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Research article

Mechanisms of Alizarin Red S and Methylene blue biosorption onto olive stone by-product: Isotherm study in single and binary systems

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ABSTRACT

The biosorption process of anionic dye Alizarin Red S (ARS) and cationic dye methylene blue (MB) as a function of contact time, initial concentration and solution pH onto olive stone (OS) biomass has been investigated. Equilibrium biosorption isotherms in single and binary systems and kinetics in batch mode were also examined. The kinetic data of the two dyes were better described by the pseudo second-order model. At low concentration, ARS dye appeared to follow a two-step diffusion process, while MB dye followed a three-step diffusion process. The biosorption experimental data for ARS and MB dyes were well suited to the Redlich-Peterson isotherm. The maximum biosorption of ARS dye, $q_{max} = 16.10$ mg/g, was obtained at pH 3.28 and the maximum biosorption of MB dye, $q_{max} = 13.20$ mg/g, was observed at basic pH values. In the binary system, it was indicated that the MB dye diffuses firstly inside the biosorbent particle and occupies the biosorption sites forming a monodentate complex and then the ARS dye enters and can only bind to untaken sites; forms a tridentate complex with OS active sites.

1. Introduction

Large amounts of dye contaminated wastewater are being released yearly from leather, cosmetics, pharmaceutical, plastics and textile industries, and results in an impending hazard to human health and the ecosystem (Cao et al., 2014; Semeraro et al., 2015). The existence of such dyes in receiving water bodies is undesirable as they cut off sunlight and reduce photosynthetic activities of autotrophic organisms (Albadarin et al., 2014). The problem is escalating because these dyes are stable and non-biodegradable (Gorgulu Ari and Celik, 2013); dyes are designed to hold colour on various materials and resist water, soap and oxidizing agents (Khataee et al., 2013). Consequently, the removal of dyes from industrial effluents is a challenging problem and it is essential to optimize dye-removal methods. The low efficiency, high cost, and in some cases, the production of toxic by-products make some physical and chemical approaches such as filtration, coagulation, photocatalytic degradation and advanced oxidation processes impractical and expensive to operate (Kabbout and Taha, 2014). Biosorption has been proven as an effective and cheap process, especially when using biowastes and agricultural by-products as the biosorbent (Albadarin et al., 2011). The search for low-cost and locally available waste materials for the biosorption of dyes continues and, recently, has been extensively accelerated (Abdolali et al., 2014; Guerrero-Coronilla et al., 2015; Guo et al., 2014; Magriotis et al., 2014; Wang et al., 2015). Olive crops cover a global cultivated area of approx. 10 million hectares. One main by-product produced in olive oil extraction and pitted table olive manufacture is olive stone. In Spain during the 2009/2010 season, olive oil and table olives world production result in 0.17 and 2.10 million tons of olive stone, respectively (The International Olive Council, 2012). This by-product is mainly turned into bioethanol or directly burnt to produce energy (Cuevas et al., 2015; Valentina et al., 2014). Using raw olive stones as biosorbent is another economic and environmental alternative. This offers the olive processing industry an opportunity to make valuable use of the huge quantities of olive stones generated every year. Therefore, olives stone (OS) was employed in this study for the biosorption of some dyes. Among the hazardous dyes, Alizarin Red S (ARS) and Methylene Blue (MB) are prime contaminants in the environment, and hence, these were selected as model dye systems. Alizarin Red S is a water soluble anthraquinone dye used extensively in the textile industry as a staining agent. It is considered to be one of the most recalcitrant and durable pollutants (Sun et al., 2011). This is due to its complex

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structures of aromatic rings that afford high optical and physico-chemical stability (Fu et al., 2011). Methylene Blue is a cationic thiazine dye commonly used in various industrial applications due to its high adsorption ability. It is not regarded as highly toxic, though, it may cause several harmful effects, such as: difficult breathing on inhalation, gastritis, severe headache, painful micturition, and methemoglobinemia-like syndromes if large amounts are swallowed (Bhattacharyya and Sharma, 2005). The studies dealing with the removal of Alizarin Red S using raw biosorbents are scarce. Previous studies on the removal of ARS onto activated materials showed that adsorption processes are very promising for pollution control (Fu et al., 2011; Zhang et al., 2001). For instance, a small amount of gold nanoparticles loaded on activated carbon (0.015 g) combined with an ultrasound device achieved a high adsorption capacity (123.4 mg/g) in 5 min (Roosta et al., 2014). On the other hand, methylene blue biosorption has been investigated widely though the removal mechanism in binary systems has not yet been clearly understood. The main objectives of this study are to investigate: (i) the chemistry and the mechanism of ARS and MB biosorption onto olive stone and the type of OS–ARS, –MB interfaces occurring; (ii) the biosorption equilibrium and kinetic experimental data required for the design and operation of column reactors; (iii) the simultaneous biosorption isotherm for the two dyes in binary systems.

2. Materials and methods

2.1. Olive stone (OS) biomass

The olive stones were crushed and 1000–355 μm fraction was chosen for the biosorption experiments without any pre-treatment. The biomass was frequently washed with boiled water and finally with distilled water to remove any adhering dirt, and dried at 110 °C for 24 h. Full characterization of OS can be found in a previous investigation (Blázquez et al., 2014). Fourier transform infrared spectroscopy and scanning electron microscopy were employed to examine the OS before and after ARS and MB biosorption. The FT-IR analyses for olive stone surfaces before and after ARS and MB biosorption were tested (KBr pressed disc technique) using a Perkin Elmer Spectrum 100 within the range of 400–4000 cm^{-1}. For the SEM analysis, OS samples were coated with gold and vacuumed (5–10 min) for electron reflection prior to analysis on a JEOL-JSM 6400 scanning microscope. The samples used for the FT-IR and SEM analyses were collected from the pH effect experiment (optimum pH).

2.2. Procedures

Alizarin Red S (342.2 g/mol) and Methylene Blue (319.8 g/mol) were purchased from Sigma Aldrich, UK. All chemical reagents were of analytical grades. Synthetic dye solutions used in the experiments were prepared with distilled water (resistivity 18.24 Ωcm). Concentrations were measured using a UV–VIS spectrophotometer (Perkin Elmer LAMBDA 25, UK) at a maximum wavelength $\lambda_{max} = 668$ nm for MB (Albadarin et al., 2014). Measurement of ARS concentration was carried out at λ_{max} = 425–514 nm (Thomas and Burgess, 2007) to minimize the pH effect on ARS concentration determination. Depending on the isosbestic point, ARS will change colour i.e. pale yellow at pH = 2.0; yellow orange at pH = 3.0–4.9; red at pH = 6.2–9.0 and violet at pH = 11 (Thomas and Burgess, 2007). The experiments of ARS and MB biosorption from aqueous solutions were carried out in a series of 50 cm^3 glass jars; samples were regularly shaken (mechanical shaker, GerhardT type LS 5) at 100 rpm and 20 °C for 72 h to ensure reaching the equilibrium. The effect of initial solution pH on the removal of ARS and MB was examined in the range of 2–9, containing 25 cm^3 of dye solution with C_o of 110 mg/dm^3 and biomass dosage of 5.0 g/dm^3. The pH was altered using 0.1 M HCl or 0.1 M NaOH. The same procedures were employed to investigate the effect of contact time and biosorption isotherms. The initial concentrations ranging from 30 to 205 mg/dm^3 for ARS and MB were employed for the contact time experiment. For the biosorption isotherm studies in single and binary systems, $C_o = 5–105$ mg/dm^3 for ARS and MB were used. The isotherm studies in binary system were investigated at pH 3.4 and 7.2. ARS and MB uptake, q (mg/g), and percentage of removal (%) were calculated according to Eqs. (1) and (2), respectively:

$$q = \left[\frac{C_o - C_e}{M}\right] \times V \quad (1)$$

$$\text{The percentage removal} = \left[1 - \frac{C_e}{C_o}\right] \times 100\% \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of ARS and MB in mg/dm^3, M is the amount of dry biomass in grams and V is the volume of the ARS/MB solution in dm^3.

3. Results and discussion

3.1. Effect of contact time and initial dye concentration

The effect of contact time on the biosorption capacity of OS for ARS and MB was studied at five different initial dye concentrations as revealed in Table 1 and Fig. 1. As expected, the biosorption capacity of OS increased with an increase in the initial dye concentrations. The ARS removal decreased from 85% to 50% as the ARS concentration was increased from 32 to 190 mg/dm^3. While the MB removal decreased from 75% to 40% when the dye concentration increased from 30 to 205 mg/dm^3. Fig. 1 shows that the biosorption at various concentrations is fast in the initial stages and steadily decreases with the progress of biosorption until the equilibrium is reached. The difference in the biosorbed concentration of ARS and MB at equilibrium (q_e) and at time t (q_t) provides the key driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases (Liao et al., 2012).

3.2. Kinetic modelling

In the current study, the pseudo first-order model (Lagergren, 1898), pseudo second-order model (Ho and McKay, 1999) and Intraparticle diffusion model (Weber and Morris, 1963) were employed to test the kinetic experimental data.

3.2.1. Pseudo first- and second-order kinetic models

The pseudo first-order model equation is given as follow:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (3)$$

The pseudo second-order equation is given as;

$$q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (4)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constants for first- and second-order models.

Table 1 summarizes the parameters of the pseudo first- and second-order kinetic models for ARS and MB biosorption onto OS. The highest R^2 values and well closer calculated q_e values to those acquired by experiments, $q_{e,exp}$, confirmed that the biosorption process for both dyes is best described by the pseudo second-order