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Adsorption performance and mechanism of methylene blue on chemically activated carbon spheres derived from hydrothermally-prepared poly(vinyl alcohol) microspheres

Zhigang Jia *, Ziyu Li, Shengbiao Li, Yanhua Li, Rongsun Zhu

School of Chemistry and Chemical Engineering, Anhui University of technology, No. 59 Hudong Road, Ma'anshan 243002, Anhui Province, PR China

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A B S T R A C T

Chemically activated carbon microspheres (CACms) are synthesized by sulfonation and carbonization of PVA (polyvinyl alcohol) microspheres, which is prepared by hydrothermal method with the assistance of $FeCl_3$. The as-prepared samples are characterized by SEM, XRD and FTIR measurement. Functional carbon microspheres with sulfonic group are found to be excellent adsorbents for cation dye removal with a higher adsorption capacity. Methylene blue (MB) as a typical kind of cation dye is chosen to investigate the adsorption performance of CACms. The parameters, such as pH, temperature, contact time, concentration of adsorbate, are employed to study the influence for adsorption capacity. The obtained results suggest that CACmc can effectively adsorb methylene blue with adsorption capacity increasing from 474.6 to 602.4 mg g^{-1} as the initial concentration increases from 20 to 300 mg/L in a wide pH range. The kinetics, isotherms and adsorption mechanism of functional CACms adsorption are discussed in detail. The adsorption data onto CACms can be fitted to pseudo-second-order model better than the pseudo-first-order model. The Langmuir adsorption model agrees well with the experimental data and the maximum adsorption capacity can reach 925.9 mg g^{-1} at 45 °C. Temperature change is found to have a significant effect on the adsorption process. The thermodynamic parameters such as the free energy, enthalpy and entropy of adsorption are evaluated and it was found that the adsorption was endothermic and spontaneous. In addition, the as-prepared CACms exhibit selective adsorption ability for MB.

1. Introduction

Synthetic dyes are indispensible to many industries and widely used in the textile, leather, paint and other application [1–4]. Up to now, 10,000 dyes have been successfully commercialized. However, the pollution of water body resulting from the dye discharge becomes much more serious with the development of modern industry. It is estimated that 10–15% of the total productions of dyes are discarded as dye effluent during dye production and dying process [5]. Dye is carcinogenic, toxic to microorganisms and causes harmful effects to human health and ecosystem [6]. The removal of dyes from wastewater has attracted much attention in recent years.

Various treatment technologies, such as adsorption [7–15], biological treatment [16], advanced chemical oxidation [17–19], coagulation/flocculation [20], electrochemical treatment [21,22] and photodegradation [23,24], have been developed to remove dyes from aqueous solution. However, it is difficult for the complete removal of dye materials while no new pollutant is produced for most of treatment methods. Adsorption can capture the dye molecular without subsequent pollution from wastewater. Removal of dyes by adsorption technologies is regarded as one of the competitive methods due to its high efficiency and economic feasibility. The adsorption technique for the removal of these toxic dyes from wastewater is intensively investigated.

Adsorbent material with high adsorption capacity and chemical stability is vital for the effective removal of pollutant [25]. Various adsorbents have been developed to remove the dyes from wastewater [26–34]. However, many adsorbent materials show relatively low adsorption capacities or the adsorption capacity was highly influenced by the variation of pH value of the solution. In fact, the practical dye wastewater differs from one another in a wide range of pH. Therefore, it is still a challenge to seek effective adsorbent materials with high adsorption capacity and satisfy the application in various conditions in view of the practical application.

Polyvinyl alcohol (PVA) is a common, nontoxic, and inexpensive organocarbon polymer. Biocompatible and nontoxic PVA microspheres are usually used a carrier for immobilization of microorganisms for wastewater bio-treatment, nanoscale Fe^0 for nitrobenzene reduction, nitrogen removal besides of biomedical applications [35–38]. In addition, PVA has preeminent mechanical strength and stability and abundant hydroxyl groups that can be easily modified with various functional groups. Based on these properties of PVA polymer, we suppose that PVA particles could be easy to be functionalized according

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* Corresponding author.
E-mail address: zjchemyue@126.com (Z. Jia).

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to the aim of wastewater treatment. In this study, chemically activated carbon sphere (CACms) derived from PVA microspheres as a new adsorption material for MB from dye-polluted water are investigated in details, and PVA microspheres are prepared by a novel hydrothermal method with assistance of $FeCl_3$. Both equilibrium isotherm and adsorption kinetics are employed to research the mechanism of adsorption of MB in solution by CACms.

2. Experimental section

2.1. Preparation of PVAms

Polyvinyl alcohol (PVA) with a degree of polymerization of 1750 and an alcoholysis degree higher than 99% was from Lanzhou Vinylon Factory (China). All the reagents used were of analytical-reagent grade. Doubly distilled water (DW) used to prepare all the solutions. In the typical synthesis, the PVA solution (5% w/w) was firstly made up by dissolving 4 g PVA into 80 mL DW, then 1 mmol $FeCl_3 \cdot 6H_2O$ was solved into the PVA solution. The above-mentioned mixture was transferred to a 100 mL Teflon-lined autoclave in the oven and then the reaction was performed at 180 °C for 12 h. Then, the autoclave was cooled naturally to room temperature. The obtained red product (PVAms) was repeatedly washed with deionized water and ethanol several times and dried at 100 °C for 2 h.

2.2. Chemical activation of PVAms

The as-prepared PVAms (500 mg) were put into a 20 mL Teflon-lined autoclave, and then 10 mL concentrated sulfuric acid (98%) was slowly added into the autoclave. The autoclave was maintained at 150 °C for 6 h. After cooling to room temperature naturally, the mixture was transferred to 200 mL DW. Then, The chemically activated carbon microspheres (CACms) were filtrated, rinsed repeatedly with DW and left to dry completely.

2.3. Characterization

X-ray powder diffraction measurements were performed on a Bruker D & Advance X-ray powder diffractometer with graphite monochromatized CuKa ($\lambda = 0.15406$ nm). A scanning rate of $0.05° s^{-1}$ was applied to record the pattern in the 2 range of 10–70°. The morphologies of samples were observed by means of an AMARY-1000B (Germany Bruker) scanning electron microscope. Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded by IR Presitige-21 FTIR (Shimadzu).

2.4. Adsorption test of CACms for MB

The adsorption of MB from aqueous solution was performed by using batch technique in a thermostatic shaker bath. MB aqueous solution with different initial concentrations (50 mL, 5–300 mg/L) was prepared in a 50 mL conical flask, and CACms (5 mg) were added. The temperature of the dye solution was set as 25 °C, 35 °C and 45 °C, respectively. The pH of solution can be tuned with HCl solution (2 M) or NaOH solution (2 M). The MB concentrations were measured by visible spectrophotometer (721 Model, Shanghai Scientific Instrument, Co., Ltd) at 664 nm. After adsorption, the equilibrium adsorption amount (q_e) of CACms for MB dye was calculated by using following equation (Eq. (1)).

$$Q_e = \frac{v(C_0 - C_e)}{m} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of dye solution, respectively; v is the volume of dye solutionand m (g) is the weight of CACms.

3. Results and discussion

3.1. Characterization of PVA microspheres and CAPVA microspheres

The phase composition of PVAms and CACms is analyzed by XRD, respectively. As shown in Fig. 1a, the broad Bragg diffraction peak in the regions of $2\theta = 14.7–23.3°$ confirms the amorphous nature of PVAms microsphere [39]. The diffraction peaks at $2\theta = 33.4, 35.6, 62.5°$ are attributed to the ⟨104⟩, ⟨110⟩ and⟨106⟩ of α-Fe_2O_3 [40], indicating that a small amount of α-Fe_2O_3 are also produced besides of the PVAms due to the addition of $FeCl_3$ during the hydrothermal process. For the sample of CACms, as shown in Fig. 1b, the broadened peak near 25°, which could be attributed to the ⟨002⟩ diffraction peak of graphite, indicated that chemical activated process for PVAms result the formation of a relatively better carbon framework in the obtained carbonation material with sulfuric acid [41]. At the same time, the diffraction peak related with α-Fe_2O_3 can not be observed, suggesting the removal of the formed α-Fe_2O_3 phase due to the acid resolution effect during the sulfonation process.

The morphologies of PVAms and CACms samples are observed by SEM technique. As shown in Fig. 2a, the PVAms sample reveals spherical morphology with average diameter of 4 μm. The surface of the *as*-obtained PVA microspheres is smooth besides of the adherence of some pie-like shape (Fig. 2b). Through chemical activation of concentrated sulfuric acid, the as-obtained sample still maintains sphere-like morphology with smooth surface (Fig. 2c), and pie-like shape almost disappears except for the circle trace left on the sphere surface of the CACms (Fig. 2d).

Surface functional groups of the pure PVA raw materials, PVAms and CACms were detected by Fourier transform infrared spectrometry (FTIR). As shown in Fig. 3a, a band at 3430 cm^{-1} of the spectrum for pure PVA is assigned to OH^- stretching vibration [42], the absorption band at 2922 cm^{-1} and 1390 cm^{-1} attributed to the C—H stretching vibration and in-plane bending vibration of methene (—CH_2—) on the ploymer chain [43,44], respectively. The peak at 1041 cm^{-1} corresponds to C—O stretching vibration of PVA chain [45]. The spectrum of PVA microspheres as shown in Fig. 3b, the new absorption band around 1730 cm^{-1} corresponds to the carbonyl function group (C═O) stretching frequency, indicating chemical rearrangement reaction occurs for the PVA molecular and results the formation of PVAms [46]. Furthermore, some peaks at 541 and 463 cm^{-1} in fingerprint region can be ascribed to the adsorption bands of α-Fe_2O_3 [47]. In Fig. 3c, the peak intensity of the spectrum for pure PVA raw material assigned to —OH stretching vibration is lower than that of FTIR spectrum of the pure PVA raw materials and PVAms. This finding is apparently due to the fact that the chemical activation of sulfuric acid initiated bond cleavage, leading to dehydration and elimination reactions that release volatile products such as water and other chemical substances. In other words, sulfuric acid breaks many bonds in the

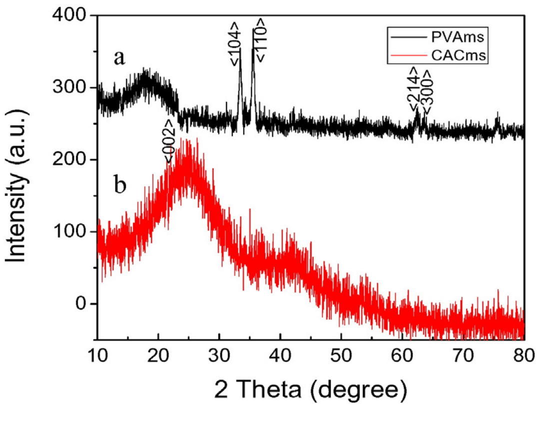

Fig. 1. XRD patterns of PVAms and CACms.