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Characterization and adsorption behaviors of a novel synthesized mesoporous silica coated carbon composite☆

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A B S T R A C T

A novel mesoporous silica coated carbon composite (denoted SEG) with hierarchical pore structure has been successfully prepared in an aqueous solution that contains triblock copolymer template, aluminum chloride, siliceous source and expanded graphite. Textural property and morphology of the SEG composite were characterized by the combination of X-ray diffraction, N_2 adsorption–desorption, scanning electron microscopy, transmission electron microscopy and Fourier transform infrared measurements. Results show that mesoporous silica is steadily and uniformly grown on the surface of the graphite slices and the thickness of the silica layer can be finely tuned according to the silica/C molar ratio in the initial reaction solution. This newly synthesized SEG composite shows greatly increased adsorption capacity to methylene blue than the pristine expanded graphite in the batch tests. Both Langmuir and Frendlich models were further used to evaluate the adsorption isotherms of methylene blue over expanded graphite and SEG samples with different silica contents. Finally, pseudo-second-order model was used to describe the kinetics of methylene blue over expanded graphite and the silica-carbon composites.

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1. Introduction

Most of the organic dyes and pigments used in textile, paper and plastic industrial fields are toxic and carcinogenic even at low concentrations [1]. These dyes discharged into water are difficult to decompose because they are very stable to light and oxidation reactions [2,3]. So it has great significance to remove dyes from wastewaters for reducing water pollution and protecting our living environments. Many methods such as physical, chemical and biological methods have been investigated to remove dye materials from waste water [4–9]. Among those proposed techniques, adsorption has been proved to be a very efficient method for water decontamination and carbon materials are the most widely used adsorbents because of their diversities [6–11].

Expanded graphite (EG) is a well known carbon material which was invented by Carburet Company in 1968 [12]. Similar to the other carbon

materials, EG is widely used in gasketing, adsorption, electromagnetic interference shielding, vibration damping and other fields due to its excellent properties such as compatibility, spring-back, flexibility, heat conducting, anti-acid, anti-base, and so on [12,13]. Different from the other carbon materials, EG normally has worm- or accordion-like morphology and possesses lots of micrometer-ranged interconnected pores, which are constructed from the opened graphite flakes [14]. As a result, EG is very useful in the adsorption of large molecular organic pollutants, especially heavy oil [15]. However, the large pores in EG also limit its application in capture of small organic molecules [16,17].

Herein in this work, a mesoporous silica layer was grown onto the pores of EG to generate mesopores inside the EG particles *via* a facile hydrothermal method. A novel hierarchical mesoporous silica-carbon composite (denoted SEG) containing both of mesopores and micrometer-sized pores was thus obtained. This silica-carbon composite was used as adsorbent to remove dyes from wastewater and it presents much higher adsorption capacity to the organic methylene blue (MB) than EG in the batch tests.

2. Experimental

2.1. Material synthesis

Expanded graphite (EG) was prepared according to the reported method [18]. Mesoporous silica-carbon composite was synthesized by

a traditional hydrothermal method. In a typical synthesis, 1 g of Pluronic P123 and 2.42 g of AlCl$_3$·6H$_2$O were dissolved in 37.5 g of deionized water. 0.125 g of EG was then added into the solution and the mixture was stirred for 24 h at room temperature. After that, 2.08 g of tetraethylorthosilicate (TEOS) was introduced ($r_{SiO_2/C}$ = 0.96). The resulting mixture was stirred for 24 h at 318 K and then hydrothermal treated at 373 K for another 24 h under static conditions. The as-synthesized sample was filtered, washed, dried and calcined at 823 K for 5 h to remove the template. The finally obtained composite was denoted SEG. To study the effect of the silica content in SEG, different amounts of EG were introduced into the solution for adjusting the $r_{SiO_2/C}$.

2.2. Characterization

XRD patterns of the EG and SEG were recorded on a Bruker D8 Advance diffractometer with Cu K$_\alpha$ radiation. N$_2$ physisorption iso-therms at 77 K were measured using a Belsorp II system, in which the samples were outgassed at 473 K for 4 h prior to testing. The Brunauer–Emmett–Teller (BET) surface area was calculated with the relative pressure ranging from 0.04 to 0.20, while the total pore volume was derived from the amount adsorbed at the relative pressure of about 0.99. The pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method according to the adsorption branches. SEM images were taken with a Hitachi S-4800 scanning electron microscope. TEM was performed on a JEM-2100 electron microscope. FT-IR spectra of powdered samples suspended in KBr pallets were recorded on a Bruker Vertex 70 spectrometer.

2.3. Adsorption performance test

The stock solution of methylene blue (MB) was prepared in distilled water. Batch tests were typically carried out by adding 50 mg of EG or SEG samples into set of 100 ml plastic flasks containing 50 ml of MB solutions with different initial concentrations (20–120 mg·L^{-1}). The mixtures were shaken for desired duration at room temperature with the speed of 50 r·min^{-1}. For the study of kinetic adsorption behavior, the mixtures were shaken at appropriate time of 5, 10, 15, 30, 60, 90 and 120 min respectively. For obtaining the adsorption isotherm, experiment was carried out for 2 h to obtain equilibrium. After that, the filtrate was collected and analyzed using a UV-2450 spectrophotometer at maximum wavelength around 665 nm.

The amount of dye adsorbed onto SEG sample was calculated from the mass balance equation as:

$$Q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where Q_e (mg·g^{-1}) is the amount of MB adsorbed per gram of SEG at equilibrium; C_0 (mg·L^{-1}) and C_e (mg·L^{-1}) are the initial and equilibrium liquid-phase concentration of dye; V (L) is the volume of the solution and M (g) is mass of the dry adsorbent.

3. Results and Discussion

3.1. Structure and morphology of the mesoporous SEG composite

Fig. 1a shows the low- and wide-angle XRD patterns of the SEG composite ($r_{SiO_2/C}$ = 0.96). SEG possesses one diffraction peak at 2θ of 0.89° (Fig. 1a, insert), which is a reflection of the presence of mesopores in the composite. Wide-angle XRD patterns reveal that EG has typical diffraction peaks at 2θ of 26.52° and 54.6° with corresponding d-spacings of 0.3358 nm and 0.1679 nm, which can be indexed to the hexagonal graphite (002) and (004) crystal faces (JCPDS No. 41-1487) [14, 19]. The same (002) and (004) diffraction peaks of the SEG composite shift to a bit lower values and appear wider, which is due to some

disorientations of the graphite sheets when EG was modified by the silica coating [14]. According to the data calculated from the (002) diffraction peaks (Table 1), there is a certain increase of 0.0003 nm in the interlayer spaces of EG sample. Moreover, the intensities of the two EG characteristic peaks are dramatically declined in SEG composite because of the coated amorphous silica in the pores of EG.

SEM images of SEG clearly demonstrate that the silica layer is steadily and uniformly grown on the surface of the graphite slices in SEG composite (Fig. 1b). Moreover, the grown silica on EG is not a single layer but multiple layers. Small irregular silica particles can be observed on the surface of the SEG sample. The thickness of the silica-covered carbon layer in SEG is nearly 50–75 nm (Fig. 1b, insert). TEM results show the presence of both long-range ordered and less-ordered mesopores in SEG composite (Fig. 1c–1e). Both twisting worm-hole like pores (Fig. 1d) and straight channels (Fig. 1e) are visible in the TEM images of SEG. The main pore size of the SEG composite observed from TEM images is around 7.05 nm. In addition, TEM image also confirms that the mesoporous silica layer is stably and regularly grown on the surface of graphite slice in SEG (Fig. 1c).

In order to investigate the formation process of such interesting silica-carbon composite, SEG composites with different SiO$_2$/C molar ratio ($r_{SiO_2/C}$ = 0.96, 0.48, 0.24 and 0.16) were carefully synthesized and examined by SEM. It is shown that EG is composed of thin smooth graphite slices and these graphite slices are curved and loosely connected to each other (Fig. 2a). The thin graphite flakes of EG became thicker when they were modified by silica coatings (Fig. 2b–2e). Furthermore, the thickness of the silica layer decreases according to the reduction of the $r_{SiO_2/C}$ in the initial reaction solution (Fig. 2b–2e). The amount of the silica coating in SEG plays very important role in improving the adsorption property of the SEG composite. N$_2$ physisorption results will give more information about the SEG composites synthesized with different $r_{SiO_2/C}$.

Fig. 3 presents the N$_2$ adsorption–desorption isotherms and corresponding BJH pore size distributions of EG and SEG composites with different SiO$_2$ coatings. EG has a type II isotherm according to the IUPAC classification, which is typical for powders with large pores [20]. The hysteresis loop of EG is identified as type B of de Boer classification, associating with slits shaped pores [20]. The N$_2$ adsorption–desorption isotherms of SEG composites are type IV with H3 hysteresis loops (Fig. 3a, curve a–d), which are obviously different from that of EG. All SEG composites show a one-step capillary condensation, which indicates uniform mesopores, while a two-step capillary evaporation is observed in the desorption branches, which are typical characteristics for plugged mesoporous silica materials [21]. The special two-step branched desorption isotherm is inconspicuous in sample with $r_{SiO_2/C}$ of 0.16 but obvious in other SEG composites. The plugs/constrictions in the SEG composites are related to the aluminum species and the weak acidities of the original reaction mixtures [21]. During the synthesis of mesoporous silica, the hydrolysis and condensation of siliceous source can be slowed under weak acidic conditions near the isoelectric point of silica. As a result, the transition process of micelles' 'sphere-to-rod' will take longer and plugs and/or constrictions are easily formed in the final mesopores if large amounts of salts existed in the reaction system [21]. In present study, the presence of plenty aluminum chloride leads to the generation of weak acidic reaction condition and the formation of constrictions/plugs in the mesopores. Furthermore, a distinctive limitless adsorption of SEG at high relative pressures can be observed, indicating the presence of macropores.

According to the BJH analysis, the SEG composite with the highest SiO$_2$ content ($r_{SiO_2/C}$ = 0.96) has a much narrower pore size distribution (PSD) curve than the other SEG composites (Fig. 3b). All SEG composites have the same PSD centered at 7.05 nm, which is approximately consistent with the above-mentioned TEM results.

Table 2 gives the physisorption results of expanded graphite (EG) and the mesoporous silica-carbon SEG composites with different amounts of silica coatings. EG has a very small surface area of about