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Removal of basic and reactive dyes using ethylenediamine modified rice hull

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Abstract

Wastewaters from textile industries may contain a variety of dyes that have to be removed before their discharge into waterways. Rice hull, an agricultural by-product, was modified using ethylenediamine to introduce active sites on its surface to enable it to function as a sorbent for both basic and reactive dyes. The sorption characteristics of Basic Blue 3 (BB3) and Reactive Orange 16 (RO16) by ethylenediamine modified rice hull (MRH) were studied under various experimental conditions. Sorption was pH and concentration dependent. Simultaneous removal of BB3 and RO16 occurred at pH greater than 4. The kinetics of dye sorption fitted a pseudo-second order rate expression. Increase in agitation rate had no effect on the sorption of BB3 but increased uptake of RO16 on MRH. Decreasing particle size increased the uptake of dyes in binary dye solutions. Equilibrium data could be fitted into both the Langmuir and Freundlich isotherms. Maximum sorption capacities calculated from the Langmuir model are 14.68 and 60.24 mg/g for BB3 and RO16, respectively in binary dye solutions. This corresponds to an enhancement of 4.5 and 2.4 fold, respectively, compared to single dye solutions. MRH therefore has the potential of being used as an efficient sorbent for the removal of both dyes in textile wastewaters.

Keywords: Sorption; Rice hull; Ethylenediamine; Reactive dyes; Basic dyes

1. Introduction

Dye, a constituent that is widely used in textile, paper, plastic, food and cosmetic industries is an easily recognized pollutant. Its presence, even in very low concentration, is highly visible and will affect aquatic life as well as food web. Many dyes are difficult to degrade, as they are generally stable to light, oxidizing agent and are resistant to aerobic digestion (McKay and Sweeney, 1980). Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and nonbiodegradable characteristics.

The conventional methods of color removal from industrial effluents include ion exchange, activated carbon adsorption, membrane technology and coagulation (Nigam, 2000). Amongst all, the sorption process by activated carbon has been shown to be one of the most efficient methods to remove dyes from effluents (Malik, 2002). However, relatively high operating costs and problems with regeneration of the spent carbon hamper its large-scale application (Janoš et al., 2003). This subsequently led to search for more economical alternative sorbent. A number of investigations have shown that agricultural by-products such as date pith, sawdust, corn corb, barley husk, rice hull and bagasse pith have the potential of being used as alternative sorbent for the removal of dyes in textile wastewater (Banat et al., 2003; Garg et al., 2003; Robinson et al., 2002; Low et al., 2000; Low and Lee, 1997; McKay et al., 1988). Chemical modifications of these materials enhanced their sorption capacities and thus usefulness in the treatment of wastewater. These materials, in general, possess high sorption capacities for either positively or negatively charged dye molecules, but not both. It is not uncommon to find textile industries using a mixture of

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different types of dyes for different applications. Hence there is a need to have sorbents capable of removing different types of dyes either singly or simultaneously.

Previous work in our laboratory has shown that modification of rice hull using ethylenediamine (EDA) yielded a material capable of removing both Cr(VI) and Cu(II) (Tang et al., 2003). In this paper, we reported the performance of EDA modified rice hull (MRH) as a sorbent for a cationic dye Basic Blue 3 (BB3) and an anionic dye Reactive Orange 16 (RO16) from single and binary dye solutions.

2. Methods

2.1. Sorbent

Rice hull was collected and washed several times to ensure the removal of dust and ash. It was subsequently rinsed several times with distilled water and dried overnight in an oven at 50 °C. The dried rice hull was ground to pass through a 1 mm sieve and labeled as natural rice hull (NRH). Modification of NRH was optimized by varying the treatment temperature and the ratio of NRH to EDA. Consequently ethylenediamine modified rice hull (MRH) was prepared by treating NRH with EDA in a ratio of 1.00 g rice hull to 0.02 mole of EDA in a well-stirred water bath at 80 °C for 2 h.

2.2. Sorbates

Synthetic dye solutions of BB3 and RO16 were used as the sorbates in this study. Their structures are illustrated in Fig. 1. The cationic dye BB3 (C.I. = 51004, 40% dye content) and anionic dye RO16 (C.I. = 17757, 50% dye content) were used without further purification. All dye powders used in this study were purchased from Sigma-Aldrich Pte. Ltd. (United States of America). Concentrations of dye solutions prepared were calculated taking the dye content into consideration. Standard dye solutions of 2000 mg/L were prepared as stock solutions and subsequently diluted when necessary.

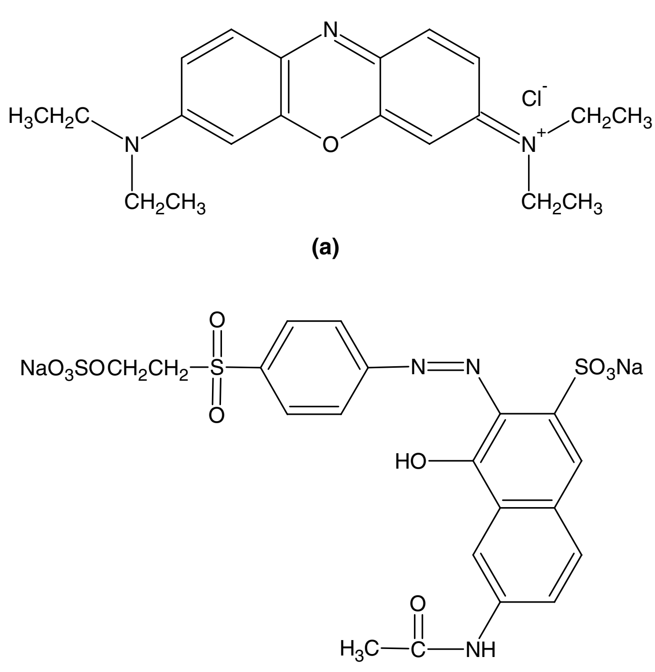

Fig. 1. The structures of (a) Basic Blue 3 and (b) Reactive Orange 16.

2.3. Batch experiments

All the batch experiments were carried out in duplicate and the results given are the means with a relative standard deviation (RSD) of less than 5%. RSD is defined as

$$\mathrm{SD} \times \frac{100\%}{\overline{X}} \tag{1}$$

where SD = standard deviation, $\overline{X}$ = mean of the measurements. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. Sorption experiments were performed by agitating 0.05 g of sorbent in 20 mL of 100 mg/L dye solution in a centrifuge tube at 150 rpm on an orbital shaker for 8 h at room temperature (25 ± 2 °C) unless otherwise stated. The sorbent–sorbate mixture was then centrifuged at 3.0×10^3 rpm for phase separation. The supernatant was analyzed for its dye concentration using a Shimadzu 160B (Kyoto, Japan) double beam UV–vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption; for BB3, $\lambda_{max} = 654$ nm and for RO16, $\lambda_{max} = 494$ nm. Dilutions were carried out when measurement exceeded the linearity of the calibration curve.

In the study of comparative uptake of dyes, the dye binding capacities of MRH and NRH for BB3 and RO16 in single and binary dye solutions were compared. A quantity of 0.05 g of each sorbent was shaken in 20 mL of 100 mg/L dye solution at 150 rpm for 4 h.

To study the effect of pH, a series of 100 mg/L single and binary dye solutions of BB3 and RO16 were prepared. The initial pH of the dye solutions was adjusted to the range of 2–10 by adding dilute HCI or NaOH. No buffer was added to maintain constant pH. At the end of experimentation pH of dye solutions were measured. Each dye solution was shaken with 0.05 g sorbent for 4 h.

Contact time experiments were performed using BB3 and RO16 dye solutions, both single and binary, with concentrations ranging from 50 to 100 mg/L. The samples were withdrawn and analyzed for their dye concentrations at predetermined intervals. The effect of agitation rate was investigated by varying the agitation rates from 50 to 250 rpm using dye solutions of 100 mg/L. The effect of particle size on dye sorption was studied by sieving the MRH into three different sizes ranging between 105–250, 250–315 and 315–1000 μm.

Sorption isotherms were obtained by varying the dye concentrations from 5 to 150 mg/L for single and binary