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ORIGINAL ARTICLE

Application of *Casuarina equisetifolia* needle for the removal of methylene blue and malachite green dyes from aqueous solution

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KEYWORDS

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Abstract This study investigated the potential of *Casuarina equisetifolia* needle (CEN) on the removal of two important dyes, methylene blue (MB) and malachite green (MG), by batch adsorption experiments. Characterisation of CEN's functional groups was done using Fourier Transform infrared spectroscopy while elemental analysis was carried out using CHNS analysis and X-ray fluorescence. The experiments were carried out by varying the adsorbent dosage, pH, ionic strength, contact time and initial dye concentration. The pseudo-second-order kinetics model best represented the experimental data for both CEN-MB and CEN-MG systems. The Weber–Morris intraparticle diffusion model showed that intraparticle diffusion is not the rate-limited step for both adsorbates, while the Boyd model suggested both systems could be controlled by film diffusion. The Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were used for describing the adsorption process. Of these, the Langmuir model best represented both adsorbents systems (CEN-MB and CEN-MG) giving maximum adsorption capacity (q_m) of 110.8 and 77.6 mg g^{-1}, respectively, at 25 °C. Thermodynamics studies showed that both adsorption systems are spontaneous and endothermic.

1. Introduction

Methylene blue (MB) and malachite green (MG) belong to dye classification of thiazine and triarylmethane, respectively. Both of these dyes are cationic dyes as they form positively charged molecules (Fig. 1) when dissolved in water. MB is not only used as a dyestuff in textile industry but also as medicine. Methemoglobinemia [1], psoriasis [2], West Nile virus [3] and Duck hepatitis B [4] are some of diseases/conditions that use MB in the treatment. The negative effects of acute exposure to MB may include increase heart rate, nausea, Heinz body formation, headache and gastritis [5,6]. MG has fungicide, ectoparasiticide and disinfectant properties and is heavily used in fish farming industry to control fish parasites and diseases [7]. However, studies revealed that MG is lethal to freshwater fish in both acute and chronic exposure, cytotoxic to mammalian cells as well as a multi-organ toxin which effect the liver, spleen, kidney, heart, eye, skin, lung and bone [8,9].

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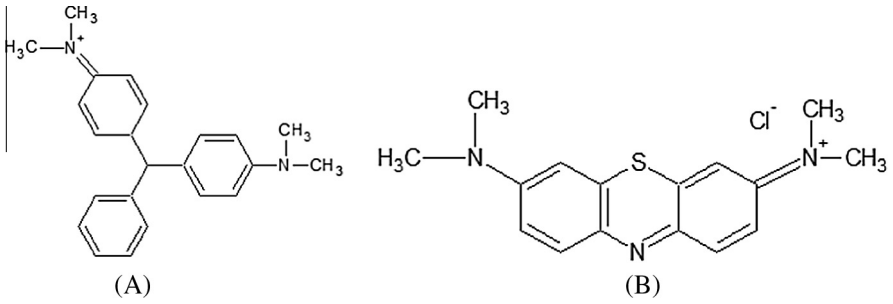

Figure 1 Molecular structure of (A) malachite green, and (B) methylene blue.

In addition to these, both dyes are resistant to biodegradation and thus, could hinder the aquatic activities and cause unpleasant sight to the water bodies due to their intense colour.

Adsorption treatments are simple with no side product as the pollutants are adsorbed on the surface of the adsorbent and in many cases, can be regenerated and reused. Activated carbon is widely used for this purpose as it has excellent adsorption properties due to its high surface area and porous structure. However, its application is limited due to its expensive cost [10]. Growing interest in finding new materials for adsorption treatment has developed many researches on materials that have low or no values such as water fern [11], agro-wastes [12,13], yeast [14,15], fungus [16], clay [17] and mud [18]. In addition to good removal of pollutants from aqueous solution, these materials are abundant, environmental friendly and low cost, making adsorption treatments to be more attractive than the conventional treatments such as photodegradation [19] and catalytic degradation [20].

This study aims to investigate the potential of *Casuarina equisetifolia* needle (CEN) as an adsorbent for the removal of MB and MG from aqueous solution. CEN is available world-wide and the usefulness of the tree ranged from timber production, material for mulching, landscaping, fuel and as wind breaker at coastal areas. Many other parts of the plant tissues were used in adsorption studies such as untreated CEN to adsorb methyl violet 2B [21] and removal of Cr(VI) [22], tree bark to adsorb Cu(II) [23], activated carbon derived from seed husk for Cr(VI) removal [24].

2. Materials and methods

2.1. Chemicals and instrumentations

All chemical reagents were used without further purification. Malachite green oxalate (MG), 90% dye content ($C_{23}H_{25}N_2{\cdot}C_2HO_4{\cdot}0.5C_2H_2O_4$, M_r 463.50 g mol^{-1}) and methylene blue (MB), 82% dye content ($C_{16}H_{18}N_3ClS{\cdot}3H_2O$, M_r 373.90 g mol^{-1}) were purchased from Sigma–Aldrich. 1000 mg L^{-1} of dye stock solution was prepared by dissolving the required amount of dye in distilled water. pH was adjusted using 0.1 mol L^{-1} NaOH (Univar) and 0.1 mol L^{-1} HNO_3 (AnalaR) and measured with Thermo Scientific Orion 2 Star pH Benchtop. Potassium nitrate (Sigma–Aldrich) and sodium chloride (GPR) were used in the determination of point of zero charge and ionic strength, respectively. The absorbance of MG and MB dye solutions were measured at wavelength 618 nm and 664 nm, respectively, using Shimadzu UV-1601PC UV–visible spectrophotometer (UV–vis). Distilled water was used throughout this study.

The functional groups of CEN were determined using Shimadzu IR Prestige-21 spectrophotometer for Fourier transform infrared spectroscopy (FTIR) analysis using KBr disc method. The elemental CHNS compositions of CEN were determined using the Thermo Scientific Flash 2000 Organic Elemental Analyzer CHNS/O, while the rest of the elements were determined using X-ray fluorescence (XRF) spectrophotometer (PANalytical Axios^{max}).

2.2. Sample preparation

CEN was collected from the garden in the Universiti Brunei Darussalam. The branches and twigs of *C. equisetifolia* were carefully removed from the collected pile. CEN was then washed with distilled water to remove any dust particles and dried in an oven at 70 °C until a constant weight was achieved. Dried CEN was then blended using Panasonic MX-J210GN blender and sieved to different sizes.

2.3. Batch experiment procedure

All adsorption experiments were carried out at predetermined mass of CEN with 20 mL dye solution in 125 mL Erlenmeyer flask. All mixtures were agitated at 250 rpm using an orbital shaker, at room temperature and ambient pH (unless otherwise stated). Prior to the adsorption experiment, effect of particle sizes was investigated with three particle sizes ($>$ 500 mm, 355–500 mm and $<$ 355 mm) with 100 mg L^{-1} dye. The effect of adsorbent dosage was carried out from 0.01 g to 0.08 g of adsorbent at interval of 0.01 g with 100 mg L^{-1} dye. The effects of pH (2–8), contact time (5–240 min), ionic strength using NaCl (0–0.8 mol L^{-1}), and temperature (25–55 °C) were carried out using the predetermined CEN particle size and dosage.

The experimental data were characterised with four kinetics models (Lagergren-first-order, pseudo-second-order, Weber–Morris intraparticle diffusion and Boyd models), while the three isotherm models included in this studies are the Langmuir, Freundlich and Dubinin–Radushkevich models.

The amount of dye adsorbed per gram of CEN, q_e (mmol g^{-1}), was calculated using:

$$q_e = \frac{(C_i - C_e)V}{M_r m} \quad (1)$$