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Phragmites australis: An alternative biosorbent for basic dye removal

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ABSTRACT

This study is aimed at investigating the removal of methylene blue (MB) from aqueous solutions using a reed species, *Phragmites australis* as an adsorbent. *P. australis* was modified by means of a chemical treatment, assuring the alteration of hydroxyl groups to sulphonyl groups. Experiments were performed in the batch mode to determine the adsorption dynamics of the modified and untreated *P. australis*. The impact of several influential parameters such as initial pH, initial dye concentration and contact time on the adsorption capacity of *P. australis* was evaluated. The adsorption capacity of raw *P. australis* was found to improve significantly by modification reaction. The maximum sorption capacities of the raw and modified biomass were found to be 22.7 mg/g and 46.8 mg/g at initial MB concentration of 250 ppm, biosorbent dosage 0.25 g and initial dye solution of pH of 6.5, respectively. Dye adsorption equilibrium data were fitted well to the Langmuir isotherm rather than the others. The rate of adsorption followed the pseudo second-order kinetic model. Thermodynamic parameters for both raw and modified biomass showed that the adsorption of MB was favorable and spontaneous. Results showed that both *P. australis* and its modified form have a potential as an eco-friendly adsorbent for the removal of methylene blue from aqueous solution.

1. Introduction

Dyes are frequently used in many industries, such as, textile, paper, food, spices and cosmetics, primarily to color products (Ravi et al., 2005) and are released mostly into aquatic systems which is a major problem due to their negative effects (carcinogenic, mutagenic and potentially toxic) on all living organisms in aquatic systems (Forgacs et al., 2004; Kabra et al., 2011). Discharge of these types of contaminants is evaluated as an issue of concern (Metivier-Pignon et al., 2003) due to not only toxicity but also esthetic reasons.

The textile and clothing industries are among the most important sectors in the Turkish economy. The Turkish textile industry, which is listed in the world's top 10 exporters, is the 2nd largest supplier to the EU (TR, 2014). Its environmental impact is substantial due to its usage of large amounts of processed water and generation of high amounts of polluted wastewater (Imtiazuddin et al., 2012; Husain and Hussain, 2012). The color change is the first reagent to be noticed in aquatic systems and wastewater. Textile dyes, even if present in very small amounts in water (e.g., less than 1 ppm for some dyes), are extremely visible and undesirable (Banat et al., 1996; Robinson et al., 2001). Methylene blue (MB) is a thiazine cationic dye and is used extensively in coloring cottons, wools, silk, dying paper and temporary hair colorant. It can cause some harmful effects, for example eye burn, inhalation problems, heartbeat increase, nausea, vomiting, shock, mental confusion (Maurya et al., 2006; Vilar et al., 2007; Tan et al., 2008; Wang et al., 2008; Vijayaraghavan et al., 2008). Because of the harmful effects, different physical, chemical and biological methods are used for the removal of textile dyes and dye products in wastewater and water (Ghoreishi and Haghighi, 2003). These techniques are coagulation, ozonation, electrolysis, cation exchange membranes, electrochemical degradation, sonochemical degredation, enhanced ultrafiltration and adsorption (Robinson et al., 2001; Aksu, 2005; Wu et al., 2008; Fan et al., 2008; Abbasi and Asl, 2008; Zaghbani et al., 2008). In all these methods, adsorption is the best technique for the removal of coloring materials (Kapdan and Kargi, 2002; Jain et al., 2003; Ho and McKay, 2003; Dabrowski, 2001), owing to lower costs, flexibility and simplicity of design and ease of practicality (Rafatullah et al., 2010).

Biological materials (e.g., algae, fungi, microbial cultures, and aquatic plants) have recently been used as bioadsorbent in several studies (Marungrueng and Pavasant, 2007; Fu and Viraraghavan, 2000; Yu et al., 2009; Low et al., 1995; Pathomsiriwong and Reanprayoon, 2012). However, studies associated with aquatic

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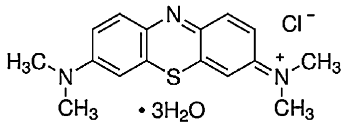
Table 1
Basic properties of methylene blue.

Molecular structure	Molecular weight (mol/g)	λ (nm)
	373.90	665

plants are fairly limited. For example, Low et al. (1993) and Pathomsiriwong and Reanprayoon (2012) studied the biosorption capacity of *Hydrilla verticillata* on dyes. They reported that dried *H. verticillata* was able to remove the dyes efficiently and rapidly. In another report, Khan et al. (2012) showed that water hyacinth roots could be used for the removal of MB.

Phragmites australis, commonly known as reed, was used in this study. It is a large perennial grass found in wetlands throughout temperate and tropical regions of the world. It can grow up to 6 m high and is long-lived (Aysu, 2014) and contains high amounts of lignin and cellulose (Lenssen et al., 1999). Properties of *P. australis* not only provide a potentially inexpensive material for wastewater treatment, but also help surface modification by means of great numbers of hydroxyl groups (—OH) on its surface. *P. australis* has thus been used for years for the removal of heavy metals and metalloids from aquatic systems and waste water (Ye et al., 1997; Vymazal et al., 2007; Bonanno and Giudice, 2010; Kumari and Tripathi, 2015). However, the studies carried out regarding the removal of textile dyes are limited. Chen et al. (2010) studied the adsorption of methyl orange and methyl violet from aqueous solutions with activated carbon derived from *P. australis*.

Relying upon the facts that the studies on raw *P. australis* are fairly limited and the advantages on use of this aquatic plant such as easy access or low-cost production are highly considerable in terms of practical potential with future prospective, the objective of the present work was set to investigate its effectiveness as an adsorbent for the removal of the widely used dye MB. Within this scope, the adsorptive properties of *P. australis* were also experimented on its modified form to explore the probable improvements. The impact of key operational parameters such as solution pH, sorbent dosage and contact time on MB adsorption by both raw and modified *P. australis* was tested to optimize the adsorption process in a batch mode.

2. Materials and methods

2.1. Chemicals/reagents

The reactive dye methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$) was purchased from Merck (Germany) and used without further purification (Table 1). In this experiment, the synthetic dye solution with various concentrations was prepared dissolving MB in distilled water, and the pH of aqueous solution was adjusted to the desired value by addition of NaOH (0.1 M) or HCl (0.1 M).

2.2. Preparation and modification of P. australis biomass

P. australis samples were collected from the lower catchment area of Kapulukaya Dam Lake in Kırıkkale Province. They were firstly cleansed with river water and then washed with distilled water for the removal of particles and dirt. Plant parts were dried at 70 °C in a hot air oven for 48 h (Vardanyan and Ingole, 2006; Sahu et al., 2007). The dried biomass was grinded with a blender. Hereafter, it is denoted as the raw adsorbent.

The raw biomass of *P. australis* (10 g) was poured into NaOH solution (1 M, 50 ml) containing epichlorohydrin (1 ml) and stirred for 5 h at 50 °C. After the reaction, the plant biomass was then washed with deionized water. The epichlorohydrin-modified plant material was converted to obtain sulphonyl groups. For this purpose, the epichlorohydrin-modified plant (≅10 g) was refluxed with sodium sulfite (Na_2SO_3, 30 g) dissolved in 57.5 ml isopropyl alcohol and 225 ml water in a round bottom flask at 80 °C for 4 h. The filtered product was washed several times with distilled water. The product was then refluxed with 0.5 M H_2SO_4 for 2 h at 80 °C to convert to remaining epoxy groups into diol (Anirudhan and Senan, 2011), and hereafter, it is denoted as the modified adsorbent. It was stored at room temperature until use.

2.3. Characterization studies

The FTIR spectra of raw and modified *P. australis* were obtained using a Bruker Vartex 70 V model Fourier Transform Infrared Spectrometer.

The surface morphology of raw, modified and MB adsorbed *P. australis* samples were examined by using a scanning electron microscope (JEOL, JSM 5600), after coating with gold under reduced pressure.

2.4. Batch experiments

The ability of raw and modified *P. australis* biomass to remove MB was tested in batch assays. All the experiments were conducted in a series of 250 ml flasks by mixing biomass with aqueous MB solutions. The parameters studied were pH (2–10) and contact time (10–240 min) at an initial dye concentration of 50 mg/l at laboratory ambient temperature (approximately 25 ± 1 °C) in 50 ml pH adjusted solutions. The initial pH of dye solution was previously adjusted with 0.1 M NaOH or 0.1 M HCl solutions.

To determine the effect of initial methylene blue concentrations on dye removal by aquatic plant biomass, dye concentrations were varied ranging from 5 mg/l to 300 mg/l at pH 6.5 and constant agitation (150 rpm). After reaching the equilibrium time, the supernatant solution was separated from plant biomass by centrifugation. The amount of residual dye was determined at 665 nm, which is the maximum wavelength adsorption of MB, by means of a UV–vis spectrophotometer (SpectroScan 80 DV).

In all experiments, the difference between the initial dye concentration (C_o) and the equilibrium concentration (C_e) was calculated and used to calculate the adsorptive capacity (q) and percentage removal as follows:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\text{Dye removal efficiency (\%)} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (2)$$

where q is adsorption capacity in milligrams per gram; C_o and C_e are, respectively, the initial and final dye concentrations after treatment for certain periods of time (mg/l); V is the volume of each dye solution in ml, and m is the total amount of modified plant biomass in grams.

The reusability of the raw and the modified plant materials was evaluated by an adsorption/desorption experiment. Following the termination of MB adsorption, a 0.1 M HCl solution was added to the medium by agitating magnetically at 150 rpm at 25 °C for 2.0 h to measure desorption capacity for each sample.

2.5. Isotherm studies

Adsorption isotherm experiments were conducted by equilibrating raw and modified plant biomass in Erlenmeyer flasks