol consecutively. Finally, nano Fe^0/OMC slurry was dried (approximately 100 °C) using an electric furnace (DK-98-II, Tianjin Taisite Instrument, China) and stored in a N_2-purged chamber before use.

Characterization of solid-phase Fe^0/OMC was carried out using XRD, BET surface area and porosity analysis.

The XRD patterns were conducted with Cu Kα radiation using a Rigaku D/MAX-rA wide-angle goniometer, continuous scans from 10° to 70° and a scanning speed of 8.0°/min.

N_2 adsorption/desorption isotherms were measured with the BET and porosimetry analyzer (JW-BK 122W, Beijing, China) at liquid nitrogen temperature (77 K). The pore size distribution stem from the nitrogen sorption branch was processed with the BJH (Barrett–Joyner–Halenda) method.

2.3. Batch experiments for bromate removal

Dissolve 1.18 g $NaBrO_3$ in 1000 mL ultrapure water to obtain the stock solution of bromate and dilute the stock solution to the desired concentrations during the experiments. Batch adsorption studies were conducted in 250-mL capped conical flasks (Tianjin) containing 100 mL bromate solutions. All the experiments were conducted on a digital freeze water-bath thermostatic rotary shaker (SHA-2(A), Jinnan Instrument Manufacturing, China). Samples were collected and filtrated before to detect the concentrations of BrO_3^- and Br^-. We use 0.1 mol/L NaOH and HCl solutions to attain the desired pH value with a pHS-3C pH meter (Shanghai Precision & Scientific Instrument, China).

All bromine concentrations were measured using a single-column ion chromatograph, and the details were reported in our previous paper [30]. The total iron levels were measured using an atomic absorption spectrophotometer (TAS-990, Beijing Purkinje General Instrument, China).

To investigate the effect of reaction temperature and initial bromate concentration on the removal efficiency of bromate, we conducted two sets of experiments at different time intervals (1, 5, 10, 15, 30, 60 and 120 min). In one set, 1000 μg/L BrO_3^- solutions were treated with 0.35 g/L nano Fe^0/OMC at different temperatures (288, 298 and 308 K). (Note: the dose of nano Fe^0/OMC 0.35 g/L was based on the effect of dosage on the bromate removal (see Supplemental data, Fig. S1).) In the other set, different initial concentrations of BrO_3^- (1.0, 3.0, 6.0 and 10.0 mg/L) were mixed with same concentration of nano Fe^0/OMC at 298 K. All the experiments were done in triplicate.

3. Results and discussion

3.1. Characterization of nano Fe^0/OMC composite

The wide-angle XRD patterns of the three different samples were shown in Fig. 1. For the pure Fe^0 and Fe^0/OMC samples, there was an obvious peak at 45°, then follows a weak diffraction peak at 65°. This is consistent with the results of a previous report by Nurmi et al. [31]. The peak at 45° of nano Fe^0/OMC is weaker and broader than that of pure Fe^0. The phenomenon of peak broadening at 45^0 may be due to the smaller grain size of iron [32] or the lesser percentage of iron on OMC than pure Fe^0.

N_2 adsorption/desorption isotherms and pore size distribution plots obtained for the nano Fe^0/OMC and OMC composite are shown in Fig. 2. The sample exhibits a type IV isotherm with H3-type hysteresis loop based on the International Union of Pure and Applied Chemistry (IUPAC) classification [33]. The type IV isotherm correlates with the capillary condensation, and the H3-type hysteresis loop at a P/P_0 range of 0.2–0.8 indicates an interconnected porous system and percolating pore connectivity [34]. The pore size distribution (Fig. 2(a)) shows that the pores of all the nanoparticles are below 50 nm. The data show a narrow pore size distribution and a most probable diameter of 2.65 nm for nano Fe^0/OMC. The slight decrease in the porosity of nano Fe^0/OMC material may indicate the blocking of some pores in OMC by iron particles [24].

Pristine Fe^0/OMC particles were found to have a higher specific surface area of 118 m^2/g than pure Fe^0 (Table 1). In comparison with OMC, the BET area of Fe^0/OMC is smaller. This decrease may be associated with the inlay of iron particles on the OMC surface and the block of pores due to the iron [24]. For Fe^0 and OMC particles, values of the surface areas were found to be 35 m^2/g and