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Study of antagonistic effect in the simultaneous removal of two textile dyes onto cellulose extracted from *Posidonia oceanica* using derivative spectrophotometric method

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ABSTRACT

The sorption of Acid Blue 25 (AB) and Direct Blue 86 (DB) was investigated in single and binary aqueous systems using cellulose extracted from *Posidonia oceanica* as sorbent by employing a batch experimental set-up. First order derivative spectrophotometric method was successfully applied to the simultaneous analysis of AB and DB concentrations with overlapping spectra in their bicomponent mixtures. The single and multi-component Langmuir and Freundlich isotherm models were applied to describe the experimental equilibrium adsorption data of both the dyes. The data fitted more adequately to mono-component Langmuir isotherm model than mono-component Freundlich isotherm model, while the revisited extended Langmuir isotherm model best predicted the multi-component sorption data, suggesting sorption selectivity toward DB dye. The maximum monolayer dye uptake capacity of extracted cellulose in single dye system was determined as 0.623 mmol g^{-1} and 0.057 mmol g^{-1} for AB and DB, respectively. It was observed that the equilibrium uptake amounts of AB and DB dyes in binary mixture onto extracted cellulose decreased considerably with increasing concentrations of the other dye resulting in their antagonistic effect.

1. Introduction

Adsorption has proven to be a promising and cost effective method for the removal of both inorganic [1] and organic [2–5] pollutants from contaminated water. Cost is an important parameter for the selection of the sorbent materials in designing sorption system. In recent years, attention has been focused on the research and development of various low cost alternative sorbents for dyes removal, including sawdust [6], agricultural wastes [7–10], activated sludge from sewage-treatment plant [11] and bio-available materials such as clay [12,13], chitin [14], algae [15], cotton fiber [16], which seem to have good potentials for the treatment of textile effluents by sorption on solid surfaces.

Dyes are complex aromatic substances essential in many industries such as textile, paper, paint, leather and pharmaceutical. Compared with natural dyes [17], synthetic dyes are superior in terms of color availability, permanency, easiness to use, quick-setting and ensured by accurate formulas [5]. However, most of the dyes are stable to light, heat and many oxidizing agents, and more difficult to be biodegraded. With the introduction of strict environmental legislation, effluents containing dyes require proper treatment prior to discharge, not only for their high chemical oxygen demand (COD), suspended solids and toxic breakdown products, but also for color, which is not only highly visible and undesirable, but also harm the environment and cause health problems to humans and aquatic animals.

Although many studies focused on the improvement of sorption performance for dyes in mono-component dye system by various sorbents, most industrial effluents contain a mixture of several dyes and little attention has been given to multi-component dye systems sorption. In multi-component dye systems, an important problem is to analyze the dyes simultaneously in mixtures. Spectrophotometric methods are more economic and simpler, compared to methods such as chromatographic techniques [18], capillary electrophoresis [19] and electrochemistry [20], which have several drawbacks, such as the need for complex sample pre-treatments, the usage of toxic solvents, and the resulting waste products. Because of the severe overlapped zero-order absorption spectra, the use of traditional spectrophotometric techniques is difficult without any separation steps. Derivative spectrophotom-

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etry, which is based on the analysis of derivative spectra, is a very useful analytical technique to resolve binary and ternary solutions with overlapping [21]. By measuring the derivative values, at the wavelengths where other components undergo zero, the best linear responses are obtainable, which enables the determination of each individual compound concentration in the presence of others.

Posidonia oceanica, a local biomass abundant on the coasts of Tunisia, has shown its effectiveness in removing organic (textile dyes [22–25]) and inorganic pollutants (heavy metals [22,23]). The cellulosic material namely cellulose and hemicellulose, represent the major constituent of the *P. oceanica* (62%) with a relatively high lignin (27%) [26]. In our research, the cellulose extracted from the marine plant is used as sorbent for two anionic dyes sorption in single and binary systems.

Acid Blue 25 (AB) and Direct Blue 86 (DB), widely used in dyeing wool, silk, cotton, nylon, leather and paper, are both water soluble dyes. In this study, these two anionic dyes were selected as model compounds to evaluate the competitive sorption of dyes in binary solutions onto extracted cellulose.

For this study there are two main objectives: the first is the simultaneous analysis of the AB and DB dyes in binary solutions using the first-order derivative spectrophotometric method, the second is the competitive sorption of AB and DB dyes onto extracted cellulose.

2. Theory and adsorption models

The recovery studies were performed to check the accuracy of the first order derivative method used to determine of the dye concentration in binary solutions. In this recovery study, the binary dye solutions of AB and DB containing different concentrations of each dye were prepared and the first order derivative spectra of the binary mixtures were recorded.

The recoveries (%), errors (%) and average percentage errors (%) between the theoretical (C_t) and measured concentrations (C_m) were calculated using Eqs. (1)–(3), respectively. In Eq. (3), N is the number of measurements.

$$\text{Recovery}\ (\%) = \frac{C_m\ (\text{mg L}^{-1})}{C_t\ (\text{mg L}^{-1})} \times 100 \tag{1}$$

$$\text{Error}\ (\%) = \frac{C_m\ (\text{mg L}^{-1}) - C_t\ (\text{mg L}^{-1})}{C_t\ (\text{mg L}^{-1})} \times 100 \tag{2}$$

$$\text{€}\ (\%) = \frac{\sum_{i=1}^{N} |(C_m - C_t)/C_t|}{N} \times 100 \tag{3}$$

The prediction of multi-component equilibrium data was always complicated due to the competitive effects involved. Multi-component isotherm models have been derived from the mono-component isotherm. However, using the parameters of mono-component isotherm model alone, may not fully describe the synergetic and antagonistic interactions adsorption behavior of dye mixtures [27].

Extended Langmuir isotherm is the most generally used model in multi-component system and was expressed as follows [28]:

$$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}} \tag{4}$$

where $q_{e,i}$ is the equilibrium sorption capacity of dyes (mmol g^{-1}), $C_{e,i}$ and $C_{e,j}$ are the equilibrium concentrations of dyes in mmol L^{-1} in binary system, and $q_{m,i}$ and $K_{L,i}$ are maximum sorption capacities (mmol g^{-1}) and Langmuir constant (L mmol^{-1}), respectively, obtained from single solute system [29].

For binary system such as AB and DB mixtures, the extended Langmuir equation above becomes:

$$q_{e,AB} = \frac{q_{m,AB} k_{L,AB} C_{e,AB}}{1 + K_{L,AB} C_{e,AB} + K_{L,DB} C_{e,DB}} \tag{5}$$

$$q_{e,DB} = \frac{q_{m,DB} k_{L,DB} C_{e,DB}}{1 + K_{L,DB} C_{e,DB} + K_{L,AB} C_{e,AB}} \tag{6}$$

The applications of extended Langmuir model to represent sorption equilibrium data in binary system have been reported in many studies [30–32]. From the previous studies, it was known that the evaluation of equilibrium data using extended Langmuir model was performed by inserting the values of q_m and K_L parameters in single system to calculate theoretical q_e and with comparison with experimental one. In binary system, the sorption potential on the sorbent surface is affected by several interactions or competition between sorbate species. Consequently, it is obvious that both K_L and q_m parameters from single Langmuir model cannot be adequately used to describe sorption behaviors in binary system. Kurniawan et al. [33] proposed a revisited mathematical equation for q_m and K_L parameters for binary sorption system:

$$q_{m(bin)} = q_{m,AB(sin)} \theta_{AB} + q_{m,DB(sin)} \theta_{DB} \tag{7}$$

$$K_{L,AB(bin)} = K_{L,AB(sin)} \exp\left(-\frac{\theta_{DB}}{\theta_{AB}}\right) \tag{8}$$

$$K_{L,DB(bin)} = K_{L,DB(sin)} \exp\left(-\frac{\theta_{AB}}{\theta_{DB}}\right) \tag{9}$$

where θ_{AB} and θ_{DB} are constants representing fractional loading of each sorbate on the sorbent surface.

By substituting Eqs. (7)–(9) into extended Langmuir model:

$$q_{e,AB(bin)} = \frac{(q_{m,AB(sin)}\theta_{AB} + q_{m,DB(sin)}\theta_{DB}) K_{L,AB(sin)} \exp(-(\theta_{DB}/\theta_{AB})) C_{e,AB(bin)}}{1 + K_{L,AB(sin)} \exp(-(\theta_{DB}/\theta_{AB})) C_{e,AB(bin)} + K_{L,DB(sin)} \exp(-(\theta_{AB}/\theta_{DB})) C_{e,DB(bin)}} \tag{10}$$

$$q_{e,DB(bin)} = \frac{(q_{m,AB(sin)}\theta_{AB} + q_{m,DB(sin)}\theta_{DB}) K_{L,DB(sin)} \exp(-(\theta_{AB}/\theta_{DB})) C_{e,DB(bin)}}{1 + K_{L,AB(sin)} \exp(-(\theta_{DB}/\theta_{AB})) C_{e,AB(bin)} + K_{L,DB(sin)} \exp(-(\theta_{AB}/\theta_{DB})) C_{e,DB(bin)}} \tag{11}$$

The empirical extended form of the Freundlich isotherm model [34] restricted to binary mixtures can be given by Eq. (12):

$$q_{e,i} = K_{F,i} C_{e,i} \left(\sum_{j=1}^{N} a_{ij} C_{e,j} \right)^{n_i - 1} \tag{12}$$

where $q_{e,i}$ is the adsorption amount of each component i, $C_{e,i}$ and $C_{e,j}$ the concentrations of i and j at equilibrium, n_i and $K_{F,i}$ the Freundlich constants obtained for i in a single component system, and a_{ij} the competition coefficient for adsorption of component i in the presence of component j.

For binary-systems (AB + DB), the isotherm can be written as:

$$q_{e,AB} = K_{F(AB)} C_{e(AB)} (a_{AB/DB} C_{e(AB)} + a_{DB/AB} C_{e(DB)})^{n_{AB} - 1} \tag{13}$$

$$q_{e,DB} = K_{F(DB)} C_{e(DB)} (a_{DB/AB} C_{e(DB)} + a_{AB/DB} C_{e(AB)})^{n_{DB} - 1} \tag{14}$$

The plotting of Eqs. (10) and (11) versus binary experimental data for Langmuir isotherm model, and Eqs. (13) and (14) for Freundlich isotherm model were using Origin 6.0 software. The θ_{AB} and θ_{DB} parameters were obtained by nonlinear fitting, the values