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Synthesis of ferromagnetic ordered mesoporous carbons for bulky dye molecules adsorption

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ABSTRACT

The magnetic mesoporous carbon materials have been synthesized by chemical activation followed by reduction of $Fe(NO_3)_3$ under N_2 condition. All these materials possess dual-pore mesopore texture (2.8–2.9 nm and 3.5–4.1 nm), large surface areas (975–1321 m^2/g), and high pore volumes (0.85–1.08 cm^3/g). The adsorption capability and behavior of four dyes, methylthionine chloride (MC), methyl orange (MO), rhodamine B (RB), and gongo red (GR), were carried out on these magnetic bimodal mesoporous carbon materials. All the materials show the well adsorption capacity of the four dyes (highest reach 768 mg/g). After investigating the adsorption isotherms of these dyes, they all fit the typical Langmuir adsorption model. And the adsorption amount is mainly affected by BET surface area and the structure/size matching between adsorbent and adsorbate. With the highest BET surface area and 1D short mesopore structure, the sample shows the larger adsorbing capacity for the smaller molecular dyes (MC, MO). Moreover, the 1D long mesopore is benefit to absorb the dye with 1D long chain structural molecule (GR), while the storage capacity of RB (2D molecular structure) on 1D mesoporous adsorbent is the lowest.

1. Introduction

The discharge of dye wastewater from textile industry has become one of the most serious pollutants in water. Various treatments for removal dyes have been reported, such as adsorption [1–14], photodegradation [15–19], biodegradation [20,21], etc. Among these techniques, adsorption on carbon material, such as activated carbons, activated carbon fibers, and mesoporous carbon [22–28], is one of the most efficient and frequent methods on removal dyes and decoloration. Active carbon, with large surface area and pore volume, thermal stability, chemical inertness, non-toxicity, and strong interaction with the organic dye molecule, was usually used as the adsorbent, but the micropore size limits the transfer of bulky dye molecules from the surface of active carbon into the pores. And the ununiform pore size also makes the low occupation of the pore. For example, Walker et al. [29] reported that only 14% of pores can be occupied by the dye on the adsorption experiment of three kinds of acidic dyes on the activated carbon.

With the highly ordered mesoporous structure and the tunable and uniform pore size (from 2 to 50 nm), the mesoporous carbon materials are desirable for the adsorption of bulky molecule. Wang et al. synthesized the carbon materials with a large capacity for the immobilization of biomolecules, and the adsorption capacity for cytochrome c could reach to 732 mg/g [30]. Zhuang et al. demonstrated an ordered mesoporous carbon has the highly efficient adsorption on bulky dye molecules [31], these results indicated that mesoporous carbon materials really exhibited excellent performance in the adsorption for dyes in wastewater.

As we known, there are main two factors that can affect the adsorption of organic species in aqueous solution: (1) the interaction between the adsorbent and the adsorbate, including, electrostatic, hydrogen bonding, acid–base interaction, and hydrophobic interactions; (2) the pore texture of the adsorbent, including, pore size, surface area, and pore volume etc. [32]. For the first factor, the surface modification was usually used to adjust the chemical nature of the adsorbent to improve its adsorption capacity. Adsorption tests were conducted in batch reactors under various conditions where the effect of pH, temperature, contact time, dye concentration, and adsorbent dose were studied [33]. The adsorption of four different organic dyes on porous xerogels also was studied by understanding the factors affecting the adsorption capacity of the xerogels. They vary the hydrophobicity and the textural properties of the xerogels as well as the solution pH [34]. For the second factor, many methods were used to improve the pore structure, such as erosion by acid or basic and physical activation by CO_2 etc. Fir wood was first carbonized, then was soaked in KOH solution, and last underwent CO_2 gasification [35]. Several researchers have studied the liquid-phase adsorption of bulk molecular on mesoporous activated carbons, confirming that the pore size distributions of activated carbons are the key factor in determining how these

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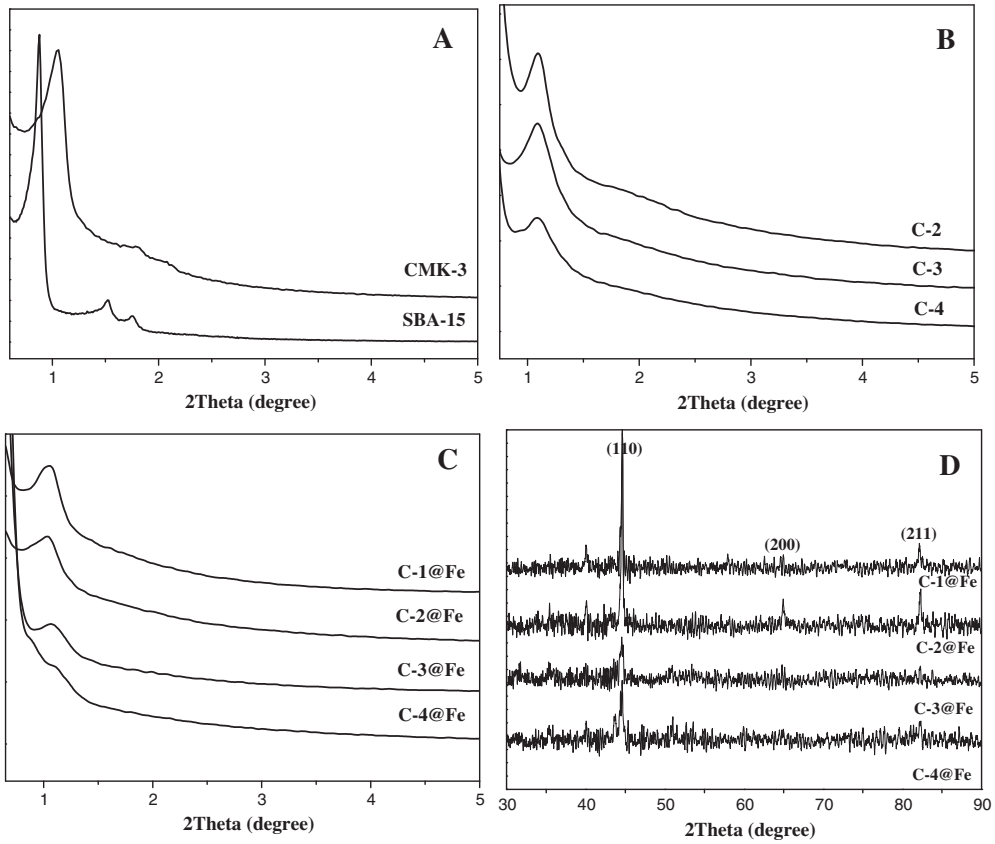

Fig. 1. Small-angle XRD patterns of (A) SBA-15, CMK-3, (B) C-2, C-3, C-4, (C) C-1@Fe, C-2@Fe, C-3@Fe and C-4@Fe and wide-angle XRD patterns of (D) C-1@Fe, C-2@Fe,C-3@Fe and C-4@Fe.

materials are applied to adsorption processes. Kim et al. [36] reported that surface area and pore structure of ordered mesoporous carbons had a significant effect on the adsorption capacity of methyl mercaptan, and that this effect was dependent on the molecular sizes of the compounds as well.

However, the carbon powders are difficult to separate from solution and it can be caused secondary pollution. The conventional separation approach normally involves filtration or centrifugation procedure, which is rather complex, expensive and could not be utilized widely. At present, magnetic separation as a promising strategy has been paid more and more attention due to the fact that it can be easily separated under an applied magnetic field.

In this paper, dual-pore mesoporous carbon materials with magnetic have been synthesized by chemical activation followed by reduction of $Fe(NO_3)_3$ under N_2 condition. Four dyes, methylthionine chloride (MC), methyl orange (MO), rhodamine B (RB), and gongo red (GR), were employed as model dye molecules, and the adsorption capacity and behavior were discussed in terms of surface area, pore size, and the structural matching between adsorbent and the adsorbate in details.

2. Experimental

2.1. Chemicals

Poly(ethylene glycol) – block – poly(propylene glycol) – block – poly(ethylene glycol) triblock copolymer Pluronic P123

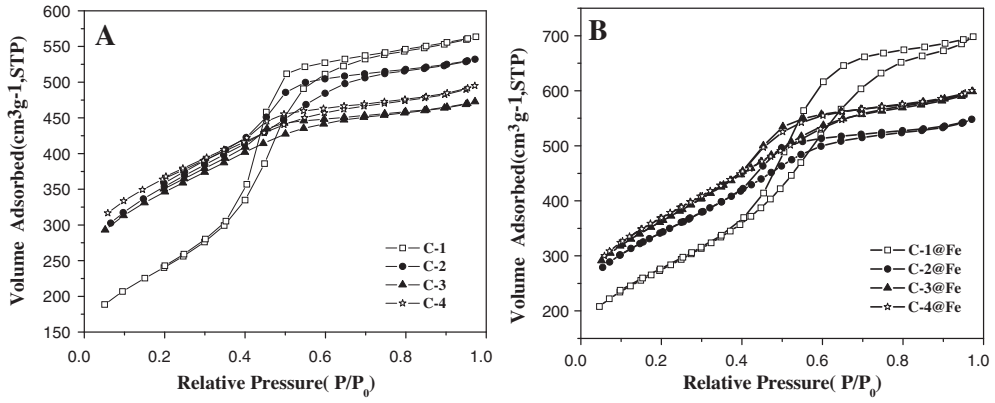

Fig. 2. Nitrogen sorption isotherms for (A) C samples and (B) C@Fe samples.