Selective Adsorption of Anionic Dye from Solutions by Modified Activated Carbon

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Received: 8 September 2017 / Accepted: 30 November 2017 / Published online: 18 December 2017
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Abstract
A new adsorbent (AC–BP–V) was synthesized by activated carbon, which was used to remove anionic amaranth from aqueous solutions. The adsorption capability, adsorption isotherm and kinetics of the AC–BP–V were studied. X-ray photoelectron spectroscopy (XPS) and zeta potential were employed to characterize the adsorbent. Experimental results indicated that AC–BP–V adsorbent exhibited high-selectivity adsorption and efficiency for anionic dyes. Adsorption behavior of the modified activated carbon from aqueous solution was investigated by varying the parameters such as pH, contact time and amaranth concentration, and the optimum adsorption pH was 1. The equilibrium data fitted well with the Langmuir isotherm, and the obtained kinetic data obeyed the pseudo-second-order kinetic model. The maximum adsorption capacity was 216.92 mg/g. The new adsorbent (AC–BP–V) has obvious selectivity to anionic dyes. The results indicated that electrostatic interaction was the main mechanism for the adsorption of anionic amaranth.

Keywords Anionic dyes · Modified activated carbon · Selective adsorption · Electrostatic interaction

1 Introduction
With the rapid development of the global industry, organic dyes, such as amaranth and lemon yellow, have been widely used in modern industry. Meanwhile, a large amount of industrial wastewater containing residual dye was produced [1,2]. According to the survey, more than 700,000 tons of dyes are produced in the world every year [3]. And about 2% of them are discharged arbitrarily; in addition, the loss of some reactive dyes in the dyeing process can be up to 50% [4]. Unfortunately, dyes have usually complex aromatic molecular structures and excellent stability, and it is difficult to be adsorbed. That dye wastewater causes great harm to people and environment. Therefore, it is necessary to find an effective and economical method for the treatment of dye wastewater [5,7].

In recent years, the researchers have studied a variety of treatment methods to improve the dye wastewater, which can be roughly divided into three categories. The first category is the chemical treatment methods, such as oxidation and photochemistry. The second category is defined as the physical processing methods, for example adsorption, membrane filtration and ion exchange. The third kind is called biological degradation methods, such as aerobic and anaerobic biodegradation [8,11]. In these methods, adsorption is considered as a promising method due to the advantage of simpler operation, lower cost and more efficient removal. Various adsorbents including activated carbon have been widely used for the removal of dye wastewater [12,13]. However, the adsorption capacity and selectivity were found to be lower. Therefore, the surface modification of activated carbon was employed to improve the removal ratio of organic dyes [14,15]. Recently, the literature has reported that the organic compounds or heavy metal ions are treated by grafting functional groups to improve the removal ratio of dyes. So, how
to improve the adsorption capacity of activated carbon is the main concern of people at present [16].

In the work, a new adsorbent (AC–BP–V) was prepared via grafting vinylimidazole onto the activated carbon. The ionic liquid adsorbent was characterized by XPS, zeta potential and \( \text{N}_2 \) adsorption–desorption measurement. In addition, adsorption performance of a new adsorbent for anion dyes was also investigated by various factors such as contact time, pH and concentration. The adsorption isotherm and kinetics were investigated to further understand the adsorption mechanism. And the selective adsorption experiments were verified.

2 Materials and Methods

2.1 Materials

Activated carbon was purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (China). Thionyl chloride, 3-bromo-1-propanol, cupric bromide, 4,4′-bipyridine and 1-vinylimidazole were supplied by Aladdin Chemical Reagent Co., Ltd. (China). \( \text{N}_2, \text{N}-\text{Dimethylformamide (DMF)} \) was obtained from Zhiyuan Chemical Reagent Co., Ltd. (China). HCl and NaOH were used to adjust the pH value of the solution.

2.2 Synthesis of Adsorbent

In the first step, 10 g of activated carbon and 120 mL of concentrated nitric acid (65 ∼ 68%) were mixed and stirred for 12 h in three bottles. Then the activated carbon (AC–COOH) was washed with distilled water until pH 7. In the second step, 7.5 g of activated carbon (AC–COOH) and 10 mL thionyl chloride were mixed and stirred under 80 \( ^\circ \)C for 24 h in three bottles, and then washed five times using \( \text{N}_2, \text{N}-\text{Dimethylformamide (DMF)} \), resulting in AC–COCl. In the third step, 6 g of activated carbon (AC–COCl) and 10 mL of 3-bromo-1-propanol (BP) were mixed, under the condition of 80 \( ^\circ \)C for 24 h, and washed with DMF. In the fourth step, 0.25 g of cupric bromide, 0.5 g of 4,4′-bipyridine, 5 mL of 1-vinylimidazole (V), 50 mL of DMF and 5 g of activated carbon (AC–BP) were mixed and stirred. The reaction was carried out under the atmosphere of \( \text{N}_2 \), at 90 \( ^\circ \)C for 24 h. Finally, the mixture was separated using centrifugation and washed by alcohol and dilute ammonia. After drying, the product activated carbon is defined as AC–BP–V. The synthesis process is shown in Fig. 1.

2.3 Analysis

X-ray photoelectron spectroscopy (XPS) was carried out by SPECS-GmbH spectrometer. Zeta potential measurements were taken using a ZetaPALS (phase analysis light scattering) was employed to analyze the zeta potential, Brookhaven Instruments Corp., the USA) with a voltage of 110–240 V and frequency of 50–60 Hz. Dye concentrations of aqueous solution were recorded using a UV spectrophotometer (UV-2401PC, Shimadzu, Japan).

2.4 Batch Adsorption Experiments

The adsorption amount of amaranth on AC–BP–V was detected by adsorption experiments. Usually, 10 mL of amaranth and 20 mg of AC–BP–V were added into a centrifugal tube and shaken at room temperature for 10 h. After centrifugation, the concentration of dye in the supernatant was determined. The adsorption amount was calculated as follows [17]:

\[
q_e = \frac{(C_0 - C_e)V}{M},
\]

where \( q_e \) is the adsorption quantity (mg/g). \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of amaranth (mg/L), respectively; \( V \) is the volume of solution; and \( M \) is the weight of the AC–BP–V adsorbent.

Batch kinetic experiments were performed via adding 20 mg of AC–BP–V to 10 mL of amaranth solution with different initial concentrations and mixing in a thermostatic shaker at 25 \( ^\circ \)C. The contact time was from 60 to 900 min, and 11 samples were obtained. The supernatant solution of amaranth was collected and analyzed. Each experiment was repeated three times, and the average value was recorded.