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Organic dyes removal using magnetically modified rye straw

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ABSTRACT

Rye straw, a very low-cost material, was employed as a biosorbent for two organic water-soluble dyes belonging to different dye classes, namely acridine orange (acridine group) and methyl green (triarylmethane group). The adsorption properties were tested for native and citric acid–NaOH modified rye straw, both in nonmagnetic and magnetic versions. The adsorption equilibrium was reached in 2 h and the adsorption isotherms data were analyzed using the Langmuir model. The highest values of maximum adsorption capacities were 208.3 mg/g for acridine orange and 384.6 mg/g for methyl green.

1. Introduction

Enormous amounts of dyestuff are consumed annually by various sectors of industry, e. g. textile, paper, leather, plastics, rubber, cosmetics, pharmaceuticals and food industries [1]. These compounds or their metabolites cause concern for human health because of their toxicity, carcinogenity and mutagenity [2,3] and also due to high persistence in environment and non-biodegradable characteristics [4]. Moreover, the colored dye effluents can block the penetration of sunlight and oxygen which are both essential for various aquatic forms of life [5].

Many techniques have been employed to eliminate dyes from waste water. These methods involve e.g. ion exchange, coagulation and flocculation, oxidation and various forms of degradation (photo-, bio- and chemical-) [4,6]. Among them, adsorption is considered to be superior because of the high efficiency and subsequently economical value [7].

In recent years, many plant materials have been tested as low-cost adsorbents for various xenobiotics, such as organic dyes, heavy metals, radionuclides or endocrinne disruptors. For instance, wheat straw [8], barley straw [9], rice straw [10], rice husks [11], sawdust [1], tea waste [5], peanut husks [12], spent coffee grounds [13], coffee husks [14], spent grain [15], fruit peels [16] and sugarcane bagasse [17] have been succesfully used for organic dyes removal.

Rye straw represents a very interesting material that can be obtained in large amount and for low price. Nevertheless, there are only few publications focused on utilization of rye derivatives for xenobiotics removal. One of them describes adsorption of Cr (VI) [18] and the second one removal of azodyes [19].

Native plant materials usually show lower maximum adsorption capacities. Nevertheless, these values can be significantly increased using a suitable method such as treatment with various acids, hydroxides or combination of both; also less common carbonization or hydrolysis have been reported recently [9,11].

A successful combination of nonmagnetic powdered material with magnetic nano- or microparticles (often bound on the surface or within the pores of the modified material) results in a formation of magnetically responsive (bio)composites which exhibit response to external magnetic field. Magnetic materials facilitate and accelerate many manipulations, also in difficult-to-handle materials (including raw extracts, blood and other body fluid, environmental samples, cultivation media, suspensions, etc.) [20]. Originally diamagnetic materials can be easily and selectively separated using a permanent magnet, an appropriate magnetic separator or an electromagnet. Magnetic separations can also be performed in large scale due to the existence of industrial magnetic separators, currently employed e.g. in kaolin decolorization, steel industry, mineral beneficiation, etc. [20].

The aim of this paper is the comparison of adsorption properties of native and chemically modified rye straw, both in nonmagnetic and magnetic versions for organic dyes adsorption and a demonstration of the promising potential of this type of plant-based material.

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2. Materials and methods

2.1. Materials

Rye straw was supplied by the farm Tomsik in Horni Dubenky (Czech Republic). Ferrous sulfate heptahydrate and sodium hydroxide were from Sigma-Aldrich (Czech Republic), citric acid from Lachema (Czech Republic), acridine orange (CI (Colour Index) 46005) and methyl green (CI 42585) from Loba Feinchemie (Austria).

2.2. Preparation of rye derivative

Before all experiments, rye straw was cut into smaller pieces (ca. 5 cm), milled and sieved to obtain fine particles about 0.1–2 mm in diameter.

2.3. Magnetic modification

Magnetic modification was carried out according to the described procedure [21] using microwave-synthesized magnetic iron oxide nano- and microparticles. Briefly, 1 g $Fe(SO_4)\cdot 7H_2O$ was dissolved in 100 mL of water and solution of NaOH (mol/L) was added dropwise under stirring until the pH reached the value 12 and the precipitate of iron hydroxides was formed. Then the suspension was diluted up to 200 mL with water. The beaker was inserted into a standard kitchen microwave oven (700 W, 2450 MHz) and treated at maximum power for 10 min. Finally, the formed magnetic particles were repeatedly washed with water until the pH was neutral.

To prepare magnetic biosorbent derivate, 1 g of straw was thoroughly mixed with 2 mL of magnetic iron oxide nano- and microparticles suspension (1 part of completely sedimented magnetic particles and 4 part of water) and then this mixture was dried at 60 °C for 24 h.

2.4. Citric acid–NaOH modification

The chemical modification of rye straw was performed as described previously [2]. Citric acid (0.5 mol/L) was added to rye straw in a ratio 12:1 (v/w). This mixture was stirred for 30 minutes and dried at 50 °C for 24 h. The termochemical reaction between rye straw and citric acid (CA) was carried out by increasing the temperature to 120 °C for 60 min. After cooling at room temperature, the CA-modified straw was thoroughly washed with distilled water to obtain neutral pH and filtered. Then a solution of NaOH (0.1 mol/L) was added to the filtrated residues in a ratio 12:1 (v/w) and the mixture was stirred for 90 min. Finally, the CA–NaOH modified straw derivative was extensively washed with distilled water to remove alkali residuals and dried at 50 °C for 24 h.

2.5. Adsorption of dyes on rye straw biomass

Testing of the adsorption properties slightly differed for untreated and chemically modified dye straw. In case of untreated derivative, 30 mg of biosorbent was mixed with 1 mL of distilled water and then 1–9 mL of dye (mg/mL) was added, while in the

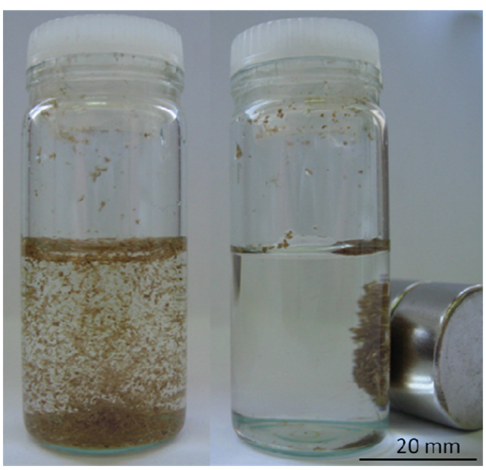

Fig. 1. Magnetic separation of magnetically modified rye straw using NdFeB permanent magnet (diametre: 20 mm; height: 10 mm; remanence: 1 T).

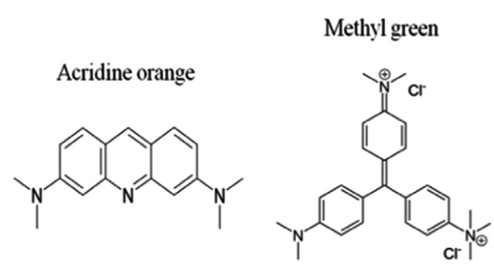

Fig. 3. Chemical structures of acridine orange and methyl green.

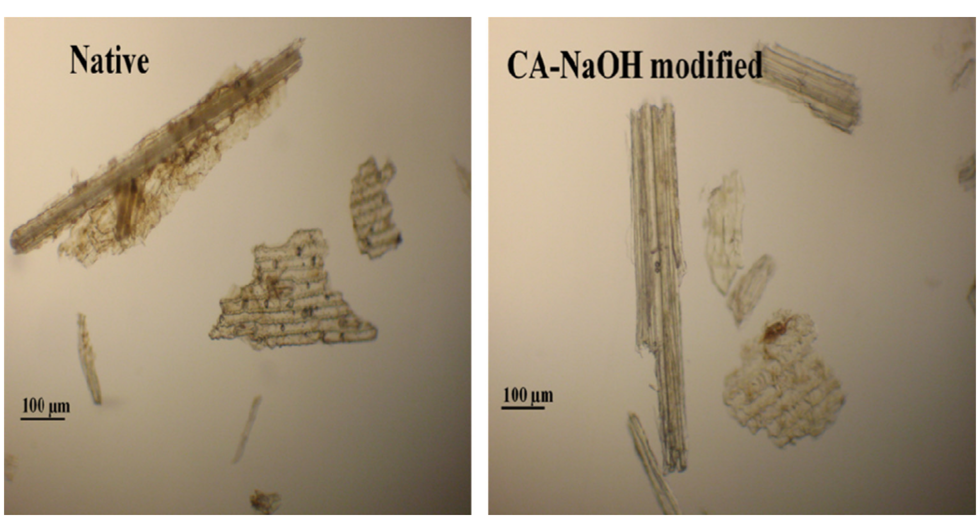

Fig. 2. Structures of native (left) and chemically modified (right) rye straw adsorbents.