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Application of raw peach shell particles for removal of methylene blue

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ABSTRACT

A possibility to apply raw, powdered peach shells (PS) as a biosorbent for water purification was studied. The PSs are locally available as a solid waste in a fruit juice factory; methylene blue (MB) was chosen as representative of common pollutants in textile industry wastewater. The phase composition of prepared particles was identified by XRD. The particle morphology was characterized by FE-SEM, while the size distribution was measured by a laser light-scattering particle size analyzer. The BET specific surface area was determined from N_2 adsorption/desorption experiments. The effect of operating parameters: the biosorbent amount (50–1000 mg/100 mL), contact time (10–180 min), solution pH (2–12) and initial concentration (10–100 ppm) on biosorption efficiency was examined. Optimal conditions for MB removal were found to be: the biosorbent amount of 400 mg/100 mL and pH 5.5. A high efficiency of MB removal was established after 180 min: 99% for $[MB]_i = 10$ ppm and 76% for $[MB]_i = 100$ ppm. Biosorption is well described by the Freundlich- and BET-type isotherms, implicating heterogeneous adsorption sites and interconnections between adsorbed molecules. The FTIR spectroscopy results indicate hydrogen bonding between the dye and the biomass. The obtained results shown that raw peach shell particles could be used as an efficient low-cost biosorbent for dye removal from water.

Introduction

Increased industrial, agricultural and domestic activities resulted in the production of large amounts of wastewater containing a number of toxic materials which are continuously polluting the available fresh water [1]. In several countries, the removal of pollutants is considered a priority issue for drinking water and wastewater treatment [2]. Among various developed technologies for water purification, sorption is proven as a superior one because of its cost-effectiveness, simplicity of operation, insensitivity to toxic pollutants, *etc.* [3]. Due to their wide availability, low cost and environmental safety, natural materials such as kaolin, zeolites, coal, *etc.*, are the most commonly used sorbents for the removal of pollutants from wastewater [4–6]. Besides, in the past several years there has been an increased interest in testing a biomass as a (bio)sorbent for wastewater treatment. Generally, waste biomass has been used for the preparation of activated carbon which has further been used for the removal of water pollutants [7–11]. Having in mind that biomass contains a large amount of water (50–60%) the following question arises: does the pyrolysis process pay off? However, waste biomass could be used as a sorbent even in a raw form [12]. The removal efficiency of raw biomass is lower than that of active carbon but it is an available/cheap material; at the same time, the use of biomass as an agricultural solid waste brings solution to the environmental problem of its storage [13].

The aim of this paper is to demonstrate the applicability of peach shells, a used biomass, classified as waste in fruit juice factories, as a biosorbent for methylene blue–a potential pollutant in textile industry wastewater. Peach stone shells have so far been used to prepare active carbon; it has been found that after chemical activation with H_3PO_4 followed by carbonization, the prepared materials show a large capacity for methylene blue sorption [14]. In this study, the idea is to determine the sorption capacity of the raw material. Accordingly, the raw biomass was characterized and its efficiency for biosorption of methylene blue was examined under different experimental conditions: the biosorbent amount, solution pH, contact time, and dye concentration were varied. Finally, we have proposed the biosorption mechanism.

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Materials and methods

Preparation of the biosorbent material

Waste peach shells (PS) from Vino Župa, Aleksandrovac, Serbia, fruit juice factory were used as the raw material for removing non-degradable toxic dye from water solutions. The collected peach shells were washed several times with boiled water to remove the adhering pulp, and subsequently dried at room temperature. After drying, PSs were manually crushed and separated from kernels; shells were milled in vibromill and sieved in different fractions. For experiments presented in this paper, the particle fraction of $<100\,\mu m$ was used. Before the biosorption experiments, PS particles were washed with 0.01 M HCl to clean out surface impurities, subsequently washed with distilled water to negative test on Cl^- ions and dried for 24 h at 80 °C in a drying oven. The dried PSs were stored in a container.

Characterization of the biosorbent

The PS biomass was characterized using an X-ray diffractometer (XRD, Philips PW-1050) with $CuK\alpha_{1,2}$ radiation (40 kV, 20 mA). The data were collected over a 2θ range 10–70° with a step size of 0.05° and a counting time of 5 s per step. The phase composition was identified by comparing the recorded data with those reported in the Joint Committee of Powder Diffraction Standards (JCPDS) database. The morphology of PS particles was observed by field-emission scanning electron microscopy (FE-SEM; SUPRA 35 VP, Carl Zeiss). The PS sample for the FE-SEM analysis was dispersed in ethanol, in an ultrasonic bath (low-intensity ultrasound, at a frequency of 40 kHz and power of 50 W), for 30 min; after dispersion, a few drops were filtered through a cellulose acetate membrane. The membrane was put on a carbon tape on an aluminum stub and carbon-coated for electron reflection. Before the analysis, the sample was vacuumed for 15 min. The particle size distribution of the PS sample was measured by a laser light-scattering particle size analyzer (PSA) (Mastersizer 2000; Malvern Instruments Ltd., Malvern, Worcestershire, U.K.). Prior to the measurement, the sample was dispersed in distilled water (22 °C), in an ultrasonic bath (at a frequency of 40 kHz and power of 50 W), for 10 min. The specific surface area (SSA) and the porous properties of the PS biomass were determined based on N_2 adsorption–desorption isotherm at −195.8 °C using ASAP 2020 (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to the measurement the biosorbent was degassed, at 110 °C for 10 h under reduced pressure, to remove moisture or adsorbed contaminants which could be present on the surface. The SSA was calculated according to the Brunauer–Emmett–Teller (BET) method from the linear part of the N_2 adsorption isotherm [15]. The total volume of pores (V_{tot}) was given at $p/p_0 = 0.998$. The mesopore volume (V_{meso}) and pore size distribution were analyzed according to the Barrett–Joyner–Halenda (BJH) method from the desorption isotherm [16]. The micropore volume (V_{micro}) was evaluated by *t*-plot method. Fourier transform infrared (FTIR) spectroscopy was used to determine the surface functional groups of the PS biomass and to identity the groups which participate in bonding between PS and MB. The samples of PS biomass before and after the biosorption process were recorded on a BOMEM (Hartmann & Braun) spectrometer using the KBr pellet technique, in the spectral range of 400–4000 cm^{-1}. The spectral resolution was 4 cm^{-1}.

Methylene blue

The biosorptive activity of PS particles was studied by the biosorption of a non-degradable dye methylene blue (MB). Methylene blue is a cationic dye, with the chemical formula $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ and a molecular weight of 373.9 g/mol; MB shows an intense absorption peak in the visible region, at 665 nm. A stock solution of 1000 ppm was prepared by dissolving 1.0 g of methylene blau (Methylen blay B extra, E. Merck, Darmstadt, Germany) in 1 L of distilled water. The MB solutions for biosorption experiments were prepared by diluting the stock solutions to the appropriate concentrations.

Effect of the PS amount on the MB biosorption

The effect of the biosorbent dose on the efficiency (%) of MB biosorption was investigated using different amounts of PS, in particular 50, 100, 200, 300, 400, 500, 600, 800 and 1000 mg. In each experiment, the appropriate amount of PS was added in 200 mL glass containing 100 mL of MB in a concentration of 20 ppm. During the experiments, the solutions' pH (∼5.5) was not changed. After 180 min the MB dye concentrations were measured.

Effect of the solution pH on the MB biosorption

The effect of the solution pH on biosorption was studied in a pH interval from 2 to 12. In each of the experiments 100 mL of 20 ppm MB solution was used. The pH was measured by a pH-meter (Hanna Instruments HI 3222) and adjusted to the appropriate value with 0.1 M HCl and 0.1 M NaOH solutions. After the pH adjustment, the solutions were mixed with 400 mg of PS. After 180 min the MB dye concentrations were measured.

Effect of the MB solution concentration and contact time on the biosorption

In order to determine the effects of the MB concentration and contact time on biosorption efficiency, an amount of 400 mg of PS biomass was mixed with 100 mL of MB solution. The tested concentrations of MB were 10, 20, 50 and 100 ppm, while the contact time was changed from 10 to 180 min.

To keep the mixture in suspension, all of the above-mentioned biosorption experiments were performed under constant stirring of 600 rpm on magnetic stirrer; temperature was kept constant at 22 °C. In each experiment, 3 mL of aliquots was withdrawn in appropriate time intervals and centrifuged at 4000 rpm during 5 min to remove PS particles from the solution before the absorbance measurement. The residual concentration of the MB pollutant after biosorption was calculated according to the absorbance value at 665 nm determined by measurements performed on a Cintra 101 UV–vis spectrophotometer (GBC Scientific Equipment Inc., Hampshire, IL, US) in the wavelength range of 300–800 nm. All tests were performed in triplicate to avoid wrong interpretation due to possible experimental errors. Standard deviations were calculated giving the experimental error below 2%.

Mechanism of biosorption

To understand the mechanism of adsorption different isotherm models have been developed during the years. In most cases, adsorption does not follow a simple law and a single model is not always convenient; commonly adsorption results from the superposition of at least two mechanisms. In this paper, to describe the mechanism of methylene blue dye biosorption on peach shell biomass, the Langmuir, Freundlich and BET isotherm models, as most commonly used, were tested. The Langmuir model is based on the assumptions that the surface is homogeneous containing a finite number of adsorption sites, and that the adsorption occurs through the formation of a monolayer of