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Adsorption of anionic and cationic dyes on ferromagnetic ordered mesoporous carbon from aqueous solution: Equilibrium, thermodynamic and kinetics

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ABSTRACT

Ordered mesoporous carbon (Fe-CMK-3) with iron magnetic nanoparticles was prepared by a casting process via SBA-15 silica as template and anthracene as carbon source, was used as a magnetic adsorbent for the removal of anionic dye Orange II (O II) and cationic dye methylene blue (MB) from aqueous solution. TEM and magnetometer images showed that the iron magnetic nanoparticles were successfully embedded in the interior of the mesoporous carbon. The effect of various process parameters such as temperature (25–45 °C), initial concentration (100–500 mg L^{-1}) and pH (2–12) were performed. Equilibrium adsorption isotherms and kinetics were also studied. The equilibrium experimental data were analyzed by the Langmuir, Freundlich, Temkin and Redlich–Peterson model. The equilibrium data for two dyes adsorption was fitted to the Langmuir, and the maximum monolayer adsorption capacity for O II and MB dyes were 269 and 316 mg g^{-1}, respectively. Pseudo-first-order and pseudo-second-order kinetic and intraparticle diffusion model were used to evaluate the adsorption kinetic data. The kinetic data of two dyes could be better described by the pseudo second-order model. Thermodynamic data of the adsorption process were also obtained. It was found that the adsorption process of the two dyes were spontaneous and exothermic.

1. Introduction

Synthetic organic dyes have emerged as important pollutants in the environment due to their worldwide application in many industries, such as textile, paper, printing, food, and cosmetics [1]. Many dyes and pigments are inert, toxic and difficult to biodegrade when discharged into waste streams. In addition, the presence of dyes and pigment in water are highly visible and affects the water transparency, resulting in reduction of light penetration, and oxygen gas solubility in water. According to the literature, it is estimated that more than over 7×10^5 t dyes are discharged annually to the aquatic ecosystem [2]. The great majority of dye wastewater is colored effluent. The discharge of highly colored dye effluents into the environment is currently one of the world's major environmental problems for both toxicological and esthetical reasons.

A variety of treatment methods, including chemical oxidation [3], biodegradation [4], photocatalytic degradation [5] and adsorption [6] have been developed to remove dyes from wastewater. Among these techniques, adsorption is the most favorable method for removal of dyes because of its simple design, ease of operation, and high-performance removal efficiency of toxic substances. Using various carbon materials as adsorbent for dyes has been widely studied due to their large surface area and high adsorption capacity. Some researchers have studied the production of activated carbon from bamboo [7], tire [8], mangosteen peel [9], sawdust [10], oil palm [11], and sludge [12]. Activated carbons were also used as adsorbents for molecules with large diameters. However, the applications of activated carbons are restricted due to the presence of micropores. Mesoporous (2–50 nm) carbon, as carbon material adsorbent, with open pore structure, high specific surface area, high thermal stability, good chemical stability and large pore size could favor the dye adsorption of different molecular structures. Some papers have reported the preparation of order mesoporous carbon from rice husks [13], wood materials [14] and waste tires [8]. In addition, mesoporous carbon can also be prepared using template method, mainly including soft and hard template. In the soft template method, self-assembly of organic molecules which generates the nanostructures, and molecules or

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moieties are manipulated at the molecular level and spatially organized in nanospaces by the chemical interactions between templates and carbon precursors. Mesoporous carbon with uniform pores can be synthesized using this method, but the pore structure arrangements of these carbons are disordered. Hard template synthesis method using post-synthesized templates served as formworks to synthesize ordered mesoporous carbon. The porous structures of the mesopore carbon are predetermined by the templates resulting in the mesopore carbons having well-defined nanostructures. In addition, the porous structure and the pore diameters can be tuned by using this method. Some groups have synthesized ordered mesoporous carbon using various mesoporous silica or aluminosilicate as a hard template [15].

In most water treatment processes, the carbon powder materials dispersed in the treated solutions are quite difficult to separate that even could result in secondary pollution. Conventional separation technologies mainly include the process of filtration or centrifugation procedure, which is rather complex, uneconomical and cannot be widely utilized. At present, magnetic separation as a prospecting technology is an attractive alternative due to the fact that it can be easily separated by means of an external magnetic field [16,17].

In previous work, we used sucrose as the carbon precursor to prepare ordered mesoporous carbon CMK-3, but the synthesized mesoporous carbon had little or no graphitic character [18]. In this paper, we attempt to use ordered mesoporous SBA-15 silica as hard template and anthracene serves as the carbon precursor to prepare ordered mesoporous carbon CMK-3, then iron magnetic nanoparticles are loaded on the graphitic mesoporous carbon framework via a simple wetness impregnation process, in which ferric chloride ($FeCl_3{\cdot}6H_2O$) was the iron source. The ordered mesoporous Fe-CMK-3 exhibited high surface area, large pore volume, and narrow uniform pore size distribution. In the adsorption experiments, the ordered mesoporous Fe-CMK-3 as an adsorbent for the removal of the anionic dye Orange II and cationic dye methylene blue (MB) from aqueous solution. It indicated that the Fe-CMK-3 was of high performance in adsorption of the two dyes. The effects of contact time, dyes initial concentration, pH, ionic concentration and temperature were investigated. Adsorption isotherms and kinetics also were determined to elucidate the adsorption mechanism of MB and OII molecules onto the Fe-CMK-3. Moreover, the experimental data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. Thermodynamic data of the adsorption were also calculated.

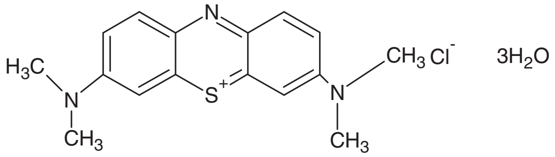
2. Materials and methods

2.1. Materials

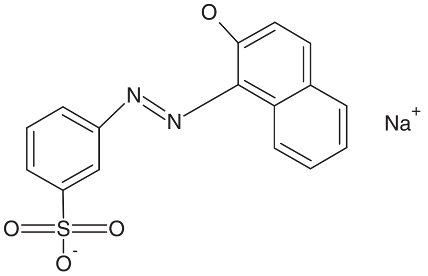
Triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), anthracene, HCl, NaOH, NaCl, H_2SO_4, $FeCl_3{\cdot}6H_2O$ were purchased from Sigma–Aldrich. All other reagents were of analytical grade. Anionic dye Orange II (O II) and cationic dye methylene blue (MB), were selected as the targeted adsorbates in this study. Two dyes molecular characteristics and structure were illustrated in Fig. 1 and Table 1.

2.2. Synthesis of mesoporous carbon Fe-CMK-3

The Fe-CMK-3 samples were synthesized by a nanocasting process using SBA-15 silica as template and anthracene as the carbon source. The synthesis procedure has slightly been revised by Jun et al. reported [19]. The SBA-15 template was prepared using the triblock copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich) as the structure-directing agent and tetraethyl orthosilicate (TEOS, 98%, Aldrich) as the silica source. The triblock copolymer Pluronic P123 was dissolved in hydrochloride solution at 40 °C. Then TEOS was added to the above mixture solution under magnetic stirring. The molar composition ratio of the final mixture was $TEOS{:}P123{:}HCl{:}H_2O = 1{:}0.0165{:}5.755{:}191.61$. The solution was magnetically stirred at 40 °C for 24 h and then transferred into an autoclave for 24 h under static conditions for hydrothermal treatment at 100 °C. Subsequently, the mixture was filtrated, dried and washed with distilled water and then calcined at 550 °C for 12 h to remove the organic template P123.



(a) Methylene blue (MB)



(b) Orange II (O II)

Fig. 1. Chemical structures of MB and O II.

The Fe-CMK-3 samples were synthesized by the following the procedure (Scheme is shown in Fig. 2): First of all, the mesoporous carbon CMK-3 products were obtained by impregnating 2 g of SBA-15 template with 5 mL aliquots of 0.4 g anthracene in acetone containing 0.28 g sulfuric acid. The solution was magnetically stirred until it was dried. Then the mixture was heated at 160 °C for 8 h to initiate carbonization. The impregnation and carbonization treatment processes were repeated under the same condition until the entire anthracene precursor solution was consumed (reached 3 g). Afterward, the mixtures were placed in a quartz glass tube and heated at 400 °C for 4 h, and then further carbonized under nitrogen at 800 °C for another 4 h (at a rate of 5 °C min^{-1}). Finally, the product CMK-3 was filtered and washed with 1 M NaOH solution ($V_{deionizedwater}{:}V_{ethanol} = 1{:}1$) for 1 h at 100 °C to dissolve the silica template, and then dried at 105 °C for 12 h. Subsequently, 0.5 g of CMK-3 was dispersed in 0.2 g $FeCl_3{\cdot}6H_2O$ and 5 mL ethanol and then the mixture was stirred under magnetic stirring for 6 h at room temperature, The sample was evaporated at 50 °C. The obtained dried sample was then subjected to polymerization and carbonization at 900 °C for 4 h under nitrogen atmosphere [20].

The textural characterization of the CMK-3 and the Fe-CMK-3 were performed using Powder X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Micrometitics ASAP 2020 surface area analyzer. The low-angle XRD pattern of sample CMK-3 and Fe-CMK-3 are shown in Fig. 3. The sample Fe-CMK-3 showed three well-resolved XRD peaks as well as CMK-3, which can be indexed as the (1 0 0), (1 1 0) and (2 1 0) reflections of the 2-D hexagonal symmetry (p6mm), indicating that the sample still a had good structural order after the modification. In addition, It was noted that the intensity of the (1 0 0) reflection peak was weaker than that of the CMK-3, this indicates that the ordered mesostructure system was slightly destroyed upon loading the iron nanoparticles.