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Efficient removal of anionic and cationic dyes from aqueous systems using spent Yerba Mate "Ilex paraguariensis"

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ABSTRACT

The overarching aim of this work was to assess the performance of low cost and readily available biomass, Yerba Mate (Y-Mate), for the removal of Orange II dye (OII) and Methylene Blue (MB) as a function of solution pH, dosage and particle size at different initial dye concentrations and contact time. The data was quantitatively described through appropriate isotherms and kinetic equations. OII biosorption on Y-Mate significantly decreased with increasing pH from 2 to 6, whereas, MB biosorption increased steadily with increasing pH. The Sips isotherm model best represented biosorption isotherms for both contaminants. Under the experimental conditions explored, the Langmuir maximum biosorption capacities reached 47 and 52 mg/g for OII and MB, respectively. The biosorption kinetics were well represented with the pseudo second-order equation. Surface area and point of zero charge (PZC), thermo-gravimetric analysis (TGA), scanning electron microscope (SEM), fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analytical techniques were considered to characterise the surface chemistry of Y-Mate. The analysis indicated that the mechanisms of Y-Mate towards both anionic and cationic dyes are mainly through the co-action of $\pi-\pi$ interaction and hydrogen bonding, while electrostatic attraction had an additional effect on the biosorption.

1. Introduction

Large amounts of water are being consumed yearly by the textile industry. In turn, water generated from dye rinse processes and exhausted dye-baths contains unfixed dyes and are generally extremely coloured. Dyes discharged from other sources such as; pulp industries, cosmetics and pharmaceuticals are considered as potent contaminants released into the natural water resources. When discharged, these coloured dye-contaminated effluents affect light penetration in the water and their degraded by-products are toxic to aquatic organisms and animals [1]. There is no single technique effective for satisfactory treatment of these effluents, but combinations of different biological and physical–chemical techniques can remove the majority of the organic content of the textile wastewaters. As a result, a final refining treatment is additionally essential to eliminate the remaining colour. This final step is crucial for potential water recycle [2]. Biosorption and adsorption provide successful and resourceful processes for the removal of dyes from wastewater, especially when readily available and inexpensive materials are used [3–6]. Adsorbents essentially add towards the ultimate performance throughout a biosorption/adsorption process, so in recent years, engineers and scientists have put considerable effort into the discovery and advancement of novel and highly effective adsorbents [7]. Table 1 provides a comparison of the Biosorption/adsorption capacities of various materials for the removal of dyes from aqueous solutions [8–13].

Yerba Mate (Y-Mate) is one of the most common tea-like hot drinks in South America and areas of the Mediterranean. There is a huge amount of exhausted yerba mate; approx. 280,000 tons of Yerba Mate are produced yearly in Argentina alone. It is considered a good source of natural polyphenols (an extracted adsorbent) [14] and has been used as a precursor to the manufacture of activated carbon [15] because it has abundant free amino, hydroxyl and carbonyl groups on its carbon structure. However, the capacity of Yerba Mate as a biomaterial for the elimination of pollutants from aqueous solutions has been underestimated. Methylene blue (MB), a heterocyclic basic dye, is frequently used in textile industries for dyeing purposes and also has medical applications such as; staining tissues, an antidote for cyanide poisoning and for the treatment of methemoglobinemia at therapeutic dosages [16]. Even though MB is not extremely hazardous, its presence in water can cause some negative consequences on human health [17–21] and so, it is essential to remove MB from wastewater. Acid orange or Orange II (OII), like most other azo dyes, is discarded in industrial wastewater and presents serious health threats. It is a toxic dye

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Table 1
Comparison of sorption performance for various dyes with different sorbents appeared in the literature.

Material	Targeted dye	C_o (mg/L)	Isotherm fitted and q_{max} (mg/g)	Removal mechanism	Reference
Pistachio by-product	C.I. reactive red	50–200 mg/L	Sips isotherm, 109.53 mg/g	Physical mechanisms	[7]
Water hyacinth leaves	Amaranth dye	10–500 mg/L	Langmuir isotherm, ~70 mg/g	Chemical mechanisms	[8]
Chemically modified masau stones	Orange II	50–300 mg/L	Langmuir isotherm, 136.8 mg/g	Chemical mechanisms	[9]
Calcined bones	Safranin (Basic Red 2)	20–100 mg/L	Langmuir/Freundlich isotherms, 93.12 mg/g	Physical mechanisms	[10]
Beach bivalve shells	Methylene blue	5–50 mg/L	Langmuir isotherm, 1 mg/g	Physical mechanisms	[11]
Graphene oxide (GO)	Acid Orange 8 and Direct Red 23	10–50 mg/L	Langmuir/Redlich-Peterson isotherms, 29.0 and 15.3 mg/g	Physical mechanisms	[12]
Yerba Mate "Ilex paraguariensis"	Orange II and Methylene blue	25–400 mg/L	Sips isotherm, 47 and 52 mg/g	Physical mechanisms	this study

and its consumption can be lethal, as it is carcinogenic and can cause tumours [22]. The concentration of these selected dyes in wastewater effluents can be as low as 1 mg/L, however, they are a good choice for testing the performance of sorbents whose mesoporosity suggests their application for sorption of liquid pollutant [12]. Therefore, the main aim of this study is to assess the biosorption capacity of Y-Mate as an efficient material for the bio-removal of OII and MB dyes from aqueous solutions. The effects of experimental controlling conditions for example: solution pH, biosorbent dosage, Y-Mate particle size and initial dye concentration, and contact time are considered in order to observe and demonstrate their effect on the biosorption isotherms and associated kinetics. Various analytical techniques, namely: TGA, FTIR, XPS and SEM have been considered to offer a comprehensive insight into possible biosorption mechanisms that govern the interaction between dye molecules and the Y-Mate biosorbent.

2. Experimental methods

2.1. Y-Mate biosorbent

Yerba Mate (Y-Mate) biomass was collected and mechanically crushed. Then, the Y-Mate was repeatedly washed with boiled water and lastly with distilled water, and dried in a conventional oven at 110 °C for 24 h to remove any moisture that may be found in Y-Mate. After sieving, three different particle sizes (75–250, 250–500 and 710–1000 μm) were formed in order to be used for the biosorption processes. The specific surface area of Y-Mate for the three different particle sizes 75–250, 250–500 and 710–1000 μm was measured by the N_2-BET method as 23.11, 20.74, 18.29 m^2/g, respectively. The point of zero charge (PZC) of the Y-Mate biosorbent was determined as 4.7 using the procedure in [23].

2.2. Chemicals

Orange II sodium salt (OII), dye content ~85 %, and methylene blue (MB), dye content ≥ 82% were obtained from Sigma Aldrich, UK. Deionized water (resistivity 18.24 Ωcm) was utilized for preparing dye solutions.

2.3. Y-Mate biosorbent characterisation

The Y-Mate surface characteristics before and after biosorption were determined using FTIR Spectroscopy: using a Perkin Elmer Spectrum 100 within the range of 400–4000/cm (KBr pressed disc technique). SEM was used to check the topography of Y-Mate before and after biosorption (gold coating and vacuumed (5–10 min)) former to analysis on a JEOL-JSM 6400 scanning microscope. XPS analysis was mainly employed to confirm the functional groups on the Y-Mate surface. The Kratos ULTRA spectrometer was used for the XPS measurements: sample temperature = 20–30 °C; X-ray Gun mono Al Kα 1486.58 eV; 150 W (10 mA, 15 kV) and pass Energy = 160 eV for survey spectra and 20 eV for narrow regions. Thermo-gravimetric analysis (TGA) for the unloaded and loaded Y-Mate was completed using PerkinElmer TGA 4000 at a heating rate of 10 °C/min from 20 °C to 500 °C under nitrogen purging (50 mL/min). The sample weight was 10 mg.

2.4. Dyes biosorption

The biosorbent was put in glass jars, dye solutions with predetermined concentrations added and the jars firmly sealed. Then, all suspensions were agitated at 110 rpm using a GerhardT type shaker for 24 h at ~20 °C. The pH of various suspensions was altered by adding either 0.05 M HNO_3 or NaOH. UV–vis spectrophotometer (Perkin Elmer LAMBDA 25, UK) was used for concentration measurements at a maximum wavelength $\lambda_{max} = 478$ nm for OII and $\lambda_{max} = 668$ nm for MB. All experiments were performed in duplicate and the change in colour, pH, and electrical conductivity (EC) was monitored. The results obtained are an average (with 5% accuracy).

2.4.1. Influence of pH and biosorbent dosage

Solution pH 2–9; $C_o = 100$ mg/L; shaking time 24 h at 110 rpm; dosage 4 g/L; T = 20 °C.

For the dosage effect study, Y-Mate dosage 1–6 g/L; solution pH 3 for OII and pH 6 for MB; $C_o = 100$ mg/L; shaking time 24 h at 100 rpm; T = 20 °C. The pH was not controlled during the sorption but the final pH was systematically recorded.

2.4.2. Effect of contact time and dye initial concentration

For the isotherm studies, solution pH 3 was used for OII and pH 6 for MB; $C_o = 25$–400 mg/L; shaking time 24 h at 100 rpm; dosage 4 g/L; T = 20 °C. For the contact time experiment, same pH values and dosage were used at room temperature with $C_o = 100$, 200 and 400 mg/L. The solutions were mixed under magnetic stirring at an agitation speed of 200 rpm. At predetermined timed intervals, samples (1 mL) were withdrawn.

2.5. Isotherms and kinetics modelling

The removal efficiency (%) and dye uptake, q (mg/g), can be calculated using Eqs. (1) and (2), respectively:

$$\text{The percentage removal} = \left[1 - \frac{C_e}{C_o}\right] \times 100\ \% \quad (1)$$

$$q = \left[\frac{C_o - C_e}{M}\right] \times V \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of dyes in mg/L, respectively. V is the volume in liters and M is the quantity of biosorbent in grams.

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