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Short Communication

Kinetics and thermodynamics of basic dye sorption on phosphoric acid esterifying soybean hull with solid phase preparation technique

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Abstract

In this paper, the solid phase preparation method of a cationic sorbent, which bears hydroxyl groups of phosphoric acid derived from esterified soybean hull (ESH), was reported. The sorption kinetics and thermodynamics of two basic dyes, acridine orange (AO) and malachite green (MG), from aqueous solution onto ESH were investigated with a batch system. The isothermal data of dye sorptions followed the Langmuir model better than the Freundlich model. The maximum sorption capacity (Q_m) of ESH for AO and MG was 238.1 mg/g and 178.57 mg/g, respectively. The dye sorption processes could be described by the pseudo-second-order kinetic model. The thermodynamic study indicated that the dye sorptions were spontaneous and exothermic. Lower temperatures were favorable for the sorption processes.

Keywords: Kinetics; Thermodynamics; Basic dye; Sorption; ESH

1. Introduction

Dyes are extensively used in various industries, particularly in textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries. It is reported that over 100,000 commercially available dyes exist and more than 7×10^5 metric tones of dyes are produced worldwidely every year (Pearce et al., 2003; McMullan et al., 2001). Dye wastewater discharged from various industries causes certain hazards and environmental problems. From the environmental viewpoint, the removal of dyes from wastewater is a great mission, since some dyes and their metabolites may be toxic, carcinogenic, mutagenic, as well as teratogenic (McKay et al., 1985; Gregory et al., 1991).

It is difficult to remove the color from wastewater because dyes are not only stable to light and heat but also resistant to oxidation and biodegradation. Since biological aerobic/anaerobic treatment is ineffective for removing dyes from wastewater, other methods of treatment need to be explored. The activated carbon is the most popular sorbent for wastewater treatment. However, certain factors limit its applications such as the high cost and regeneration trouble. At present, there is a growing interest in using other low cost sorbents for dye removal. Many lignocellulosic materials, including bagasse pith (McKay et al., 1987), coconut husk (Low and Lee, 1990), banana pith (Namasivayam et al., 1993), coir pith (Namasivayam and Kadirvelu, 1994), sunflower stalks (Sun and Xu, 1997), corncob, barley husk (Robinson et al., 2002), kudzu (Allen et al., 2003), rice husk (Vadivelan and Kumar, 2005), pine sawdust (Özacar and Sengil, 2005), peanut hull (Gong et al., 2005), lemon peel (Kumar, 2007) and kohlrabi peel (Gong et al., 2007), had been used as low cost dye sorbents. Some lignocellulosic materials also had been chemically modified for improving their dye sorption capacity (Low and Lee, 1997; Marchetti et al., 2000; Ong et al., 2007).

In this paper, the solid phase preparation technique of a cationic sorbent derived from modified soybean hull was reported. The soybean hull was thermochemically esterified

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by phosphoric acid (PA) with urea as catalyst. Up to now, to the best of our knowledge, the solid phase preparation technique of PA esterifying lignocellulosic materials has not been described. The sorption kinetics and thermodynamics of esterified soybean hull (ESH) as a cationic sorbent for removing two basic dyes, acridine orange (AO) and malachite green (MG), from aqueous solution were investigated with a batch system.

2. Methods

2.1. Preparation of soybean hull and esterifying agent

Soybean hull, supplied by a local vegetable oil factory, was washed with tap water to remove soil and dust, and then dried at 50 °C for overnight. The dried soybean hull was ground and sieved, and the 420–850 μm fractions were retained for the further thermochemical esterification.

The esterifying agent was prepared by dissolving 1.67 g of urea in 1 L of 0.5 M PA, and its pH was adjusted to 3.5 with NaOH.

2.2. Esterification of soybean hull

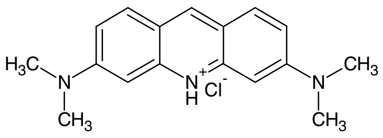
The ground soybean hull was mixed with esterifying agent at the ratio of 1:12 (hull:esterifying agent, w/v) and stirred for 30 min. The mixture was dried at 50 °C in a forced air oven for 24 h. The thermochemical reaction between PA and soybean hull was conducted by raising the oven temperature to 120 °C for 90 min. After that, the cooled ESH was washed extensively to neutral pH with distilled water. Then the ESH was filtrated and suspended in 0.1 M NaOH at suitable ratio and stirred for 60 min. Finally, the ESH was washed thoroughly with distilled water to remove residual alkali, dried at 50 °C until the weight was constant and preserved in a desiccator as sorbent for further use.

2.3. Preparation of cationic dye solution

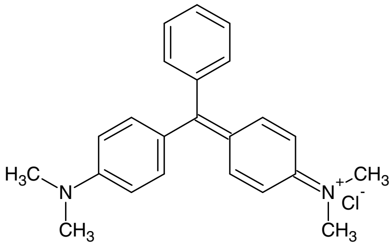
AO and MG, in commercial purity, are two basic dyes of acridine type (CI No. 46,005, FW = 301.83, $\lambda_{\max} = 490$ nm) and triphenylmethane type (CI No 42,000, FW = 364.9, $\lambda_{\max} = 617$ nm), respectively. Their chemical structures are shown in Fig. 1. Dye stock solutions (500 mg/L) were prepared and then diluted to different initial concentrations for sorption experiments.

2.4. Experimental methods

The batch sorption experiments were carried out in 250 mL flasks containing 100 mL dye solutions with different concentrations or initial pH in a shaker rotated at 150 rpm. Different doses of ESH were added to each flask, and then the flasks were sealed up to prevent change of volume of the solutions during the experiments. After shaking for predetermined time intervals at predetermined temperatures, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration/centrifugation. The dye concentrations in the supernatant solutions were determined by spectrophotometry.



Acridine orange



Malachite green

Fig. 1. The chemical structures of AO and MG.

To detect the effects of pH on dye sorptions, the initial pH of dye solutions were adjusted with dilute HNO_3 or NaOH using a pH meter. After sorption, the pH of supernatant solution was again adjusted with a buffer (pH 6) for avoiding color change caused by different initial pH.

The experiments were conducted in duplicate and the negative controls (without sorbent) were simultaneously performed to ensure that sorption was not by the container but sorbent.

3. Results and discussion

The preliminary experiments indicated that the maximum dye sorption ratios were reached and the percentages of sorbed dyes kept basically unchangeable in AO ($pH \geqslant 4$) and in MG ($pH \geqslant 6$). For this reason, the pH 6 was selected as the optimum pH for the other experiments. For 250 mg/L of dye solutions, the maximum dye sorption percentages were reached by 2.0 g/L or up of ESH. So, the ESH dosage of 2.0 g/L was chosen for the further experiments.

3.1. Sorption isotherm

The effects of initial dye concentrations on dye sorptions were investigated. When the dye concentrations were increased from 50 to 500 mg/L, the percentages of sorbed AO and MG decreased from 98.06% to 85.36% and from 98.42% to 68.52%, respectively. But the amount of dye sorbed on ESH increased from 24.52 mg/g to 213.4 mg/g in AO and from 24.61 mg/g to 171.3 mg/g in MG. When the ESH dosage was fixed, the percentages of sorbed dyes decreased consequentially with the increase of initial dye concentrations due to the active sites of ESH exhausted.