

Synthesis of Magnetic Activated Carbons for Removal of Environmental Endocrine Disrupter Using Magnetic Vector

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磁気ベクトルを用いた環境中の内分泌攪乱化学物質除去のための磁性活性炭の合成

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In this study, magnetic activated carbons (MACs) were synthesized by a chemical processing, adding iron (II and III) sulfates and alkali (aqueous NaOH solution) to the suspension of activated carbons at room temperature. Fine magnetite particles with some tens nanometer in diameter were precipitated on the surface of activated carbons. MACs prepared by this chemical precipitation processing could rapidly adsorb several pollutants such as bisphenol A and nonylphenol. In addition, MACs were easily collected with a permanent magnet and may be suitable for collection in a simple magnetic separation system.

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1. Introduction

There are a number of serious environmental problems, especially, in water and soil polluted with various heavy metal ions (Cd, As, and Pb etc.) and endocrine disrupting chemicals. With increasing environmental issues, it is gravely important to remove volatile organic compounds, polyhalogenated compounds, and environmental endocrine disrupters from soil, underground water, lake, and river. In order to solve these serious problems, the studies about various adsorbents such as activated carbon, silica-gel and zeolites, have been made. However, even if these harmful ions and chemicals can be removed by the usage of adsorbents, the efficient filtration and recovery of adsorbents from the purified water is difficult to carry out by conventional environmental purification methods. Recently, applications of high gradient magnetic separations are noted for environmental applications such as purification of wastewater and/or drainage from manufactory, removal of arsenic from geothermal water, and treatment of landfill leachate.^{1),2)} When these harmful compounds can be easily adsorbed to new type of adsorbents and removed by magnetic vectors, magnetic separation systems will be developed as a new technology of solid-liquid separation in the environmental field.²⁾⁻⁴⁾

Activated carbons are often used as a useful adsorbent for the removal of a variety of organic compounds and heavy metal ions.³⁾⁻⁵⁾ These adsorbents are highly inert, thermally stable, and cheap. As well-known, activated carbons have high specific surface areas due to their high adsorption abilities from the micro- and meso-pores in dilute solutions. In some cases, it may be advantageous to have activated carbon modified with the dispersion of the magnetic particles such as magnetite, that is, magnetic activated carbons (MACs). A good example is to use the magnetic supports to remove the

contaminants in solution by magnetic vectors. Also it is expected that by using magnetic separation systems, it is easy to filter and leach the adsorbents from the purified water.^{2),5),6)} Thus, the addition of magnetic properties into activated carbons is expected to be useful for the purification of the polluted waters. So, the first purpose in this study is to synthesize MACs through a chemical processing and to evaluate the adsorption ability of the harmful substances, bisphenol A (BPA), nonylphenol (NP), and methylene blue (MB) on MACs.

2. Experimental procedures

2.1 Preparation of magnetic activated carbons (MACs)

Powdered activated carbon (Mitsubishi Chemicals Co., Daiyahope 6D, 200 mesh, 50.0 g) was suspended in 500 ml of water. Precipitations of magnetite were carried out by a chemical processing as followed. A solution of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ($n=6$ to 9), 18.5 g in 1300 ml of water) and a solution of ferrous sulfate ($\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, 20.0 g in 150 ml of water) were prepared and then mixed with a magnetic stirrer. The mixed solution was successively added into a suspension of activated carbon (AC) at room temperature and then was slowly stirred for 30 min. After well-mixing, 10 M-NaOH solution was added dropwisely upto pH 10–pH 11 to this AC suspension, further mixed for 60 min, and aged at room temperature for 24 h. MACs suspension added with mixture of ferric sulfate and ferrous sulfate was filtered with a Buchner funnel and repeatedly washed with water and ethanol, and subsequently dried at 323 K.

2.2 Adsorption of methylene blue (MB), bisphenol-A (BPA) and nonylphenol (NP) by MACs

Stock solutions of MB, BPA and NP were prepared. Variable amounts of MACs were added into several 50 ml volumetric flasks of a definite concentration (0.10×10^{-4} to 6.5×10^{-4} mol dm^{-3}) for MB, BPA and NP and subsequently adsorp-

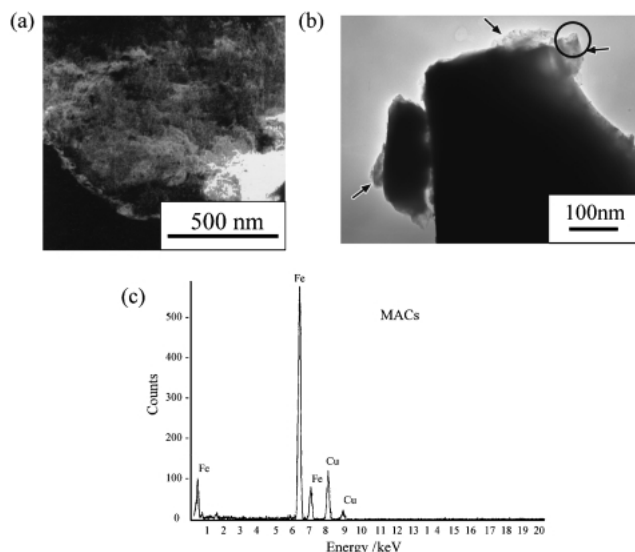


Fig. 1. SEM (a) and TEM (b) images of microstructures of magnetic activated carbon (MACs) synthesized by a chemical processing in this study. (c) shows EDS results from circle area in (b) image.

tion tests were carried out at 298 K for 24 h. For the comparison, absorption behaviors of powdered AC were also evaluated for MB, BPA and NP. After magnetically separated with a permanent magnet, the concentration of BPA in the supernatant was determined by a UV-visible spectrophotometer. The BPA concentration adsorbed on MACs was estimated from difference between initial (A_0) and arbitrary absorbance (A_s). As a demonstration of magnetic separation, the purification test of water containing with MB of $3.92 \times 10^{-4} \text{ mol dm}^{-3}$ was carried out with MACs using a permanent magnet.

2.3 Microstructural evaluation

Magnetite (Fe_3O_4) and MACs were measured by an X-ray diffractometer (Rigaku: RINT 2000) using monochromatic Cu $K\alpha$ radiation. Microstructures of MACs were observed by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

Figure 1 shows SEM and TEM images of microstructures of MACs synthesized by a chemical processing in this study. As shown in Fig. 1, MACs were successfully prepared by precipitation of magnetite on the surface of AC. In case of MACs prepared through the chemical precipitation, a number of fine magnetite particles with some tens nanometer in diameter were observed to be dispersed on the surface of AC. Also, from the results of EDS spectra for MACs (Fig. 1(c)), iron compounds like magnetite were confirmed. **Figure 2** shows XRD patterns for MACs prepared through the chemical precipitation. For the comparison, XRD results of AC and magnetite are contained in this figure. From these XRD results, samples of MACs were composed of magnetite and AC.

MACs prepared by this chemical precipitation processing could efficiently and rapidly adsorb a variety of organic compounds as well as powdered AC. Equilibrium adsorption isotherms of the unbuffered water solutions of MB and BPA on MACs are shown in Fig. 3. MB, MPA and NP were absorbed by MACs. There were great differences in the adsorption behaviors of MB and BPA between MACs and powdered AC. Adsorption amounts of MB or BPA on MACs were reduced, compared to those of powdered AC.

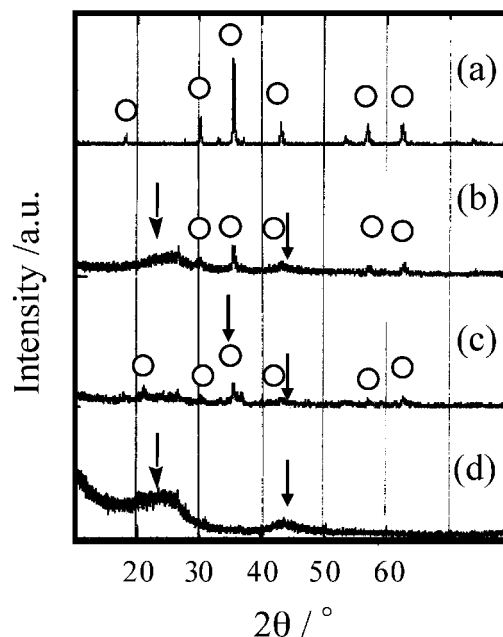


Fig. 2. XRD patterns of magnetic activated carbons (MACs), activated carbon (AC), and magnetite. (a): magnetite, (b) and (c): MAC, and (d): AC. ○ = magnetite, ↓ = AC (b) MAC without aging for 24 h and (c): MAC with aging for 24 h

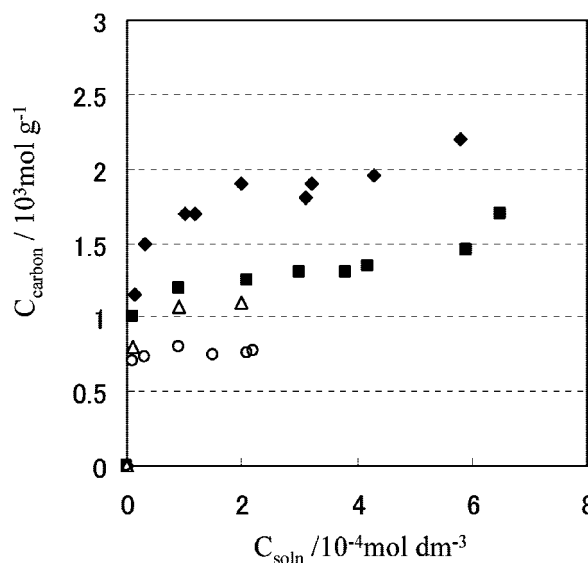


Fig. 3. Equilibrium sorption isotherms of metylene blue (MB) bisphenol-A (BPA) using monolithic AC and MACs: ◆ BPA/AC, ■ BPA/MAC, △ MB/AC, ○ MB/MAC

Adsorption of MB and BPA to MACs can be described in Langmuir isotherm, as the linear transformation data was confirmed in Fig. 4. Saturated adsorption amount was calculated from linear relationship of Langmuir isotherm in Fig. 3. From these results, maximum adsorption amounts for MB on MACs reached approximately 280 mg g^{-1} . However, in case of BPA, MACs had maximum adsorption amounts of 300 mg g^{-1} . On the other hand, powdered AC had higher adsorption abilities, 390 mg g^{-1} for MB and 430 mg g^{-1} for BPA than MACs. On the contrary, although the adsorption of NP was carried out for MACs and powdered AC, 270 mg of NP was

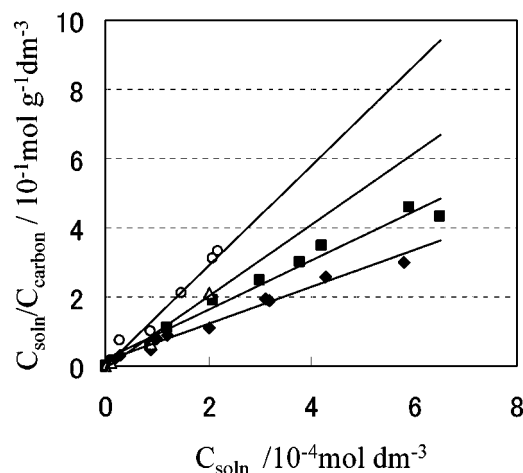


Fig. 4. Langmuir transformation of equilibrium sorption isotherms MB and BPA using monolithic AC and MACs:

◆ BPA/AC, ■ BPA/MAC, △ MB/AC, ○ MB/MAC

captured with 1 g of MACs and powdered AC. Thus, it was found that MACs possessed a little lower adsorption amounts for MB and BPA than powdered AC.

As shown in Figs. 3 and 4, 20 to 30% decrease of adsorption ability of MACs relatively to those of AC was thought to be caused by the facts that the precipitations of magnetite particles on the surface of AC diminished the adsorption sites of AC. Therefore, excess magnetization due to large amounts of the precipitation of magnetite may reduce the adsorption abilities for organic compounds, although the enhancement of magnetic character is caused by the increase of the magnetite particles amounts. The decrease of magnetites amounts decreases the magnetization, although the adsorption ability is maintained. Thus, MACs have the optimum volume of the precipitations of magnetite particles on the surface of AC and consequently, both abilities of adsorption and magnetization should be balanced by the control of microstructures for MACs. However, since the large magnetite particles possess the high magnetization, MACs added by small amounts of magnetite with large diameter may be useful as a good adsorbent and applicable for a magnetic separation. Consequently, for realization of a magnetic separation system, the development of high performance adsorbents with the minimum amount of magnetite precipitations and the crystal growth of magnetite particles may be desired.

Figure 5 shows the purification of water containing with MB with a magnetic separation using a permanent magnet. MB was completely adsorbed with MACs, as shown in Fig. 5 (c), and these MACs adsorbing MB were easily separated with a permanent magnet, leading to the magnetic separation. Furthermore, BPA adsorbed to MACs was easily washed by

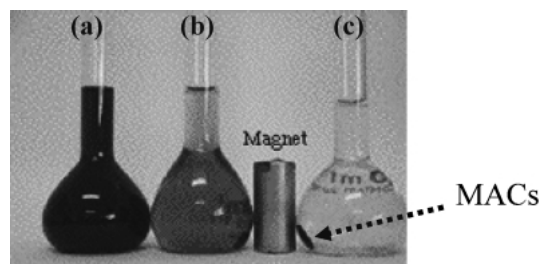


Fig. 5. Purification tests of water containing with MB using a permanent magnet. In case of (c), MACs were easily collected by a permanent magnet.

Initial concentration of MB = $3.92 \times 10^{-4} \text{ mol dm}^{-3}$.

MACs contents: (a) 0 mg, (b) 25.7 mg/50 ml, (c) 38.3 mg/50 ml.

ethanol abstraction and MACs were recovered. In addition, dried MACs could be reused for adsorption of BPA and had the similar adsorption ability as as-synthesized fresh MACs. Therefore, MACs can be recycled for the purification of waste water.

4. Conclusion

Magnetic activated carbons (MACs) were synthesized by adding iron (II and III) sulfates and alkali to the suspension of activated carbon. The products were analyzed by XRD, SEM, and TEM. The properties of absorption for MACs were evaluated by MB, BPA and NP adsorption measurement. From TEM results, fine magnetite particles with some tens nanometer in diameter were precipitated on the surface of activated carbon. MACs prepared by this chemical precipitation processing could rapidly adsorb several pollutants such as BPA and NP, although MACs had a little lower ability of adsorption MB, BPA, and NP, compared to powdered AC. MACs were easily collected with a permanent magnet and may be applicable for a simple magnetic separation system.

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