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Physicochemical modeling of reactive violet 5 dye adsorption on home-made cocoa shell and commercial activated carbons using the statistical physics theory

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ABSTRACT

Two equilibrium models based on statistical physics, i.e., *monolayer model with single energy* and *multilayer model with saturation*, were developed and employed to access the steric and energetic aspects in the adsorption of reactive violet 5 dye (RV-5) on cocoa shell activated carbon (AC) and commercial activated carbon (CAC), at different temperatures (from 298 to 323 K). The results showed that the *multilayer model with saturation* was able to represent the adsorption system. This model assumes that the adsorption occurs by a formation of certain number of layers. The n values ranged from 1.10 to 2.98, indicating that the adsorbate molecules interacted in an inclined position on the adsorbent surface and aggregate in solution. The study of the total number of the formed layers ($1 + L_2$) showed that the steric hindrance is the dominant factor. The description of the adsorbate–adsorbent interactions by calculation of the adsorption energy indicated that the process occurred by physisorption in nature, since the values were lower than 40 kJ mol^{-1}.

Introduction

With the population growth, there is an increase in the demand for industrial products. A number of industries such as textile, food, food stuffs, cosmetic, pharmaceuticals products, rubber and leather, etc., apply dyes in their final products [1,2]. The production and consumption of these industrial products result in large amounts of wastewater contaminated with dyes [3,4]. Industrial wastewater contaminated with dyes is unsafe for aquatic life, impeding light penetration and reducing the photosynthetic activity of aquatic plants [5]. The presence of dyes in the environment affects all living organisms because they have toxic and carcinogenic properties [6–8]. Therefore, it is necessary the removal of synthetic dyes from aqueous effluents.

Adsorption is one of the most employed operations for removal of dyes from industrial effluents [6–9]. Although the adsorption operation is largely used, the adsorption equilibrium still requires further elucidation. To understand the adsorption process at a first time, classical interpretations were developed using empirical models describing the adsorption process of the two considered systems (RV-5 and activated carbons) [10]. To interpret microscopically the adsorption of reactive violet 5 dye (RV-5) on cocoa shell activated carbon (AC) and commercial activated carbon (CAC) at different temperatures, a simple model named *monolayer model with single energy* [11] and a *multilayer model with saturation* [11,12], derived from statistical physics elements, were chosen and developed in this paper. The first model represents the general case of Langmuir model, assuming that a site contains n molecules and a formation of only one layer occurs. The second model, assumes that the adsorption occurs by a formation of $1 + L_2$ layers. It is possible to select other statistical physics models to test the adsorption isotherms, for example, double or triple layer models, but, all these models are tested indirectly, since are included in the *multilayer model with saturation*. In this paper and based on the simulations results, all the adsorption isotherms were interpreted using the *multilayer layer model with saturation*.

This work aimed to study the physicochemical modeling of reactive violet 5 dye adsorption on home-made and commercial activated carbons, using the adequate model in order to describe

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the dyes behavior in solution by estimation of the aggregation degree of the dye molecules based on theoretical observations, and to deduce approximately the total number of the formed layers on the adsorbent surface.

Materials and methods

Solutions and reagents

The RV-5 dye (CAS 12226-38-9; C.I. 18097; $C_{20}H_{16}N_3O_{15}S_4Na_3$, 735.58 g mol^{-1}, λ_{max} = 545 nm see Supplementary Fig. 1) with purity of 86%, was achieved from Sigma-Aldrich (São Paulo, Brazil) and was used without purification. A stock solution (5.0 g L^{-1}) of RV-5 dye was prepared by weighing a calculated amount of the dye and dissolving in deionised water. The stock solution was diluted to obtain various working solutions. The pH of the solutions was adjusted using a Digimed DM-22 pH meter, with a 0.10 mol L^{-1} NaOH and/or a 0.10 mol L^{-1} HCl.

Adsorbents

Cocoa shell activated carbon (AC) and commercial activated carbon (CAC) were used in this work. Commercial activated carbon (CAC) was supplied by Vetec (325–400 mesh). The cocoa shell activated carbon adsorbent was prepared using the following procedures [10]: an amount of 70.0 g of biomass plus 70.0 g of inorganic components (20% lime, 40% $ZnCl_2$, and 40% $FeCl_3$) and 45.0 mL of water were mixed to obtain a paste. This material was placed in a mould cylinder (253.34 cm^3), wet-shaped and dried at 25 °C for 24 h. The dried cylinder was inserted in a stainless steel reactor [10]. The reactor was thereafter heated in the tubular furnace at 10 °C min^{-1} up to 750 °C for 30 min, under N_2 atmosphere (100 mL min^{-1}). The adsorbent was later cooled down to room temperature under N_2 (25 mL min^{-1}), milled, sieved to a particle size ⩽103 μm and stored until use. This carbon material was named CC. To complete the chemical activation of the carbon, a leaching procedure described in the literature was employed [10], obtaining the cocoa shell activated carbon AC.

Batch adsorption studies

The adsorption capacity of proposed AC was compared with a well-established CAC. 50.0 mg of adsorbent and a 20.0 mL of RV-5 dye solution (300.0–1500.0 mg L^{-1}) were placed in various 50.0 mL Falcon tubes at different pH values (2.0–10.0). The mixtures were agitated between 5 and 480 min inside a thermostatic shaker (Oxylab, São Leopoldo, Brazil) from 298 to 323 K. The mixtures were centrifuged for 5 min at 10,000 rpm after the batch adsorption experiments, to separate the adsorbents from the dye solutions. When necessary, aliquots of the supernatant were diluted with deionised water at pH 2.0 before spectroscopic measurement. UV/visible spectrophotometer T90+ UV–VIS was used to quantify the final RV-5 concentration in solution, after adsorption at a maximum wavelength of 545 nm.

Adsorption models development and simulation

Generally, the adsorption isotherms form plays an important role to retrieve helpful information's in order to choose the adequate models suitable for simulation. All the adsorption isotherms of RV-5 dye on activated carbon (AC) and on a commercial activated (CAC) carbon are characterized by a simple form showing that a saturation phenomenon was appeared at high concentration, reflecting that the adsorption is finished. So, the adsorption process of RV-5 dye occurred by a formation of one layer or by a certain number of layers on the adsorbent surfaces. For the reason, two statistical physics models were selected to simulate the adsorption isotherms at different temperatures. The first selected model named by '*monolayer model with single energy*' (**model 1**) [11], it is a simple model describing the adsorption by a formation of one layer on the adsorbent surface. It is possible also to select other models describing the adsorption of RV-5 dye by a formation of two and three layers for example, but other important statistical physics model was selected gathering all these cases named by '*multilayer model with saturation*' (**model 2**) [12]. The second selected model describes the adsorption process with a formation of certain number of layers.

To develop the two adsorption models, certain hypotheses were applied: the interaction between the dye molecules was neglected, because the concentrations are lower than the dye solubility [11–13]. In addition to this, the mutual interaction between the adsorbate dyes and solvent ones was also neglected [11–13]. These hypotheses were applied to facilitate the interpretations.

Monolayer model with single energy

Firstly, it was supposed that the dye interact with the adsorption surface of AC and CAC by only one energy, and it was denoted as $-\varepsilon$ [11,14]. We assumed also that the adsorption surface containing a certain number of identical receptor sites characterized by the N_M density [1,3]. Mathematically, the first step to calculate the model is to write the expression of the partition function of a single receptor site. According to other pervious works, this partition function of one receptor site is given by [11,13,15]:

$$z_{gc_1} = \sum_{N_i=0,1} e^{-\beta(-\varepsilon_i-\mu_i)N_i} = 1 + e^{\beta(\varepsilon+\mu)} \quad (1)$$

where, $-\varepsilon_i$ (kJ mol^{-1}) is the adsorption energy of the receptor site, μ_i is the chemical potential of the adsorbed state (kJ mol^{-1}), N_i is the receptor site occupation state, β is the Boltzamm factor and T the absolute temperature (K). This function contains two simple terms describing microscopically the dye behavior on the adsorption surface. If the partition function is equal to 1, we can deduce that the receptor site occupation state N_i is equal 0 indicating that the receptor site is empty. It is clear that the second term ($e^{\beta(\varepsilon+\mu)}$) of the partition function showing that the receptor site is occupied. It is easy now to write the partition function in relation with the total receptor site (N_M density (mg g^{-1})) [11,12].

$$z_{gc_1} = (z_{gc})^{N_M} \quad (2)$$

According to other previous works, the expression of the occupied sites is given by [11,13]:

$$N_{01} = \frac{N_M}{1 + \left(\frac{c_{1/2}}{c}\right)^n} \quad (3)$$

The expression of the first selected model for simulation is given by [11]:

$$Q_1 = \frac{nN_M}{1 + \left(\frac{c_{1/2}}{c}\right)^n} \quad (4)$$

being, Q_1 the adsorbed mass (mg g^{-1}), n the number of molecules per site, $c_{1/2}$ the concentration at half saturation (mg L^{-1}) and c (mg L^{-1}) the equilibrium concentration.

Multilayer model with saturation

The second model describes the dyes adsorption with a formation of a limited number of layers.

To calculate the expression of this model, we assume that the RV-5 dye of the first layer interact with the adsorbent surface of