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Efficiency of almond gum as a low-cost adsorbent for methylene blue dye removal from aqueous solutions

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ABSTRACT

This study was aimed to use almond gum as a potential adsorbent to remove methylene blue dye from aqueous solution. The adsorbent was characterized by scanning electron microscopy and Fourier transform infrared spectrometer. The adsorption of methylene blue on almond gum material was studied as a function of almond gum dose (0.05–2 g), pH solution (3–10), contact time (up to 240 min) and initial concentration (20–200 mg L^{-1}), temperature (303.16 K, 313.16 K, and 323.16 K), and agitation(up to 250 rpm). The influence of these parameters on the adsorption capacity was studied using the batch process. The experimental data were analyzed by the Langmuir, Freundlich, and Tempkin isotherms. Results show that the data fitted well with the Freundlich isotherm (R^2 = 0.99). The maximum adsorption capacities of methylene blue onto almond gum were found to be 250 mg g^{-1}, 333.33 mg g^{-1}, and 500 mg g^{-1} at 303.16 K, 313.16 K, and 323.16 K, respectively. The kinetic data were fitted to the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and it is revealed that adsorption of methylene blue onto almond gum follows closely the pseudo-second-order kinetic model. Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) were evaluated to predict the nature of adsorption. The calculated values of ΔH, ΔS, and ΔG for uptake of methylene blue were 52.078 kJ mol^{-1}, 177.91 J mol^{-1} K^{-1}, and −18.56 kJ mol^{-1}, respectively. These results indicate the endothermic and spontaneous nature of the adsorption process. The results revealed that almond gum adsorbent is potentially an efficient and low-cost adsorbent for adsorption of methylene blue.

1. Introduction

Dyes are mainly chemical compounds constituted of two important components: chromophores; which are responsible for producing the color, and auxochromes; which enhance the affinity of the dye toward the fibers (Gupta and Suhas, 2009). Numerous dyes are linked to surfaces to impart color and are known to be resistant to the action of detergents. Synthetic dyes are widely used in several industries such as textile, paper, leather tanning, plastic, carpet, food, and cosmetics to provide color to their products (Ivanov et al., 1996; Kabdaşli et al., 1999; Sokolowska-Gajda et al., 1996). These dyes are always released in industrial waste, leading to disposal problems (Crini, 2006; Forgacs et al., 2004; Muthukumar and Selvakumar, 2004; Ong et al., 2007). Their discharges into effluents involve a significant source of pollution due to their recalcitrance nature. Furthermore dyes may impart toxicity to aquatic and plants biota and may be mutagenic and carcinogenic, causing severe damage to human life; such as dysfunction of kidneys, reproductive system, liver, brain, and central nervous system (Dinçer et al., 2007; Kadirvelu et al., 2003; Shen et al., 2009). The removal of dye pollutants from waste effluents becomes environmentally of great importance because even a small quantity of dye in water could be toxic and highly visible (Chiou et al., 2004).

Numerous removal methods such as adsorption, coagulation, advanced oxidation, membrane separation, aerobic, and anaerobic microbial degradation are used to eliminate dyes from waste water (Gupta and Suhas, 2009). Among all of these methods, adsorption is the most used regarding its cheapness and efficiency as advanced treatment employed in industries to reduce hazardous

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Fig. 1. Pictures of crude almond gum (collected from almond trees) and grinded almond gum after drying.

organic and inorganic pollutants from the effluents (Kant, 2012). Activated carbon is the most commonly used adsorbent regarding its high capacity of adsorption and microporous structure (McKay, 1982). However, due to its high price, its industrial use is still limited (EL-Geundi, 1997). Recently, several agricultural waste and residues have been tested as adsorbent, to remove dyes from waste waters, because of their low cost, low toxicity, and easy availability (Hameed, 2009). In fact, peach gum (Zhou et al., 2014), rice husk (Vadivelan and Kumar, 2005; Zou et al., 2011), yellow passion fruit waste (Pavan et al., 2008), grass waste (Hameed, 2009), banana and orange peels (Annadurai et al., 2002), and wheat shells (Bulut and Aydın, 2006) were used for dyes removal from aqueous solutions. However, most of the reported bioadsorbent materials show low adsorption capacity, limiting thus their industrial applications. Other economical, easily available, eco-friendly, and highly efficient adsorbents are still needed.

Almond gum exudate is produced by almond tree (*Prunus amygdalus*, Rosaceae family) after a mechanical injury followed by a microbial attack. Almond gum represents an abundant natural biomass worldwide and is an acidic polysaccharide composed of galactose, arabinose, xylose, mannose, rhamnose, and glucuronic acid, with molar ratios of 45, 26, 7, 10, 1, and 11, respectively (Bouaziz et al., 2015). Due to its high molecular weight and highly branched molecular structure, almond gum is insoluble in aqueous solutions, and could be a promising adsorbent for the removal of methylene blue cationic dye from waste water. Indeed, almond gum contains numerous negatively carboxylic groups that can adsorb cationic dyes such as methylene blue through strong electrostatic interactions. For this purpose, this work is devoted to study for the first time the efficiency of almond gum as a bioadsorbent to remove methylene blue dye from aqueous solutions. The influence of adsorption parameters (initial dye concentration, methylene blue dose, contact time, and optimal pH and temperature), using almond gum, was investigated. The adsorption isotherms, kinetics, and thermodynamic properties of almond gum were then discussed.

2. Materials and methods

2.1. Materials

Almond gum was collected from almond trunks (Achaak's variety) in the suburb of Sfax city (Tunisia) on April 2014. The dried almond gum was grinded to fine powder (Fig. 1) and sieved to obtain particle sizes below 100 μm, 110–250 μm, and 260–350 μm. Methylene blue was purchased from Sigma–Aldrich (SdnBhd, Malaysia) and was used as adsorbate. A stock solution of 1 g L^{-1} methylene blue was prepared in deionized water and used to generate the working solutions at different concentrations of methylene blue. The structure and characteristics of the dye used in this work are presented in Table 1. All the remaining reagents were used as received without further purification.

Table 1
Chemical properties and characteristics of methylene blue.

Generic name	Methylene blue
Chemical formula	$C_{16}H_{18}ClN_3S{\cdot}3H_2O$
Molecular volume ($cm^3\ mol^{-1}$)	241.9
Molecular weight ($g\ mol^{-1}$)	373.90
Molecular diameter (nm)	0.80
Colour index number	52.015
λ_{max} (nm)	668

2.2. Characterization of adsorbent

Dry matter of almond gum adsorbent was determined according to the AOAC (Cunniff, 1997). Total nitrogen content was determined by Kjeldahl's method (AFNOR, 1977) and the protein content was calculated using the general factor (6.25). Sugar content in almond gum was determined according to Dubois et al. (1956). Fat content was determined according to the French Association of Standardization (AFNOR, 1981). Soluble and insoluble fiber contents were evaluated as described by Prosky et al. (1988). Total ash was determined by sample's combustion in a muffle furnace at 550 °C for 4 h. Mineral levels (Na, Mg, Ca, Zn, and Cd) were measured by flame atomic absorption spectrometry (Analytic Jena ZEEnit 700 spectrometer, USA), according to Jorhem (2000). Fourier transform infrared (FTIR) spectra of raw almond gum was performed using a PerkinElmer spectrophotometer and KBr pellets (PerkinElmer Spectrum BX FTIR, USA) as described by Sila et al. (2014). The samples were exposed to radiations in the range of 4000–500 cm^{-1} with 2 cm^{-1} resolution. Scanning electron microscopy experiments were performed after coating samples with gold using a sputter coater (model JEOL, JFC-1100 E ion sputtering Device). Pictures were taken by a JEOL, JSM-5400 scanning microscope (Japan) under vacuum at an accelerating voltage of 5 kV. Images were magnified 500 and 1000 folds.

2.3. Adsorption studies

Prior to the measurement, a calibration curve was prepared using known concentrations of methylene blue. Measurements were performed using a UV–vis spectrophotometer (Shimadzu, Model UV 1240, Japan) at 668 nm; corresponding to the maximum absorption of the dye solution. Adsorption experiments were carried out in a rotary shaker at different temperatures (from 303 K to 323 K) and rotation speeds (from 100 rpm to 250 rpm) using 250 mL shaking flasks containing 100 mL dye at different concentrations