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Adsorption of Remazol Brilliant Blue R using ZnO fine powder: Equilibrium, kinetic and thermodynamic modeling studies

Kezban Ada[a], Aysun Ergene[b,*], Sema Tan[b], Emine Yalçın[b]

[a] Department of Chemistry, Faculty of Arts and Sciences, Kırıkkale University, 71450 Yahşihan-Kırıkkale, Turkey
[b] Department of Biology, Faculty of Arts and Sciences, Kırıkkale University, 71450 Yahşihan-Kırıkkale, Turkey

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ABSTRACT

Zinc oxide powders with six-sided flake-like particles were prepared by homogeneous precipitation from boiling aqueous solutions that contained excess urea and 0.075 (Z075) and 0.300 (Z300) M Zn^{2+}. The average sizes of the particles are 37 and 46 μm, while the average sizes of the crystals are ~45 for Z075 and Z300 at 1000 °C. Equilibrium, kinetic and thermodynamic studies were carried out for the adsorption of RBBR dye from aqueous solution using both types of ZnO in the form of fine powders. The effects of pH, initial dye concentration, contact time and temperature of solution on the adsorption were studied. Langmuir, Temkin and Dubinin–Radushkevich (D–R) isotherm models were used to describe the adsorption of RBBR onto ZnO powders. The Langmuir and D–R isotherm models fit the equilibrium data better than the Temkin isotherm model. The monomolecular adsorption capacity of Z075 and Z300 was determined to be 190 and 345 mg g^{-1} for RBBR, respectively. The Lagergren first-order, Ritchie second-order kinetic and intra-particle diffusion models were used for the adsorption of the dye onto ZnO powders. The Ritchie second-order model was suitable for describing the adsorption kinetics for the removal of RBBR from aqueous solution onto Z075 and Z300. Thermodynamic parameters, such as the Gibbs free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and equilibrium constant of activation ($K^{\#}$) were calculated. These parameters showed that the adsorption process of RBBR onto Z075 and Z300 was an endothermic process of a chemical nature under the studied conditions.

1. Introduction

Zinc oxide (ZnO) powders have potential applications in various fields, such as varistors (variable resistor), transducers, semiconductors, solar cells, non-linear optical materials, gas sensors, ceramics, pigments, rubber additives, photo-catalysts, rubber additives, pharmaceuticals, cosmetics and so on [1–5]. A wide number of methods have been used to prepare ZnO powders, including, homogeneous precipitation in aqueous solution of Zn^{2+} cations, hydrothermal synthesis, microwave synthesis, solution combustion, pulsed laser deposition, emulsion precipitation, ultrasonic atomization, spray pyrolysis, freeze-drying and sol–gel processes [6–15].

The microstructural and morphological characteristics of ZnO powders vary according to the selected synthesis method. ZnO powders of different shapes, such as spindle-like, rod-like, ellipsoidal, spherical, and prismatic have been synthesized by the one or more of the methods mentioned above [16–22]. On the other hand, only a few methods were reported in the literature [23] to prepare ZnO powder having flake-like particles. The aim of this study is the chemical preparation of flake-like ZnO particles using a reaction between zinc sulfate and excess urea in a boiling aqueous solution.

Synthetic dyes are extensively used for textile dyeing and other industrial applications. The total world colorant production is estimated to be about 800,000 tons/year. More than 10,000 dyes are commercially available and at least 10% of the used dyestuff enters the environment as wastes [24]. These industrial effluents are toxic and are characterized by high chemical oxygen demands (CODs)/biological oxygen demands (BODs), suspended solids and intense color [25]. Furthermore, these colored molecules are highly conjugated and can be extremely injurious to the life forms [26]. Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements and they are often difficult to degrade and/or removed by conventional physical and chemical processes [27,28].

Remazol Brilliant Blue R dye (RBBR) is one of the most important dyes in the textile industry. It is frequently used as a starting

* Corresponding author. Tel.: +90 318 3572478/1518; fax: +90 318 3572461.
E-mail address: ayergene@yahoo.com (A. Ergene).

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material in the production of polymeric dyes. RBBR is an anthracene derivative and represents an important class of toxic and recalcitrant organopollutants.

2. Materials and methods

2.1. Preparation of ZnO fine powders

The preparation and some physicochemical properties of the ZnO powders selected as materials in this study were investigated in our previous work [29]. The zinc oxide precursors were precipitated in boiling aqueous solution containing 0.075 and 0.300 M Zn^{+2} and excess urea. The powders were obtained by the calcination of the precursors at 1000 °C for 4 h. The powders that were prepared at two different concentrations are called, for the purposes of this study Z075 and Z300. Scanning electron microscopy (SEM) photographs for Z075 and Z300 were recorded (LEO 435) at 30 kV from samples covered with a gold thin film.

2.2. Preparation of dye

The general characteristics of RBBR are summarized in Table 1. RBBR (CI 61200, Reactive Blue 19) obtained from Sigma–Aldrich Company Ltd, is an anthraquinone-based dye. The concentration of the prepared dye solutions ranged between 0.5 and 10 g L^{-1} for RBBR.

2.3. Adsorption isotherms in a batch system

The three most common adsorption isotherm models were used to fit the equilibrium adsorption data. These are the Langmuir, Temkin and Dubinin–Radushkevich models. The linear form of the Langmuir equation [30–33], is expressed by

$$\frac{C_e}{q_e} = \frac{1}{q_m}K_L + \frac{C_e}{q_m} \quad (1)$$

where K_L denotes the Langmuir isotherm constant related to the affinity between the adsorbent and the adsorbate (L g^{-1}) and q_m denotes the Langmuir monomolecular adsorption capacity (mg g^{-1}). The values of q_m and K_L can be determined by plotting C_e/q_e versus C_e. Equation of the Temkin model [34–36] is given below and is plotted as q_e against ln C_e:

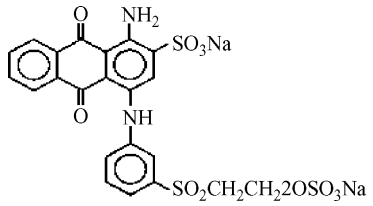
$$q_e = \left(\frac{RT}{b_T}\right)\ln K_T + \left(\frac{RT}{b_T}\right)\ln C_e \quad (2)$$

where b_T is the adsorption potential of the adsorbent and K_T is the equilibrium constant corresponding to maximum binding energy (L g^{-1}). K_T and ΔG° as follows:

$$K_T = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad (3)$$

where R is the universal constant and T is the absolute temperature.

Table 1
The characteristics of RBBR.



Molecular formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Molecular weight	626.54
Color index number	61,200
λ_{max} (nm)	595

The linear form of the Dubinin–Radushkevich model [34–37] is represented by equation:

$$\ln q_e = \ln q_m - K_{DR}\varepsilon^2 \quad (4)$$

where K_{DR} is the porosity factor (mol^2 J^{-2}), q_m (mol g^{-1}) is the monomolecular adsorption capacity of adsorbate adsorption by the powder surface and the variable ε can be related to equilibrium concentration (C_e, g L^{-1}) as follows:

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \quad (5)$$

where ε (J mol^{-1}) is the Polonyi potential, R is the universal gas constant and equal to 8.314 J mol^{-1} K^{-1} and T is the absolute temperature.

A plot of ln q_e versus ε^2 (J^2 mol^{-2}) yields a straight line, confirming the model. The mean free energy of adsorption E (kJ mol^{-1}) per molecule of the adsorbate when it is transferred from the solution to the powder surface can be calculated using the following equation:

$$E = (-2K_{DR})^{-1/2} \quad (6)$$

2.4. Kinetic models for the adsorption

To determine dye adsorption kinetics, three different kinds of kinetic models were used. The Lagergren pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models are shown below [33,34,38–41].

The pseudo-first order model is defined by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

where t is the contact time (min), k_1 is the pseudo-first-order adsorption rate constant (min^{-1}), q_e and q_t are the amount of dye adsorbed on the ZnO fine powders at equilibrium (mg g^{-1}) and at time t, respectively. The integration of Eq. (7) with the initial condition, $q_t = 0$ at $t = 0$ leads to:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

The values of the adsorption rate constant (k_1) were determined from the ln($q_e - q_t$) in terms of t.

The pseudo-second-order model is defined by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

Integrating and rearranging Eq. (9) with the initial condition $q_t = 0$ at $t = 0$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (10)$$

where dq_t/dt is the initial sorption rate (mg g^{-1} min^{-1}) and is defined as $t \to 0$ by $H = k_2 q_e^2$ where k_2 is the pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}). The value q_e is determined from the slope of t/q_t versus t and h is determined from the intercept.

Intra-particle diffusion model: The adsorption of RBBR dye onto ZnO fine powders may be controlled via external film diffusion at earlier stages and later by the particle diffusion. The possibility of intra-particle diffusion resistance was identified by using the following intra-particle diffusion model:

$$q_t = K_{dif}t^{1/2} + C \quad (11)$$

where K_{dif} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and C is the intercept. The values of q_t versus $t^{1/2}$ and the rate constant K_{dif} are directly evaluated from the slope of the regression line.