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Evaluation of performance of chemically treated date stones: Application for the removal of cationic dyes from aqueous solutions

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ABSTRACT

Chemically treated date stones (CTDS) used in this study as adsorbent for the removal of methylene blue (MB) and crystal violet (CV) from aqueous solutions in batch system. The effect of contact time, initial dye pH, temperature and initial dye concentration on the adsorptive removal process was studied. The results show that the removal of MB and CV is rapid and superior adsorption efficiency of MB and CV onto CTDS. In this study Langmuir and Freundlich isotherms were investigated for adsorption of MB and CV onto CTDS. The Langmuir isotherm has the highest correlations coefficients, with maximums monolayers capacities of MB and CV were 515.46 mg/g and 543.47 mg/g, at 50°C, respectively. Pseudo-first-order and pseudo-second- order models were studied to analyze adsorption kinetics. The result shows the adsorption kinetic is the best with pseudo-second-order model. Desorption and regeneration experiments using HNO_3 (0.1 N) eluent were only possible with CTDS, which performed well in four repeated cycles with high MB and CV removal efficiencies.

1. Introduction

The textile industry generates large amounts of wastewater containing dyes and synthetic chemical additives [1]. The presence of dyes in textile effluents even at very low concentrations is visible and undesirable. Color wastewater affects the aesthetic nature of the water and reduces the penetration of light and also the photosynthesis of aquatic organisms [2]. The releases may have major drawbacks as well on the man on his environment because of their stability and formulation [3].

The treatment of liquid effluents of these industries after finishing step is usually based on the physico-chemical and biological processes. Among the physico-chemical methods, there is the adsorption which is a simple and effective method for the elimination of many organic pollutants [4,5]. The principle of treatment by adsorption is entrapping dyes by a solid compound. In general, in the various studies conducted by scientists, activated carbon is a good for treatment of discoloration but it poses problems of high cost it saturates quickly and it should be removed after use [6].

The aim of our work is the development of new materials for use as adsorption media and can make simple purification processes and less expensive. Date stones, agricultural waste, lignocelluloses biomass, abundant in Morocco, available and no toxic, fall into this category. In fact this material has physicochemical properties that can induce significant adsorbent activity.

The treatment of lignocellulosic biomass with acids aims to activate the functional adsorption sites and that the increase of the binding capacity of the screw material of the screw to remove adsorbates. This can be achieved in several ways: by reducing the content of cellulose, lignin and hemicelluloses from the solid substrate to be processed, increasing the porosity of the matrix, or by increasing its surface area [7].

This study attempts to improve the adsorption capacity of methylene blue and crystal violet on date stones with chemical treatment by sulfuric acid H_2SO_4 (2 N) followed the sodium bicarbonate $NaHCO_3$ (1%).The methylene blue and crystal violet are dyes used in the textile industry, cationic dyes, which have been shown to have harmful effects on living organisms on short periods of exposure. Ingestion of dye through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea and gastritis. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation and methemoglobinemia [8].

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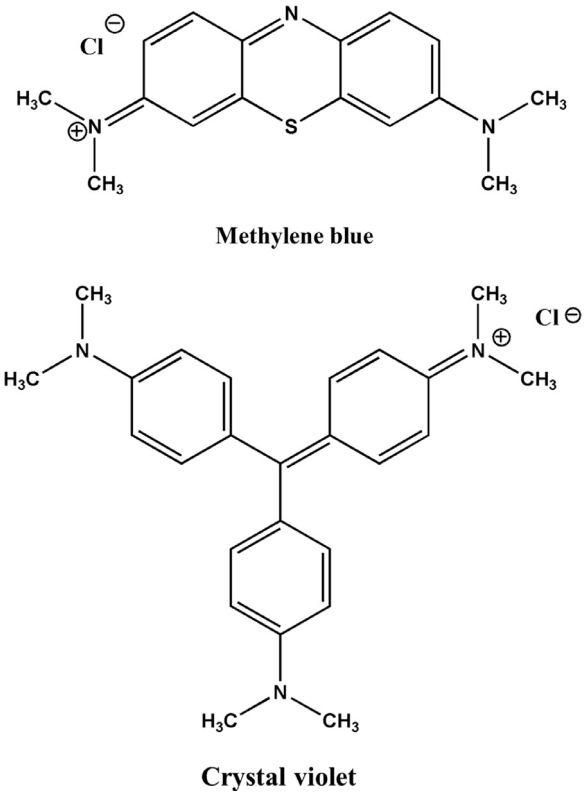

Fig. 1. Chemical structures of methylene blue and crystal violet.

Also in this study we proposed a mechanism of interactions between the functional groups available on the surface of chemically treated date stones (CTDS) and methylene blue (MB) and crystal violet (CV).

The raw and treated date stones were characterized by Fourier transform infrared (FTIR) coupled by attenuated total reflectance (ATR) technique, thermo gravimetric analysis (TGA) and Scanning electron microscopy (SEM) analysis.

Adsorption of MB and CV on CTDS was performed by varying parameters such as contact time, initial dye pH, temperature and initial dye concentration. The behavior of the equilibrium sorption was investigated using the Langmuir, and Freundlich isotherms models. Adsorption kinetics of MB and CV was tested by the pseudo-first-order and pseudo-second-order kinetics models. Desorption behavior MB and CV from CTDS was studied in batch experiments. Four adsorption-desorption cycles also evaluated. The developed CTDS demonstrates rapid and excellent removal efficacy of MB dye than that of various adsorbents reported in the literature. Finally, we propose the mechanism of interaction between the ions of MB and CV and surface CTDS.

2. Materials and methods

2.1. Preparation of MB and CV solutions

Methylene blue (molecular weight: 319.86 g/mol, chemical formula: $C_{16}H_{18}N_3SCl$, color index: 52,015) and crystal violet (molecular weight: 407.99 g/mol, chemical formula: $C_{25}H_{30}N_3Cl$, color index: 42,555), the basic dyes. A stock solution of 1 g/L was prepared by dissolving 1 g of MB or CV powder in 1 L of distilled water. The working solutions were prepared by diluting the stock with distilled water to give the appreciate concentration of the working solutions. The Chemical structures of MB and CV are shown in Fig. 1.

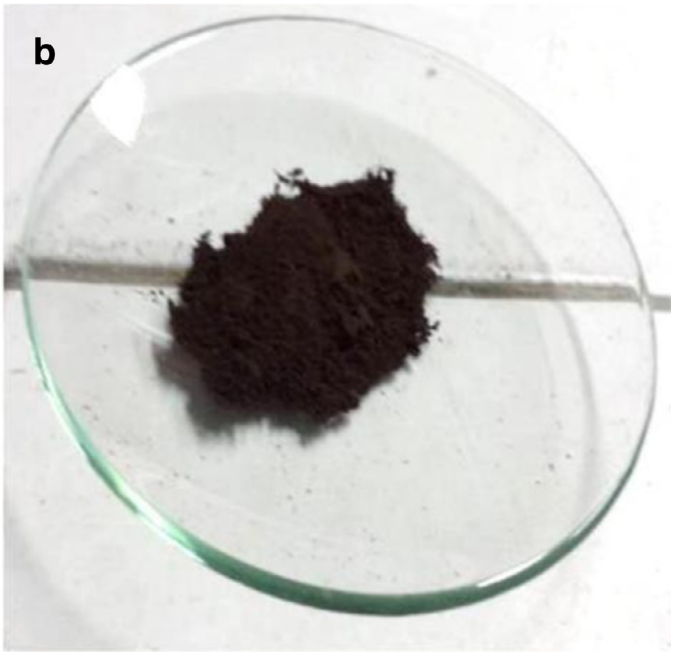

Fig. 2. Photos of original waste (a) and CTDS (b).

2.2. Pretreatment and characterization of adsorbent

Date stones (Fig. 2a) were collected in Tinghir (South East of Morocco). They are washed and placed in an oven at 105°C for 24 h, then ground on a laboratory mill Retsch SM10 and sieved to different sizes (50–100, 100–315, 315–500 and 500–1000 µm) on laboratory sieve. 1 g of the prepared date stones (50–100 µm) is mixed with 100 ml of solution sulfuric acid H_2SO_4 (2 N), well subjected to heating under reflux for 8 h. After-cooled, the support was washed with distilled water to remove excess sulfuric acid before undergoing filtration through filter paper, then washed with solution of sodium bicarbonate $NaHCO_3$ (1 %) to eliminate the

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