Adsorption of Methylene Blue on Mesoporous SBA-15 in Ethanol-water Solution with Different Proportions

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ABSTRACT: The adsorption behavior of mesoporous SBA-15 materials to methylene blue (MB) as model molecule has been studied in different proportions of ethanol-water solution. It was found that adsorption capacity and adsorption rate of SBA-15 to methylene blue were the best in aqueous solution and the worst in anhydrous ethanol solution, in addition, adsorption capacity and adsorption rate increase as the proportion of water increased in ethanol-water solution. It’s interesting that the release behavior at a specific time appeared in the adsorption process of SBA-15 to methylene blue from anhydrous ethanol solution or ethanol-water solution. The adsorption kinetics of methylene blue (MB) on mesoporous SBA-15 samples in different solution have been analyzed and discussed based on the composition, the morphology, the surface area, pore size distribution and adsorption/desorption measurements measured with scanning electron microscopy (SEM), transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption and spectrophotometer technique.

1 INTRODUCTION

In recent years, many pollutants in water bodies have increased due to high increase in various industrial activities produced a large group of chemicals that get mixed in wastewater among many aqueous pollutants. In particular, different synthetic dyes have a dramatic increase in the annual production in many industries such as textiles, paper, rubber, leather, food, plastics, pharmaceutical and cosmetics, so the removal of dyestuff in waste effluents was primary problem. At present, various treatment methods for the remove dyes from wastewater were often used, including adsorption, oxidation processes, catalytic oxidation, reverse osmosis, biological method, ultra-filtration and ion exchange were often used. However, most of these methods have serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements. Thereinto, adsorption with the advantages such as simple operation, low-cost, environmentally friendly technologies, good effect and so on, was widely employed for treating different wastes. Adsorbents such as activated alumina, palm-fruit, natural zeolite, peat, fly ash, montmorillonite, polymeric resins and activated carbon, have been carried for dye removal. Ordered mesoporous materials (OMMs) as a absorbent with high surface area,
high pore volume, and a narrow pore size distribution, have better adsorption performance for dyes. In this work, adsorption capacity and adsorption rate of mesoporous SBA-15 materials to methylene blue (MB) has been studied in different proportions of ethanol-water solution. Adsorption mechanism of SBA-15 to methylene blue based on the composition, the morphology, the surface area, pore size distribution and adsorption/desorption measurements, have been analyzed and been discussed, which hopes to provide theoretical basis for industrial wastewater treatment.

2 EXPERIMENTAL SECTION

2.1 Materials

Pluronic 123 triblock polymer (EO_{20}PO_{70}EO_{20}, M=5800; Aldrich), tetraethyl orthosilicate (TEOS, purity 99.8%; AR), anhydrous ethanol, methylene blue (AR). All the reagents were used without further purification. Distilled water was used in the experiments.

2.2 Synthesis of SBA-15

SBA-15 sample was synthesized according to the procedure reported by Zhao et al using Pluronic 123 triblock polymer as a structure-directing agent and tetraethyl orthosilicate (TEOS) as silica source. The starting composition was in the following ratio: 4 g of P_{123}, 0.041 mol TEOS, 0.24 mol HCl, 6.67 mol H_{2}O. The mixture was placed in an oven at 35 °C for 24 h, subsequently, at 100 °C for 48 h, a white solid was then collected by centrifugation. The solid was washed with deionized water for three times, and then dried at 60 °C overnight. Finally, the SBA-15 was obtained by calcining the white solid in air at 550 °C for 5 h.

2.3 Adsorption performance study

Adsorption kinetic curves of SBA-15 materials to methylene blue model molecules were investigated: 125mg sample of SBA-15 was dispersed into a 250 mL MB aqueous solution or different mixture proportions of water and anhydrous ethanol) (37.5 μM) under stirring, and then the suspension was left to stand for 12 h, during that period the mass of the residual MB dissolved in the solution was monitored by a UV-vis spectrophotometer at different interval. After that, MB-loaded SBA-15 complexes were separated by centrifugation and dried by a 24h freeze-drying process.

2.4 Characterization

The morphologies and the structures of the samples were examined by a JEOL JSM-6390LV scanning electron microscopy (SEM) and a JEM-2010F transmission electron microscopy (TEM).
The specific surface areas were estimated using the Brunauer-Emmett-Teller (BET) method with a TriStar 3000 Surface Area and Pore Analyzer (Micromeritics). The compositions of the SBA-15 samples were detected by a Fourier transform infrared (FTIR) spectrometer in transmission model (Nicolet 5700). UV-Vis spectra were measured through a TU-1901 UV-visible spectrophotometer.

3 RESULTS AND DISCUSSION

Figure 1 shows the morphology of mesoporous silica SBA-15 samples by the typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. Figure 1A displays a coupling short rod-like shapes for mesoporous SBA-15, the diameter size (~ 1 µm) of the rod is relatively uniform, and the rod can be aggregated into a wheatlike macroscopic structure. Figure 1B further confirms the internal structure of the SBA-15 particles that the parallel orientation of channels is preferably along the long axis.

The FTIR spectrum of the SBA-15 is presented in Figure 2. From the figure one can see that the absorption bands at 1094 cm\(^{-1}\), 800 cm\(^{-1}\) and 465 cm\(^{-1}\) are attributed to the stretching vibrations, bending vibrations and rocking vibrations of Si-O-Si, respectively. The broad absorption band at ~3431 cm\(^{-1}\) is assigned to O-H stretching vibrations and 1627 cm\(^{-1}\) is the bending vibrations of adsorbed water molecules.

The structure and the pores can be confirmed further by nitrogen adsorption-desorption isotherms and the corresponding pore-size distributions measurements in Figure 3. The adsorption isotherm displays a type IV isotherm with H1 hysteresis and exhibits a sharp step with a H1 hysteresis loop, which is typical of mesoporous solids. The p/p\(_0\) position of the inflection ranging from 0.65 to 0.85 confirms this structural porous characteristic. The specific
surface area was 967 m²g⁻¹ and the pore size distribution centered at about 6.7 nm calculated by the standard BET method.

Figure 2. FT-IR spectra of the SBA-15.

Figure 3. Nitrogen adsorption-desorption isotherms (A) and the corresponding pore-size distributions (the inset B) of the SBA-15.

Figure 4 shows the adsorption kinetic curves of methylene blue on SBA-15. It can be seen that adsorption rate and adsorption capacity of SBA-15 in aqueous solution was highest than that of SBA-15 in anhydrous ethanol solution and in ethanol-water mixture solution. At the first 10 min of the adsorption process, the adsorption of MB dye in aqueous solution was very rapid and reached an equilibrium, the adsorption percentage of MB dye on mesoporous SBA-15 was

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93.96%, however, adsorption rate and capacity of MB dye in anhydrous ethanol solution increased gradually, and the adsorption percentage of MB dye on mesoporous SBA-15 was only 25.15% during the first 10 min. Then we researched the adsorption of methylene blue on mesoporous SBA-15 in different ethanol-water mixture, the results showed that adsorption rate of MB dye increase as the proportion of water increased in ethanol-water solution. However, the adsorption capacity of SBA-15 in anhydrous ethanol solution and that of SBA-15 in ethanol-water mixture solution are becoming to very close with the adsorption time going when the samples stood for 12 hour. It’s interesting that the release behavior at a specific time appeared in the adsorption process of SBA-15 to methylene blue from anhydrous ethanol solution, and the phenomenon of release behavior ahead of schedule occured when the adsorption solution from anhydrous ethanol to ethanol-water mixture. The interactions, which are responsible for the adsorption of MB onto SBA-15, may be electrostatic, hydrogen bonds, and van der waals forces. The differences of the adsorption kinetic in ethanol-water solution with different proportions can be explained as due to the different interactions between the solvent and the adsorbate.

![Figure 4. The adsorption kinetic curves of methylene blue on mesoporous SBA-15.](image)

4 SUMMARY

The adsorption behavior of mesoporous SBA-15 materials to methylene blue (MB) can be influenced obviously by changing the mixing proportions of ethanol-water solution. The adsorption capacity and the adsorption rate increased with the proportion of water increased in ethanol-water solution. Another interesting result is the release behavior appeared at a specific time in the adsorption process from anhydrous ethanol solution, even the phenomenon of release behavior ahead of schedule occured when the adsorption solution from anhydrous
ethanol to ethanol-water mixture. All these phenomena will provide theoretical basis for industrial wastewater treatment.

REFERENCES


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