Preparation of bifunctional hollow mesoporous $Fe^0@C@MnFe_2O_4$ as Fenton-like catalyst for degradation of Tetrabromobisphenol A

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ABSTRACT

Nanoscale zerovalent iron (nZVI) loaded magnetic hollow mesoporous bimetallic Fenton-like catalyst, $Fe^0@C@MnFe_2O_4$, was prepared by a one-pot solvothermal method. Carbon shell of polydopamine (PDA) was formed through self-oxidation of dopamine by adding $MnFe_2O_4$ hollow spheres into dopamine solutions. Then Fe^{2+} ions were adsorbed on the surface of $PDA@MnFe_2O_4$ to obtain active nZVI *in-situ* through subsequent calcinations. Thus, the mesoporous carbon shell of $Fe^0@C@MnFe_2O_4$ had a great contribution to high adsorption capacity for concentrating TBBPA around the catalyst. The high concentration of TBBPA outside would further facilitate the transportation to the inside of the hollow catalyst to achieve a high catalytic efficiency. $Fe^0@C@MnFe_2O_4$, as an integrated adsorbent-catalyst, was used to remove Tetrabromobisphenol A (TBBPA) in aqueous solution with the presence of H_2O_2 and NH_2OH. Over 90% of TBBPA can be removed within 120 min. According to the result of ESI–MS, β-scission and debromination were involved in the degradation of TBBPA. The reused catalyst could be easily separated by using an external magnetic field in seconds. After ten cycles, the catalyst was still of good activity. The excellent removal efficiency of TBBPA might be attributed to the synergistic effect from high adsorption capacity and efficient Fenton-like catalytic reaction of $Fe^0@C@MnFe_2O_4$.

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1. Introduction

Tetrabromobisphenol A [4, 4-isopropyl-idenebis-(2, 6-dibromophenol), TBBPA] is one of the most widely used brominated flame retardants (BFRs) around the world [1]. TBBPA has been ubiquitously detected in the environment [2–7], even in tissues of humans [8] and human milk [9,10]. Due to some structural resemblance of TBBPA to the thyroid hormone thyroxine (T_4), it was suggested that they may interfere with the metabolism and transport of thyroid hormone [11,12] besides of their neurotoxicity [13], cytotoxicity [14] and immunotoxicity [15]. Thus, it's necessary to find an effective way to eliminate TBBPA from environment. Several methods have been reported to remove TBBPA from aqueous solutions, such as sorption [16], photo catalysis degradation [17], and biological degradation [18]. Among these methods, advanced oxidation processes (AOPs) have been considered as an effective way for water purification and recovery [19]. Iron salts as classical Fenton's reagents can activate H_2O_2 to generate active radicals such as •OH and $HO_2^•/O_2^{•-}$ which are known to be very effective in the destruction of many hazardous organic pollutants

in water [20–22]. However, there are some disadvantages such as a low and narrow pH range for usage and possible second environmental contaminants. The development of heterogeneous catalysts has been demanded to overcome the above shortcomings [23–26].

Mesoporous carbon materials have attracted considerable attention because of their unique textural properties, such as large surface area, controllable pore architecture, uniform and tunable pore size and chemical stability which are good for the adsorptive removal of pollutants from aqueous solution [27,28]. Xu et al. prepared adsorbents and catalysts based on multi-walled carbon nanotubes for removal and dechlorination of organic pollutants [29,30]. Liu et al. prepared a novel carbon adsorbent using PDA as a carbon source for the fabrication of carbon shell through self-polymerizing of dopamine at alkaline pH values [31]. The top coating layer of PDA can further bind with metal oxides making it easy to introduce carbonaceous materials onto magnetic metal oxides [32].

Manganese ion (Mn(II)), a common transition metal ion, can react with both •OH and $HO_2^•/O_2^{•-}$, which affect the chain propagation processes. Zhao et al. discovered that the addition of Mn(II) in Fe(III)/H_2O_2 system can promote the production of $HO_2^•/O_2^{•-}$ which would accelerate the formation of Fe(II), then the production of •OH and finally the degradation of organic

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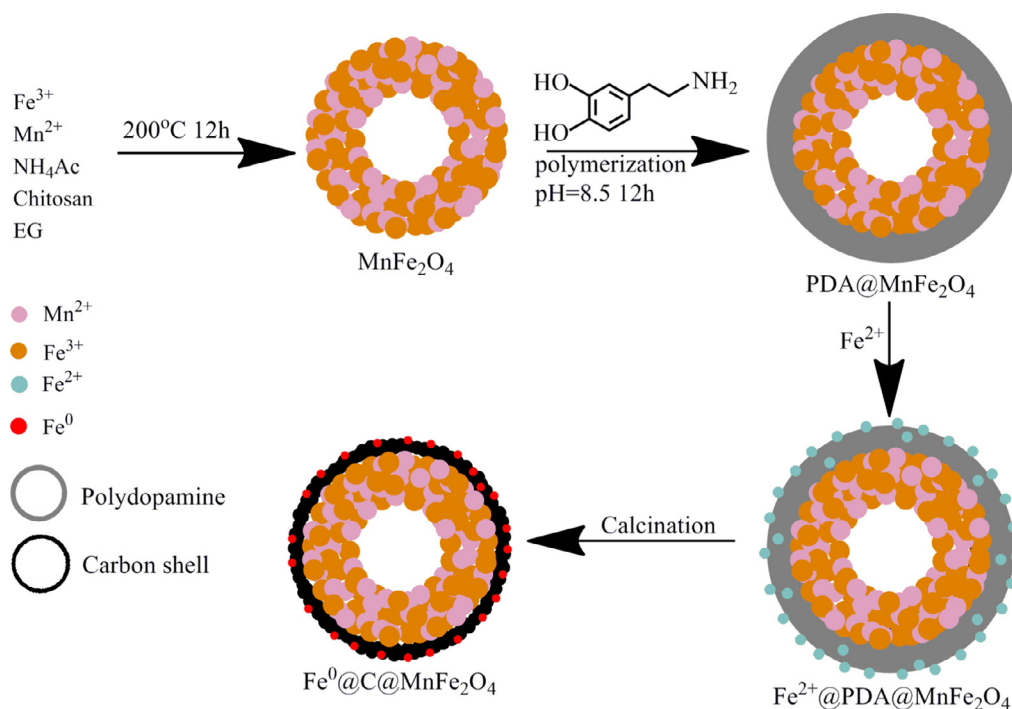**Fig. 1.** Illustration of the synthesis process for fabrication of $Fe^0@C@MnFe_2O_4$.

pollutants [33]. Meanwhile, nano zero-valent iron (nZVI) has been reported that it is able to reductively degrade hazardous organic compounds such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) [34], atrazine [35], organochlorine pesticides [36] and tetrabromobisphenol A (TBBPA) [37]. However, there are few studies focusing on the *in-situ* generation of nZVI on the mesoporous carbon@bimetallic oxide core–shell structure for the efficient removal of TBBPA.

In this study, we synthesized the bimetallic hollow magnetic spheres $Fe^0@C@MnFe_2O_4$ with nZVI loaded on the mesoporous carbon shell. The hollow magnetic spheres were characterized by using SEM, TEM, XRD, FT-IR, RT MS, VSM and BET. The removal efficiency of TBBPA was tested under varying conditions of initial pH of solutions, the dosage of catalyst, and the concentration of H_2O_2 and NH_2OH. The stability and reusability of $Fe^0@C@MnFe_2O_4$ were also examined. It was demonstrated that $Fe^0@C@MnFe_2O_4$ could be used as a potential catalyst for efficient removal of organic pollutants from water.

2. Experiment

2.1. Materials and apparatus

Tetrabromobisphenol A (TBBPA) was purchased from Aladdin Industrial Corporation. NaOH, H_2O_2 and NH_4AC were purchased from Chengdu Kelong Chemical Reagent Company (China). $NH_2OH \cdot HCl$ was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $FeCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$, Chitosan, Terephthalic acid (TA) and *N, N*-dimethylformamide (DMF) were obtained from Tianjin Guangfu Technology Development Co., Ltd. (China). Methylene chloride was purchased from Lianlong pharmaceutical chemical co., ltd (China). All reagents were of analytical grade.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the morphology and structure of $MnFe_2O_4$, $PDA@MnFe_2O_4$ and $Fe^0@C@MnFe_2O_4$. Fourier transform infrared (FT-IR) spectra were obtained by using KBr

pellets on American Nicolet Corp. model 170-SX spectrometer. The crystal structure of the $MnFe_2O_4$, $Fe^0@C@MnFe_2O_4$ and reused $Fe^0@C@MnFe_2O_4$ was obtained by XRD (Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.54056$)). Mössbauer spectroscopy studies were performed using a conventional constant-acceleration drive and a 50 m Ci 57Co: Rh Source. BET surface area, pore volume and pore diameter were measured using the BET method and the Barrett–Joyner–Halenda (BJH) method, respectively. Magnetic properties of $MnFe_2O_4$ and $Fe^0@C@MnFe_2O_4$ spheres were performed on a vibrating sample magnetometer (Lake Shore model 7304, Westerville, OH). The iron and manganese concentration were determined using inductively coupled plasma (ICP). UV–vis detection was carried out on a TU-1810 PC UV–vis spectrophotometer (Purkinje General, Beijing, China). The hydroxyl radical ($\cdot$OH) was detected by a photoluminescence (PL) technique, which was recorded on a F97Pro spectrofluorophotometer (LengGuang Industrial Co., Ltd., Shanghai, China).

2.2. Preparation of $MnFe_2O_4$ hollow spheres

$MnFe_2O_4$ magnetic hollow spheres were prepared by a one-pot solvothermal method [38]. In a typical procedure, 0.49 g of $MnCl_2 \cdot 4H_2O$ and 1.35 g of $FeCl_3$ $6H_2O$ were dissolved in 70 mL of ethylene glycol. Then 12.25 g of NH_4Ac was added to form a clear solution under magnetic stirring, followed by the adding 0.03 g of chitosan under continuous stirring at 250 rpm for 30 min. The resulting mixture was transferred into a 100 mL Teflon-lined autoclave and then heated at 200 °C for 12 h. After reaction, the autoclave was cooled to room temperature. The products were obtained by an external magnetic field and sequentially washed with distilled water and ethanol for several times and then dried in a vacuum oven at 60 °C for 24 h.

2.3. Preparation of PDA coated $MnFe_2O_4$ magnetic hollow spheres

0.1 g of $MnFe_2O_4$ in 50 mL of Tris–HCl buffer solution (1.58 g/L, pH 8.5) was sonicated for 30 min. Then 0.5 g of dopamine was