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Assessment of the biosorption kinetic and thermodynamic for the removal of safranin dye from aqueous solutions using calcined mussel shells

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ABSTRACT

Calcined mussel shells have been used as new low cost and eco-friendly biosorbent for the removal of safranin as cationic dye from aqueous solutions by biosorption technique. Batch mode experiments were conducted using various parameters such as pH, contact time, biosorbent amount and safranin concentration. Removal efficiency of safranin by the calcined mussel shells attained 87.56% using 200 mg of biosorbent and 150 mg/L as safranin concentration and for a pH above 9.2. Four kinetic models are used, pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion for the design and the optimization treatment. The kinetic analysis showed that the pseudo-second-order model had the best fit to the experimental data. Biosorption isotherms were also investigated using Langmuir, Freundlich and Temkin models. The experimental data fitted very well with both Langmuir and Freundlich isotherm models. Thermodynamic biosorption processes were found to be spontaneous, endothermic. The Gibbs energy ΔG° decreased from −1.956 kJ/mol to −2.456 kJ/mol with increase in temperature from 298 K to 313 K indicating a increase in feasibility of biosorption at higher temperature. Accordingly, calcined mussel shells were shown to be a very efficient, eco-friendly and low cost biosorbent and a promising alternative for removal dyes from aqueous solutions.

1. Introduction

Environmental pollution is one of the major problems faced by the modern world wide due to its extreme development in agriculture, medicine, energy sources and all chemical industries. Many examples of industries use dyes or pigments to colour their final products and cause seriously severe damage of environment and to public health. Among these are textile, paper and pulp, printing, iron–steel, coke, petroleum, pesticide, paint, solvent, pharmaceutics, and wood preserving [1,2]. Today it is well established that coloured compounds are among the most contaminants products in wastewater. These dyes are noxious, carcinogenic and cause a serious hazard to aquatic life organisms [3,4]. Release of dye compounds into water system without proper treatments prevent sunlight into water ecosystem and reduce photosynthesis phenomena [4,5].

Customary treatment processes may be physical, chemical and biological comprising adsorption [6,7], coagulation/flocculation [8], advanced oxidation processes [9], ozonation [10], membrane filtration [11], electroflotation [12], electrokinetic coagulation [13], electrochemical destruction [14], ion exchange [15], irradiation [16], precipitation [17] and biological treatment [18]. These methods may achieve successfully the decolorization of industrial effluents but these techniques are not simple of experimental operation. These methods also produce heavy amounts of sludge with obvious disposable problems. From these methods, biosorption proved to be the most accepted treatment method as it gives the best results and may be used to eliminate diverse types of colouring materials.

Especially, Biosorption has been set up as an efficient technology to take away dye molecules from dilute aqueous solutions by means of inactive and dead biomass [19–21]. By a large scientific research on biosorption has been practiced with metals and associated elements; the technology is now practical for the removal of particulates and all categories of organic compounds. Biosorption is usually fast method and make use of cheaper materials; for instance waste biomass from agriculture and industry being plenteous in nature, economical and require

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minute processing [22–30]. These materials have many functional groups: carboxyl, hydroxyl, sulfudryl and amino groups on their surfaces, having the ability to bind sorbate ions and molecules [31].

In order to overcome the above addressed problem, calcined mussel shells can be applied as a novel low-cost, eco-friendly biosorbent and it can play a vital role for remediation and removal dye from aqueous solutions. Safranin used in this study is a contaminant agent and is widely used as food dye in flavouring and colouring candies and cookies, textile industries, leather, paper as well as in researches related to histology, textile, cytology and bacteriology [32]. Safranin is a phenazine dye that has been used as a photosensitizer in electron- and energy-transfer reactions. Safranin is widely used as a redox indicator in analytical chemistry. Safranin has been used as an analytical reagent for the determination of nitrite in acidic medium; Safranin reacted with nitrite to form a diazonium cation, which caused the change of the reddish-orange colour of the dye solution to blue. The safranin was selected in the present study as a representative cationic dye.

In the current work, biosorption studies were carried out under various experimental factors such as initial pH, biosorbent dose, contact time, initial dye concentration and temperature. The kinetics of biosorption has been studied, and various kinetic models, such as pseudo-first-order, pseudo-second-order, and diffusion models have been tested with experimental data for their validity. The equilibrium biosorption behaviour of the biosorbent has been studied using the biosorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. Thermodynamics of biosorption process has been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

2. Materials and methods

2.1. Preparation and characterization of calcined mussel shells biosorbent

The mussel shells were collected from a popular restaurant near Casablanca in Morocco. They were repeatedly washed several times with tap water followed by distilled water and then were dried in oven at 378 K for 12 h. Mussel shells are crushed, powdered to small grains and then calcined at 1173 K for 2 h. The residue was washed with distilled water three times and dried at 353 K for 24 h. The residue was finely chopped and ground into small particles of different sizes in the range of 75–100 μm, milled in an agate mortar, washed with distilled water, dried overnight at 378 K, then calcined at a heating rate of 275 K/min to 673 K and maintained at this temperature for 4 h. The resulting material was stored in a glass bottle for further use without any pretreatment and the mussel shells calcined obtained was denominated (CMS).

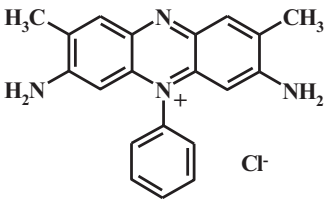

Fig. 1. Chemical structure of safranin dye.

Chemical structure of safranin is shown in Fig. 1. The CMS biosorbent is identified by X-ray diffraction (Philips X'Pert PRO), analysis of Infra-Red spectroscopy (Bruker Tensor-27) and Elemental analysis. Elemental analysis shows a high yield of Ca (60.24%) and Si (3.57%) compared to small amounts of Mg (0.90%), Al (0.41%), P (0.20%) and Sr (0.11%). While the analysis by XRD depicted in Fig. 3 shows the presence of calcite and portlandite, syn. IR spectra analysis of CMS is shown in Fig. 2. The bands at 3643 cm^{-1} are assigned to hydroxyl group stretching modes and the stretching and folding of carbonate group has been assigned to bands at 1437 cm^{-1} and 874 cm^{-1} (Fig. 2).

2.2. Determination of pH Zero Point Charge

The zero point charge pH (pH_{ZPC}) of the CMS biosorbent was measured using the pH drift method [33]. In this fact, the pH_{ZPC} of the CMS was determined by adding 20 mL of 5×10^{-2} mol/L NaCl to several 50 mL cylindrical high-density polystyrene flasks (height 117 mm and diameter 30 mm). A range of initial pH (pH_i) values of the NaCl solutions were adjusted from 2 to 12 by adding 10^{-1} mol/L of HCl and NaOH. The total volume of the solution in each flask was brought to exactly 30 mL by further

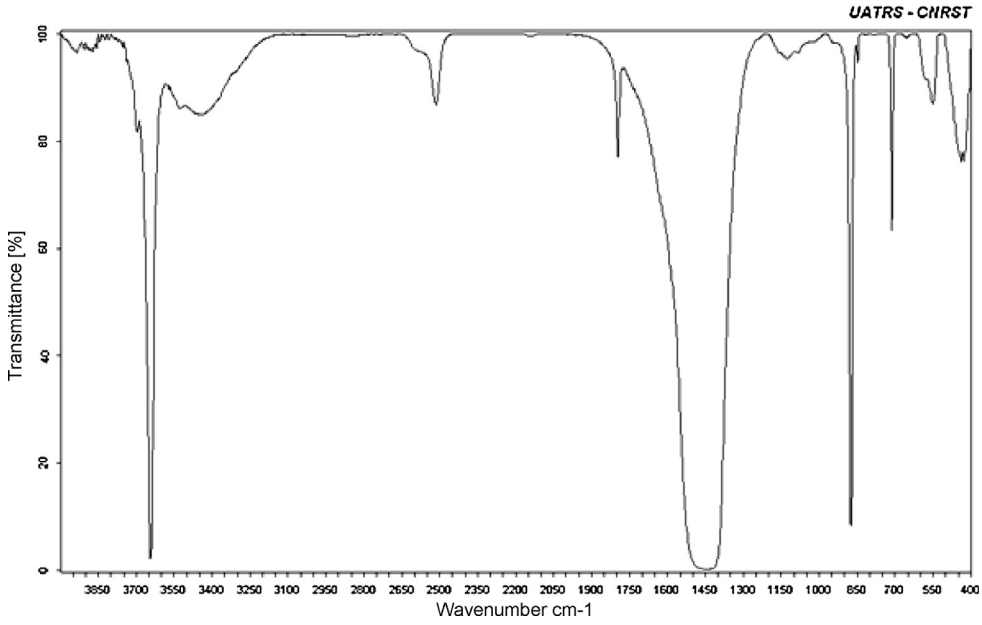

Fig. 2. IR spectra of CMS biosorbent.