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Mono and simultaneous removal of crystal violet and safranin dyes from aqueous solutions by HDTMA-modified *Spirulina sp.*

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ABSTRACT

The process of mono and binary removal of crystal violet and safranin dyes by *Spirulina sp.* (blue-green algae) modified with cationic surfactant is evaluated. The surfactant used was hexadecyltrimethylammonium bromide (HDTMA). *Spirulina sp.* was cultivated in Zarrouk's medium. The adsorptive properties of the modified *Spirulina sp.* (HDTMA-algae) were tested as a function of pH (2–10), contact time (5–180 min), temperature (25–45 °C), and initial dye concentrations (25–300 mg/L) and characterized with FTIR, SEM, EDX, XRD and BET analyses. The specific surface area of HDTMA-algae was 0.1990 m^2/g. The data were fitted to non-linear Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models and non linear pseudo-first-order and pseudo-second-order kinetic models. The adsorption was 75% and 88% at pH 2 for Crystal Violet and Safranin dye, respectively. The maximum adsorption capacities were 101.87 mg/g and 54.05 mg/g and the k_F values were 0.96 L/g and 3.56 L/g for Crystal Violet and Safranin, respectively. The kinetics of Crystal Violet and Safranin dyes onto HDTMA-algae were best described by the pseudo-second-order kinetic model. The negative values of free energy and enthalpy change indicated the feasibility, spontaneity, and exothermic nature of the adsorption process. Also, binary adsorption of Crystal Violet and Safranin dyes onto HDTMA-algae from binary dye mixtures is compared.

1. Introduction

Synthetic dye stuffs are extensively used as coloring agents in the textile, paper, leather, gasoline, pharmaceutical, and food industries (Gupta et al., 2013). Most of the synthetic dyes and their degradation products are of great environmental concern due to their widespread usage, toxic and carcinogenic and their low removal rate during aerobic wastewater treatment (Robinson et al., 2001; Khan et al., 2015; Gupta et al., 2015a).

Dyes were also usually classified based on their particle charge upon dissolution in aqueous application medium, to cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) (Gupta et al., 2015a; Zare et al., 2015; Mishra and Tripathy, 1993; Purkait et al., 2005; Gupta, 2009).

Crystal violet (CV) is a cationic dye that is widely used in textile production for dyeing cotton, acrylic, wool, and silk (Khan et al., 2015). Safranin is one of the most commonly used cationic-azine dyes, which is among the oldest known synthetic dyes. Safranin is mainly used as food dye in flavoring and coloring candies and cookies. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper (Kaur et al., 2014; Shah, 1998). CV and safranin can causes several

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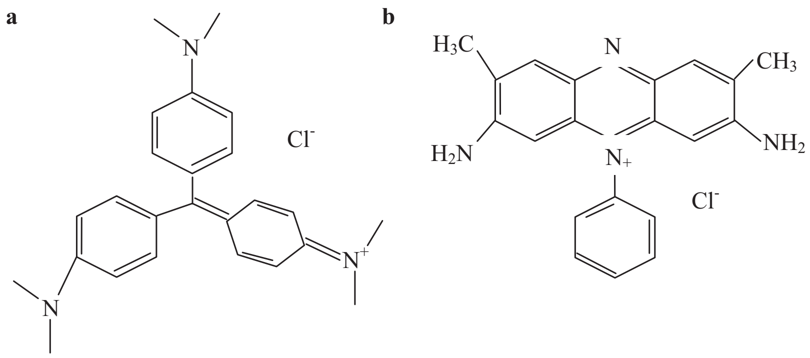

Fig. 1 – Chemical structure of CV (a) and safranin (b) (Shariati et al., 2011; Zolgharnein et al., 2015).

acute health problems such as irritation to the skin, mouth, throat, tongue, lips, and eyes as well as stomach pain (Khan et al., 2015; Kaur et al., 2014). Hence the removal of CV and safranin dyes from aqueous solutions is highly significant.

Many physical and chemical processes have been used to remove synthetic dyes from industrial wastewaters such as coagulation-flocculation (Szygula et al., 2009), membrane filtration (Alventosa-deLara et al., 2012), fenton process (Karatas et al., 2012), Photo-catalytic degradation (Gupta et al., 2011a, 2012; Saleh and Gupta, 2012), irradiation (Paul et al., 2011), ozonation (Moussavi and Mahmoudi, 2009), adsorption (El Haddad et al., 2014; Mittal et al., 2009, 2010a, 2010b; Jain et al., 2003), and biosorption (El Haddad et al., 2013). Of these methods, adsorption and biosorption have been determined to be superior due to their effectiveness, low cost, and ease of application (Kaur et al., 2014; Dotto et al., 2012; Guler and Sarioglu, 2014).

Recently, researchers have focused on the treatment of dye and heavy metal in wastewaters with organisms such as bacteria, fungi, yeast and algae (Gupta et al., 2015b). Algal biomass is generally used as a biosorbent because it is available in large quantities, is largely cultivated, is a very effective adsorbent, and is relatively inexpensive (Celekli et al., 2010; Apiratikul and Pavasant, 2008; Aksu and Donmez, 2006). *Spirulina sp.* is a photosynthetic cyanobacterium (Vonshak, 1997) and it has some functional groups such as carboxyl, hydroxyl, sulphate, and phosphate as well as amino groups (Celekli et al., 2010).

Surface modification has been proved to be an effective technology. Cationic surfactants, mostly amine salt and quaternary ammonium salt, can provide adsorbents with abundant potential for positively charged sites. Surfactants have been successfully used by many researchers for surface modificationsuch as hexadecyltrimethylammonium bromide (HDTMA), cetyltrimethyl ammonium bromide (CTAB), dodecyl benzyl dimethyl ammonium chloride, polyethylemine (PEI), and 3-(2-amino ethyl amino) propyl trimethoxysilane (APTS) (Jing et al., 2011; Yusof and Malek, 2009; Bingol et al., 2009; Owlad et al., 2010).

Up to now, most dye removal studies have focused on single dyes and the use of two or more mixtures of dye is rare (Mittal et al., 2010c; Gupta et al., 2011b; Gao et al., 2010). Adsorption studies multi component adsorbate systems can leads to improved behavior which is beneficial for practical applications (Pal et al., 2013). Morever, real industrial wastewaters contain additional metal compounds and dye complexes. For this reason, it is worth studying the adsorptive properties of modified *Spirulina sp.*, especially because there are no reports on the mutual biosorption of CV and Safranin.

The objective of this paper is to examine mono and simultaneous biosorption of CV and Safranin on a modified *Spirulina sp.* (HDTMA-algae). The biosorbent used in this study has a complex chemical and biological composition and for this reason very interesting from a theoretical viewpoint.

Spirulina sp. was modified with hexadecyltrimethylammonium bromide (HDTMA) as a low-cost biosorbent for mono and simultaneous removal CV and safranin dyes from aqueous solutions. Removal efficiency was tested with a series of batch experiments that varied solution pH, contact time, initial dye concentration, and temperature. Removal mechanisms are discussed via FTIR, SEM, EDX, XRD, and BET analyses. The equilibrium isotherms, kinetics, and thermodynamic parameters were determined for the mono-component systems to predict the nature of dye biosorption by HDTMA-algae. Simultaneous biosorption of CV and safranin dyes on the HDTMA-algae was studied with variable initial dye concentrations.

2. Materials and methods

2.1. *Chemicals*

All reagents were of analytical reagent grade and used as supplied. CV (λ_{max} CV = 590 nm) and safranin (λ_{max} safranin = 517 nm) powders were used. The chemical structures of CV and safranin are shown in Fig. 1 (Shariati et al., 2011; Zolgharnein et al., 2015).

2.2. *Cultivation of Spirulina sp.*

Spirulina sp. was isolated and cultivated in Zarrouk's medium (Zarrouk, 1966). Sun-dried *Spirulina sp.* was washed with deionized water and then oven-dried, initially at room temperature for 24 h and subsequently at 60 °C for 24 h. The dried biomass was ground into a powder.

2.3. *Preparation of HDTMA-modified Spirulina sp. (HDTMA-algae)*

HDTMA-modified *Spirulina sp.* (HDTMA-algae) was prepared as follows (Gładysz-Płaska et al., 2012). Dried *Spirulina sp.* was treated with an excess of sodium ions to enhance cation exchange capacity (CEC). Five grams of *Spirulina sp.* were contacted with 100 mL of 1 M NaCl for 24 h. After filtration, the sodium form of *Spirulina sp.* was washed several times with distilled water and air-dried. Next, 1 g of Na form *Spirulina sp.*