Molecular modeling of cationic dyes adsorption on agricultural Algerian olive cake waste

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ABSTRACT

In this research, the adsorption isotherms of Methylene Blue (MB) and Basic Yellow 28 (BY28) on agricultural Algerian olive cake waste (AAOCW) were modeled at molecular level using statistical physics and COSMO–RS theories. This molecular modeling aimed to demonstrate an alternative way to describe the interactions between dyes and adsorbents. The adsorption equilibrium isotherms of MB and BY28 on AAOCW were constructed at different temperatures. The statistical physics model was used to quantify the number of adsorbed dye molecules per site, the anchorage number, the receptor sites density, the adsorbed quantity at saturation, the concentration at half saturation and the molar adsorption energy. The COSMO–RS theory was used to quantify the interaction energies: Electrostatic, hydrogen bonding and Van der Waals. σ–Profile and σ–potential were calculated to show the ability of each of the two dyes to interact with every adsorbent site. It was demonstrated that statistical physics and COSMO–RS theories are confident ways to elucidate the interactions between dye molecules and adsorbent surface at a molecular level.

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1. Introduction

The widespread use of synthetic dyes in many industries such as plastics, paper, textile and cosmetics has caused serious environmental problems. In fact, over 10,000 different dyes and pigments are used industrially, corresponding to 7×10^5 tons annually produced worldwide, while it is estimated that 15–20% of the products used are discharged in aqueous media without adequate treatment [1,2]. Generally, dyes are categorized into three classes: cationic or basic dyes, anionic or acidic, and non–ionic or disperse dyes. In particular, cationic dyes are largely applied in the textile industry being water soluble, cost–effective and widely diffused on the pertinent market [3]. Due to their synthetic origin and aromatic structure, dye molecules are usually very stable and non–degradable in nature; moreover, they are often toxic and suspect carcinogenic [4]. Therefore, the removal of dyes from industrial wastewaters is of great and pressing interest. Typical dyes concentrations in wastewaters can reach level as high as up to 0.25 g dm^{-3}, depending on the dyes and processes used [5]. Even if many different physical,

chemical, electrochemical and biological methods have been proposed for dyes removal from polluted waters [6], adsorption has considerable advantages over them, due to a notable flexibility to high polluting load coupled with good efficiency, versatility and relatively low costs for organics removal [7].

Currently, a multitude of sorbents of various nature have been proposed for dyes capture from water [3,8]. In general, the cost of solid adsorbent is one of the main contributions to the overall economic impact of the process and, for this reason, the research is straight oriented towards the individuation of low–cost sorbents. In this scenario, agricultural waste products (AWP) can be proficiently used as adsorbent media for the removal of textile dyes, both cationic and anionic, from water [9,10]. It is interesting that most of the AWP proposed in the literature are synthesized starting from waste materials but using different combinations of physical/chemical treatments, eventually at high temperature, in evident contrast with the driving purpose of AWP use (i.e. their low cost).

Furthermore, the first and probably most important step for the evaluation of the performances of a new adsorbent is the evaluation of its adsorption capacity at equilibrium. Indeed, this parameter defines the thermodynamic limits for the application of a given adsorbents, its

potentiality and effectiveness, simultaneously influencing the kinetics of the process [11]. In turn, adsorption capacity is highly dependent on the specific adsorbent–adsorbate couple and on their energetic interactions in aqueous media [12]. Hence, a thorough characterization of the energetic interactions of the system allows determining the adsorption mechanism and, consequently, defining the optimal conditions for its application. Overall, the knowledge of these parameters and the availability of reliable models for the description of the adsorption capacity in wide ranges of operating conditions are of fundamental importance for the implementation of this type of materials in industrial water purification facilities and it makes possible the design of real low–cost treatment systems [13].

Starting from these important premises, in this work, an agricultural Algerian olive cake waste (AAOCW) was proposed for the removal of two dyes from aqueous solutions (Methylene Blue, MB, and Basic Yellow 28, BY28) taken as probe molecules. The sorbent was used as it is, without any significant (i.e. costly) pre–treatment. Adsorption isotherms were realized at three different temperature levels and in a typical range of equilibrium concentration, as retrieved from the literature. Experimental data were analysed in light of different adsorption models developed on statistical physics principles and, a dedicated energetic analysis was performed in order to determine the type of adsorbent–adsorbate interactions and to simultaneously define the contribution to adsorption of the different fractions of the adsorbent materials. To this aim, the Conductor–like Screening Model for Real Solvents (COSMO–RS) theory was applied to experimental data through quantum calculations.

2. Materials and methods

2.1. Adsorbent

The olive cake waste used as adsorbent in this study (AAOCW) was obtained nearby from a traditional olive oil extraction industry in Setif, Algeria. AAOCW was dried in open air, crushed into powder and sieved. In order to remove surface impurities and to reduce the oil present on the surface, before its use, the powder of olive cake was soaked in hot distilled water for 1 day and then washed several times with hot distilled water until the wash water resulted as clear. After this step, the material was oven dried at 100 °C. No further chemical or physical treatments were performed.

The infrared spectrum of raw olive cake waste was recorded by a FTIR spectrophotometer (Cary 640 FTIR) in range of 4500–500 cm^{-1}, in order to identify the functional groups, present on AACOW surface.

2.2. Dyes

The dyes used in the present study were Methylene Blue (MB; $C_{16}H_{18}ClN_3S$; molecular weight: 319.86 g mol^{-1}; $\lambda_{max} = 664$ nm) and Basic Yellow 28 (BY28; $C_{21}H_{27}N_3O_5S$; molecular weight: 433.52 g mol^{-1}; $\lambda_{max} = 438$ nm). These cationic dyes were purchased from Sigma–Aldrich, and used without further purification. The dye molecules were selected since are common in textile effluents. Stock solutions (1000 mg L^{-1}) were prepared in distilled water, and experimental solutions were obtained by successive dilutions in distilled water. All other chemicals used in this work were of an analytical grade.

Molecular structures of the used molecules are given in the Supplementary material.

2.3. Batch adsorption isotherms

Batch adsorption isotherms were carried out at three different temperatures (293 K, 303 K and 313 K) using 100 mL Erlenmeyer flasks in which 20 mL of MB and/or BY28 solutions with different initial concentrations (varying from 25 to 650 mg L^{-1}) were placed. The solution pH was the original of the dye aqueous solution without any further

adjustment (initial pH$_{MB}$ = 6.4; initial pH$_{BY28}$ = 5.6). Subsequently, 0.20 g of the powdered AAOCW were added to each flask and kept in a shaker under 250 rpm at desired temperature for 24 h (until equilibrium had been reached). The values of pH and adsorbent dosage were selected based on the results obtained from a preliminary study of the effect of pH and adsorbent dosage on the adsorption of MB and BY28 onto olive cake. All experiments were carried out in triplicate and blanks were performed. At the end of the operation time, the suspension was centrifuged at 2000 rpm during 5 min and the liquid supernatant was analysed by a UV–Visible Spectrophotometer (Shimadzu UV–1700) at maximum wave length of 664 nm for MB and at 438 nm for BY28 to determine the residual dye concentration. The amount of dye adsorbed per mass unit of adsorbent at equilibrium q_e (mg g^{-1}) was calculated by Eq. (1)

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, C_0 is the initial dye concentration in liquid phase (mg L^{-1}); C_e is the equilibrium dye concentration in liquid phase (mg L^{-1}); V is the volume of the dye solution (L); and m is the mass of the adsorbent (g).

3. Equilibrium isotherms modeling

3.1. Statistical physics models

The modeling analysis was carried out through the use of various adsorption models developed on the basis in statistical physics principles [14]. The adsorption process is described by the fact that a variable number of molecules interact with N_m receptor sites located on a unit of mass of the adsorbent. The grand canonical partition function describes the microscopic state of an investigated adsorption monolayer system in thermodynamic equilibrium according to Eq. (2):

$$Z_{gc} = \sum_{N_i = 0,1} e^{-\beta(-\mu-\varepsilon)N_i} \tag{2}$$

where ε is the receptor site adsorption energy; μ is the chemical potential; N_i is the receptor site occupation state (0 or 1) and β is defined as $1/k_BT$, with k_B the Boltzmann constant and T the room temperature.

AAOCW is a solid mostly composed of three major compositional fractions i.e., cellulose (cellobiose), hemicellulose (xylose) and lignin [15]. All these three units are potential adsorption sites for the investigated dyes. Therefore, heterogeneous multi-Langmuir model can be proposed as described by Gritti and Guiochon [16]. We suppose then that a monolayer adsorption takes place preferentially onto one, two or three of these units and it is assumed that each adsorption site is characterized by different adsorption energy. The mathematical expressions of the three models deriving from these assumptions are given in Eqs. (3)–(5)

- One type of adsorption sites model (**M1**) [14]:

$$Q_e = \frac{n\, N_M}{1 + \left(\frac{c_1}{c_e}\right)^n} \tag{3}$$

- Two types of adsorption sites model (**M2**):

$$Q_e = \frac{n_1\, N_{1M}}{1 + \left(\frac{c_1}{c_e}\right)^{n_1}} + \frac{n_2\, N_{2M}}{1 + \left(\frac{c_2}{c_e}\right)^{n_2}} \tag{4}$$

- Three types of adsorption sites model (**M3**):

$$Q_e = \frac{n_1\, N_{1M}}{1 + \left(\frac{c_1}{c_e}\right)^{n_1}} + \frac{n_2\, N_{2M}}{1 + \left(\frac{c_2}{c_e}\right)^{n_2}} + \frac{n_3\, N_{3M}}{1 + \left(\frac{c_3}{c_e}\right)^{n_3}} \tag{5}$$