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Fe/Cu mesoporous carbon supported alumina hollow ceramic membrane for the degradation of ofloxacin

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Abstract. Nanoscale bimetallic Fe/Cu mesoporous carbon supported alumina hollow ceramic membrane were successfully synthesized by spin-coating method. The morphology and physico-chemical properties of catalyst were characterized by XRD, SEM, TEM. The performance of the catalysts was evaluated by the adsorption degradation of ofloxacin. The results showed that the adsorption ability of supported membrane is stronger than that of pure alumina hollow ceramic membrane. Compared with single metal Fe mesoporous carbon membrane, the bimetallic Fe/Cu mesoporous carbon membrane exhibited higher removal ratio (45 % versus 90 %). The possible adsorption and degradation mechanisms are also proposed.

Introduction

The wastewater discharged from factories has characteristics of high concentration, high toxicity and high organic content, such as printing and dyeing wastewater, pharmaceutical wastewater and leather wastewater. It is difficult to achieve the emission standards with the treatment of general municipal sewage treatment system if it is discharged directly into the environment, which seriously affects the ecological environment. Therefore, efforts to develop more efficient, economical and clean water treatment technologies have become an urgent demand for wastewater treatment. At present, the heterogeneous Fenton has attracted widespread attention due to its excellent properties. The choose of catalyst is vital for the heterogeneous Fenton reaction. Mesoporous materials with large specific surface area and uniform pores are widely used, which could provide more active sites and improve the pollutant removal efficiency. But the utilization rate of the catalyst is not high in traditional heterogeneous Fenton reaction. To solve these problems, bimetallic Fe/Cu mesoporous carbon supported alumina hollow ceramic membrane were synthesized in this report. The combination of membrane filtration and mesoporous materials could not only retain the catalytic advantages of mesoporous materials, but also complete catalytic separation simultaneously, which improved utilization ratio of catalyst. The performance of the catalysts was evaluated by the adsorption degradation of ofloxacin, and the possible mechanisms are also proposed.

Experimental

Chemicals. Alumina hollow ceramic tube (length 6 cm, outside diameter 14 mm, internal diameter 8 mm, pore size 500 nm) was purchased from Nanjing Jiuwugaoke Co. Ltd. Pluronics (F127) was purchased from Sigma Aldrich. Ethanol solution of phenolic resin (20 wt%) was prepared in laboratory. Copper(II) nitrate hydrate ($Cu(NO_3)_2{\cdot}3H_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) were analytical grade and purchased from Tianjin Guangfu Chemical Co. Ltd. Absolute ethyl alcohol (CH_3CH_2OH) was used as solvent.

Synthesis of catalysts. Bimetallic Fe/Cu mesoporous carbon precursor were prepared according to the following procedure: Pluronics (F127, 1.0 g) were dissolved in absolute ethyl alcohol (14.0 g), reflux 30 min at 50 ^{o}C. Then 5.0 g ethanol solution of phenolic resin (20 wt%) was added and stirring vigorously for 10 min. $Fe(NO_3)_3{\cdot}9H_2O$ (0.23 g) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.07 g) mixing ethanol solution was added dropwise. The resultant solution was stirred continuously for 30 min. Then the solution was poured into a surface dish and evaporate at room temperature. A spin-coating method was used to coat layer in alumina hollow ceramic tube surface with obtained bimetallic Fe/Cu mesoporous carbon precursor. In brief, the alumina ceramic tube was blocking at both ends. Then the Fe/Cu mesoporous carbon precursor material was uniformly coated on the outer surface of the alumina ceramic tube. The obtained ceramic membrane was solidified at 100 ^{o}C in vacuum oven of 24 h, then calcined at 600 ^{o}C for 5 h (heating rate of 1 ^{o}C/min) in argon gas and get the Fe/Cu mesoporous carbon supported alumina hollow ceramic membrane.

Characterization. The bimetallic Fe/Cu mesoporous carbon hybrid nanoparticles were characterized by X-ray diffraction with Cu Ka radiation (= 0.154 nm) as the X-ray source. The transmission electron microscopy (TEM) was done on a Hitachi H-7650 operated at 100 kV.

Catalytic degradation of ofloxacin. The degradation of ofloxacin (30 mg/l) was conducted on the ceramic membrane surface. First, the ceramic membrane (seal up one end) was placed into the solution of ofloxacin, the other end of ceramic membrane was connected with the circulation pump to provide transmembrane pressure. Then, pH was adjusted to 5 and H_2O_2 (20:1) was added according to with molar ratio of loaded metal on ceramic membrane surface. Ofloxacin was degraded in the activity layer of bimetallic Fe/Cu mesoporous carbon on ceramic membrane surface. Through the ceramic tube carrier, the purified water was separated into the internal hollow part of membrane. The samples of through ceramic membrane were collected for UV-Vis testing at 288 nm. Finally, the ceramic tube carrier was recycled after washing with deionized water and alcohol and drying in vacuum oven.

Results and discussion

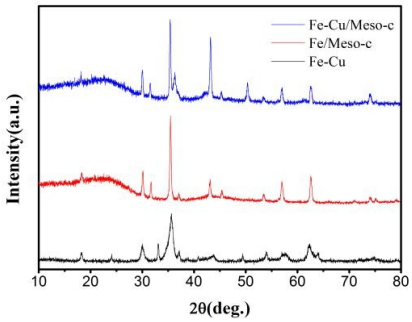

Fig.1. High-angle XRD patterns of pure Fe-Cu, Fe/Meso-C and Fe-Cu/Meso-C catalysts

Characterization of Fe/Cu mesoporous carbon. Fig.1A shows the high-angle XRD patterns of pure Fe-Cu, Fe/Meso-C and Fe-Cu/Meso-C catalysts. The diffraction peak broadened at 25° when metal oxides incorporated into mesoporous carbon, which is related to the metal nanoparticles occupied channels of mesoporous carbon. From Fig.1, the diffraction of 30°, 35°, 43°, 57° and 63° were assigned to (220), (311), (400), (511) and (440) reflections of crystalline □-Fe_2O_3 phases[1]. In addition, the diffraction of 32.5^o, 38.7^o, 46.3^o, 48.7^o, correspond to crystalline CuO phases. These results were consistent with previous studies[2], indicating that the successful Fe/Cu metal oxide crystallization and uniformly dispersion in the carbon matrix.

To further investigate the porous structure and distribution state of metal species, the Meso-C and Fe/Cu Meso-C were investigated by transmission electron microscopy (TEM) and the obtained images are shown in Fig.2. As shown in Fig.2a, the mesoporous carbon exhibits well-arranged lattice stripe and regular hexagonal pore distribution. Although bimetallic metals of Fe and Cu incorporated in the carbon framework (Fig.2b), the ordered arrangement of the lattice fringes could be observed, which indicates that the incorporation of metal nanoparticles did not destroy the structure of mesoporous carbon. In addition, the graphs clearly demonstrate that the Fe/Cu nanoparticle were well dispersed in the structure of mesoporous carbon. These characteristics ensured high catalytic activity for ofloxacin.

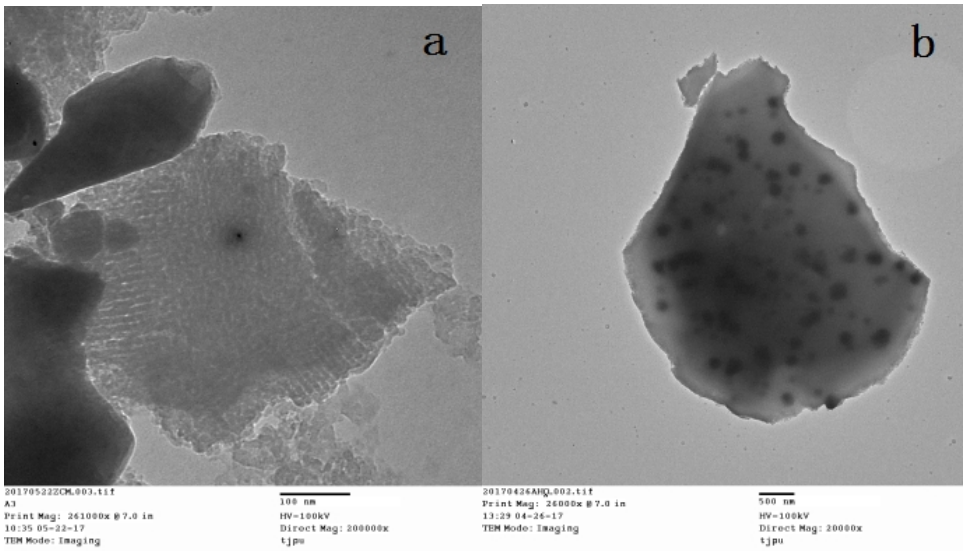

Fig.2. TEM images of Meso-C (a) and Fe/Cu Meso-C (b).

Comparison of adsorption and degradation. The adsorption degradation of ofloxacin were implemented by catalyst materials. As shown in Fig.3a, the adsorption of ofloxacin only showed slight effects by uncoated pure alumina hollow ceramic tube because of relatively larger pore size. However, the Fe/Cu mesoporous carbon coated alumina hollow ceramic membrane continuous increased to 50 % within 250 min for adsorption efficiency of ofloxacin compared with pure ceramic tube (5 %). The combination of coated ceramic membrane with H_2O_2 increased adsorption degradation efficiency of ofloxacin, reached 90 % in 30 min. These was mainly due to the large specific surface area of Fe/Cu mesoporous carbon active layer on ceramic membrane surfaces, high utilization of active sites and the separation of ceramic tube supports.

Metal contrast of active layer. The degradation of ofloxacin by different metal active layers was shown in Fig.4b. As illustrated in Fig.4b, compared with the bimetallic Fe/Cu mesoporous carbon active layer, the degradation of ofloxacin by the single metal iron mesoporous carbon activated layer ceramic membrane was significantly decreased by 50 %. It is indicating that the Fe(III) and Cu(II) on the surface of the active layer could catalyze H_2O_2 decomposition to generate ·OH radicals[3] (Wang, Zhao et al. 2013), and the synergistic effect of Fe and Cu also could promote the decomposition of H_2O_2 and produce more ·OH radicals, which increased the degradation rate.

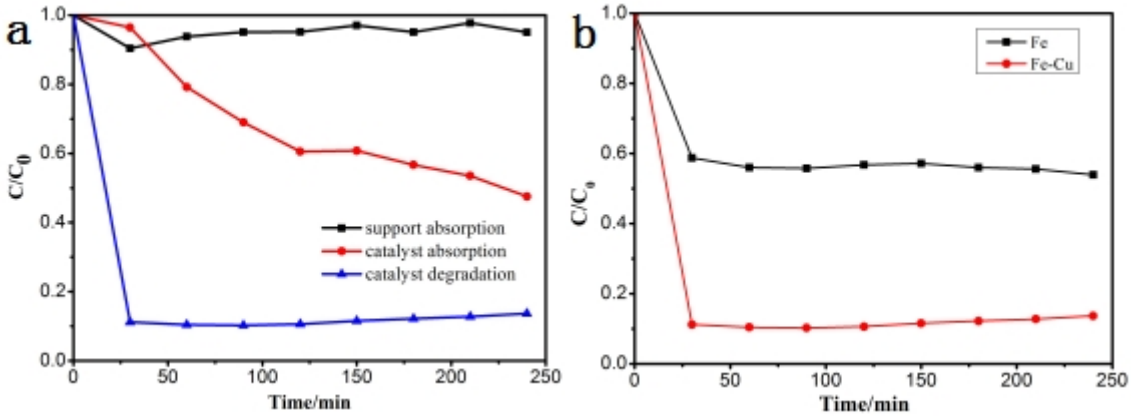

Fig.3. Comparison of adsorption and degradation of Fe-Cu/Meso-C catalysts(a);Degradation comparison of single iron and Fe-Cu metal oxides of active layer for degradation of ofloxacin(b).

Conclusions

In summary, bimetallic Fe/Cu mesoporous carbon supported alumina hollow ceramic membrane combined membrane filtration and degradation with mesoporous materials. It not only retains the characteristics of large pore size and uniform pore size of mesoporous materials, but also integrates membrane separation and further improves the material utilization and catalytic performance.

Acknowledgements

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