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Dye adsorption by resins: Effect of ionic strength on hydrophobic and electrostatic interactions

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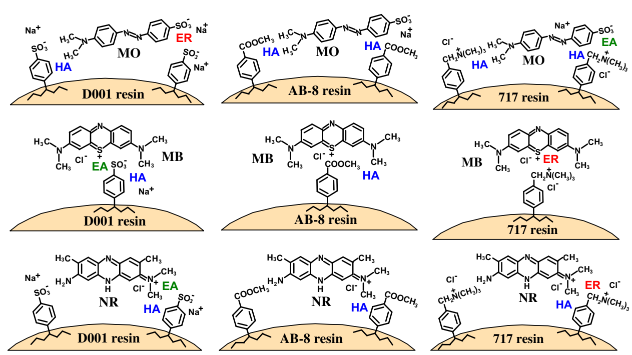
HIGHLIGHTS

- In adsorption processes, interactions between dyes and resins were studied in detail.
- The importance of hydrophobic and electrostatic interactions on adsorption were emphasized.
- Hydrophobic attraction increases with increasing ionic strength.
- Electrostatic interaction decreases with increasing ionic strength.

GRAPHICAL ABSTRACT



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ABSTRACT

Dyes are adsorbed mainly through hydrophobic and electrostatic attractions and hydrogen bonding between the dyes and the adsorbents. pH and ionic strength are two important factors affecting dye adsorption. Solution pH affects the adsorption mainly through adjusting the electrostatic interactions. While the effect of ionic strength on the dye adsorption is more complicated and is not so clear. Ionic strength may affect not only the electrostatic interactions, but also the hydrophobic interactions. In this study, the effect of ionic strength on the adsorption of three dyes onto three resins were designed and investigated comparatively and comprehensively. The selected resins with a same matrix were negatively charged D001, neutral AB-8 and positively charged 717 resins. The selected dyes were methyl orange (MO), methylene blue (MB) and neutral red (NR) with negative, positive and weak positive charges, respectively. Nine groups of combinational batch adsorption experiments were carried out using the three resins and the three dyes. There are two experiments in each group. In one experiment a solution with 1 mol/L NaCl was used, while in the other experiment a solution without NaCl was used for comparison. Our experimental results confirmed the importance of hydrophobic and electrostatic interactions on the dye adsorption. The hydrophobic attraction was found to increase with increasing ionic strength. While the electrostatic interactions were found to decrease with increasing ionic strength.

1. Introduction

Dyes have been widely used in textile, leather, paper, plastics, printing, electroplating, food and cosmetic industries [1,2]. They are considered as water contaminants [3]. The discharge of dyes into water bodies reduces light penetration and decrease the photosynthetic efficiency of aquatic plants [3]. Some of the dyes and their products have a mutagenic or carcinogenic influence on human beings [1]. Therefore, considerable attention has been paid to treat dyes before discharge [4,5]. Filtration, flocculation, precipitation, degradation and adsorption processes have been applied

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for the removal of dyes from aqueous solutions [3,6]. Among these methods adsorption is proven as a reliable and effective process in terms of flexibility, simplicity, ease of operation, low operational cost, minimum sludge production, etc. [3,6,7].

In the processes of dye adsorption, several factors are reported to affect the adsorption. These factors include adsorbent dose, initial adsorbate concentration, contact time, temperature, pH and ionic strength [3,5,8–11]. Among them, pH and ionic strength are two important factors affecting the adsorption processes. Dyes are adsorbed mainly through hydrophobic and electrostatic attractions, hydrogen bonding and surface function group interactions between the adsorbents and the dyes [12–16]. Solution pH affects not only the surface charge of the adsorbents, but also the ionization of the dyes [3]. Solution pH affects the adsorption mainly through adjusting the electrostatic interactions between the dyes and the adsorbents [11,12–15]. While the effect of ionic strength on the dye adsorption is more complicated and is not so clear [17–20]. Ionic strength may affect not only the electrostatic interactions, but also the hydrophobic interactions [17].

Although it is known that ionic strength may affect the electrostatic and hydrophobic interactions, very little is known about the detail of the effect. The present study represents an effort to gain a better understanding of this issue. The effect of ionic strength on the adsorption behavior of three dyes onto three resins was designed and investigated comparatively and comprehensively. The selected resins have a same matrix. They were negatively charged D001, neutral AB-8 and positively charged 717 resins. The selected dyes were methyl orange (MO), methylene blue (MB) and neutral red (NR) with negative, positive and weak positive charges, respectively. It would be better to use a dye without charge to replace NR. However, when a dye is purely neutral, its solubility is low and it is not easy to carry out the comparative adsorption experiments. Therefore, NR was used. MO, an anionic azo dye, has been used in textile, printing, paper, pharmaceutical and food industries [3,7]. MB, a cationic dye, has been extensively used in dyeing industry [1,21,22]. NR, also a cationic dye, has been commonly used for counterstaining nuclear in biological research. It is a pH indicator with changing color from red to yellow over a pH range of 6.8–8.0 [5]. Through the designed adsorption studies using these dyes, the effect of ionic strength on electrostatic and hydrophobic interactions were checked and discussed in detail.

2. Experimental

2.1. Resins

D001, AB-8 and 717 resins were purchased from Xi'an Lanxiao Technology Ltd. (China), Shanghai Kaiping resin Ltd. (China) and Laiyang Shuangshuang Chemical Factory (China) respectively. Some parameters of these resins are listed in Table 1. Before use all the resins were washed using de-ionized water thoroughly, filtered and finally stored in a closed container. The wet resins were used for the adsorption experiments. Water content of the resins was measured using a moisture analyzer (MB45, OHAUS) by heating the resins to 100 °C.

2.2. Organic dyes

MO, MB and NR were purchased from Tianjin Tensing Fine Chemical Research Develop Center (China), Tianjin Baishi Chemical Industry Co., Ltd. (China) and Sinopharm Chemical Reagent Co., Ltd. (China). The molecular structures of these dyes are shown in Fig. 1.

Table 1
Resins used for the adsorption experiments.

Resin	Matrix	Functional group	Particle diameter (mm)	Water content (%)
D001	Styrene-DVB	$-SO_3^-$	0.4–0.7	52.00
AB-8	Styrene-DVB	$-COOCH_3$	0.3–1.25	73.23
717	Styrene-DVB	$-N(CH_3)_3^+$	0.3–1.2	55.51

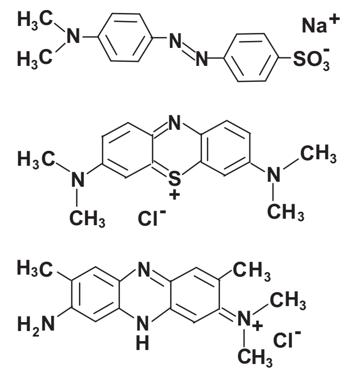

Fig. 1. Molecular structures of the dyes.

2.3. Adsorption studies

Nine groups of combinational batch adsorption experiments were carried out using the three resins and the three dyes. There were two experiments in each group. In one experiment a solution with 1 mol/L NaCl was used, while in the other experiment a solution without NaCl was used for comparison. In all the adsorption experiments, no acids or bases were added into the solutions. And all the experiments were designed to obviously present the effect of ionic strength in solutions with similar pH values. All the batch adsorption experiments were performed by mixing 0.16 g of the wet resins with 250 mL of 0.122 mmol/L dye solutions at 25 °C in a SHA-C water bath (Changzhou Guohua Co., Ltd., China) with a shaking speed of 155 rpm.

Dye concentration change was recorded on a TU-1810 UV–visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd. China) by measuring the solution absorbance at maximum absorption in suitable diluted solutions: MO at 507.50 nm in pH 2 solutions; MB at 664.50 nm in pH 7 solutions; NR at 530.50 nm in pH 5 solutions. The adsorption amount of dyes onto the resins was calculated using the following equation:

$$q = \frac{V(C_0 - C)}{m} \qquad (1)$$

where q (mmol/g) is the adsorption amount of the dyes onto the resins, V (L) the volume of the solution, m (g) the dry weight of the resins. C_0 and C (mmol/L) are the dye concentrations in the solutions before and after adsorption, respectively.

3. Results and discussion

3.1. Comparison of the adsorption results

The effect of ionic strength on the dye adsorption by the resins is shown in Figs. 2–4. In order to have a total comparison, the amount of the dyes adsorbed by the resins after adsorption for 48 h is shown in Fig. 5. The general comparative adsorption results could be summarized as follows: