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Enhanced removal of hazardous dye form aqueous solutions and real textile wastewater using bifunctional chitin/lignin biosorbent

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ABSTRACT

A new biomaterial based on chitin and lignin was prepared and applied for the removal of hazardous dye C.I. Direct Blue 71 (DB71) from aqueous solutions and wastewaters. The dye sorption on the chitin/lignin biosorbent (Ch/L) was examined depending on the initial dye concentration (50–200 mg/L), phase contact time (1–1440 min), kind of auxiliaries (NaCl, Na_2SO_4, anionic surfactant SDS) and their concentrations (1–20 g/L salts, 0.1–0.75 g/L SDS), initial solution pH as well as temperature (20–50 °C). The equilibrium and kinetic characteristics of C.I. Direct Blue 71 uptake by chitin/lignin followed by the Freundlich isotherm model and the pseudo-second order model rather than the Langmuir, Tempkin models, and pseudo-first order model. C.I. Direct Blue 71 adsorption on chitin/lignin was spontaneous (−2.86 to −8.14 kJ/mol) and endothermic (60.1 kJ/mol). The possibilities of dye elution and reuse by means of the batch method were investigated and as follows the chemical reaction is an inseparable sorption mechanism. Purification of wastewaters containing direct dyes was made with 91% efficiency after 1 h of phase contact time. For comparison, data obtained or obtained results in the DB71-chitin (Ch) system were also presented.

1. Introduction

An innovative group of materials currently often applied for removal of heavy metal ions and organic substances of various types including dyes from waters and wastewaters are hybrid and composite materials. They are made of two different components, mainly organic and inorganic ones to make a single entity with either enhanced or completely new properties. Their combination results in better physicochemical, thermal and mechanical properties compared to single components which form it. Hybrid materials can be divided into two groups depending on the nature of interactions between inorganic and organic components [1,2]. In class I hybrid materials the interactions between organic and inorganic components are weak i.e. van der Waals or hydrogen bonding. The strong bonding such as covalent or ion-covalent interactions are characteristic of class II hybrid materials [1,2]. More and more often scientists synthesize new materials based only on organic or inorganic components. In the author's opinion, such kind of materials obtained from two organic (or inorganic) biopolymers possessing different properties compared with the substrate components can be called quasi-hybrid. Possibility of synthesizing hybrid materials based on various chemical compounds allow to obtain systems of desired physicochemical properties and utilization. Additionally, some advantages of the above materials are associated with a wide applicative spectrum beginning with everyday utility means up to advanced industrial technologies including waste purification [3]. Lately the hybrid systems have been more and more often used as adsorbents characterized by great effectiveness and selectivity towards dyes of various types. González et al. [4] evaluated the adsorption capability of the chitin/graphene oxide (Chi:nGO 3:1) hydrogel towards Remazol Black (RB) and Neutral Red (NR). The optimum uptake of NR and RB was observed at pH of 5.0 and 4.0, respectively. The maximum adsorption capacities of the chitin/graphene oxide hybrid were equal to 70 mg/g for RB and 165 mg/g for NR. Relatively high values of the adsorption capacities were determined by Janaki et al. [5] for the adsorption of sulfonated anionic dyes such as Congo Red (322.58 mg/g), Coomassie Brilliant Blue (357.14 mg/g) and Remazol Brilliant Blue R (303.03 mg/g) on the polyaniline/chitosan composite. The chitosan–polyaniline/ZnO hybrid prepared through polymerization of chitosan and aniline hydrochloride in the pres-

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ence of $ZnCl_2$ exhibited good adsorption capacity towards C.I. Reactive Orange 16 amounting 476.2 mg/g [6]. The ionic liquid-coated Fe_3O_4-chitosan-graphene oxide prepared by Li et al. [7] was applied for methylene blue adsorption and the maximum adsorption capacity was 262 mg/g. Extremely high adsorption capacity (1825 mg/g) of the carboxylmethyl cellulose (CMC) based adsorbent was determined for methyl orange [8]. Eosin Y, C.I. Reactive Black 5 and Congo Red were removed by the polyaniline coated lignin-cellulose composite with high efficiency compared with the unmodified lignin-cellulose material [9–11]. According to Nair et al. [12] the chitosan–alkali lignin composite (ChAL) was an effective sorbent for removal of the anthraquinonic dye – Remazol Brilliant Blue R (RBBR), and Cr(VI) from aqueous solutions. The maximum adsorption capacity of ChAL composite for RBBR was 111.11 mg/g while for chitosan it was only 76.92 mg/g [12]. Interesting synthesis of a new kind of the biopolymer EC/Cs composite network based on cellulosic fibres extracted from an aquatic weed, water hyacinth *Eichhorniacrassipes* (EC), TiO_2 nanoparticles and chitosan was proposed by El-Zawahry et al. [13]. The experimental results indicated that the composite can be applied for removal of C.I. Reactive Black 5 from its dye-bath effluent. The maximum sorption capacity was found to be 0.606 mg/g [13]. The biocomposite prepared from magnetized chitosan-coated lignocellulose exhibited ultra-high adsorption capacity (up to 1184 mg/g), rapid adsorption rate, and excellent reusability (with removal efficiency up to 99.48% in the tenth cycle) towards C.I. Acid Red 18 [14].

C.I. Direct Blue 71 belongs to the *tri*-azo dyes and is extensively applied in the textile industry for cellulose, cotton, viscose, and silk dyeing as well as for leather and paper coloration. It is well known that not only azo dyes such as C.I. Direct Blue 71 but also their intermediate products of degradation are toxic for aquatic fauna and flora as well as for human body [15–17]. Therefore they and should be carefully removed from industrial streams and wastewaters. For this purpose such materials as $CoFe_2O_4$ and $CoFe_2O_4$ loaded ZnO nanoparticles [15], chemical modified cucumber peel [17], raw and chemically modified sunflower stalks [18,19], different types of activated carbons [20], anion exchange resins of various basicity [21], nanocomposite of chitosan and multi-wall carbon nanotubes [22] or biosilica/alginate nanobiocomposite [23] were used. However, there are still few literature reports about application of hybrid sorbents, especially those based on chitin, for C.I. Direct Blue 71 removal. In the light of the above, the authors synthesized a new material from chitin powder and kraft lignin for removal of hazardous dye C.I. Direct Blue 71. Kinetic and equilibrium studies were performed in order to evaluate its sorption efficiency towards dye.

2. Experimental

2.1. Materials

α-Chitin powder from crab shells (technical grade, Sigma-Aldrich, Germany) was combined with kraft lignin (reagent grade, Sigma-Aldrich, Germany) in the presence of 15% hydrogen peroxide (Chempur, Poland).

C.I. Direct Blue 71 dye (Sigma-Aldrich, Germany) is tetrasodium 3-[(*E*)-{4-[(*E*)-{4-[2-(6-amino-1-oxo-3-sulfonatonaphthalen-2(1*H*)-ylidene)hydrazino]-6-sulfonatonaphthalen-1-yl}diazenyl]naphthalen-1-yl}diazenyl]naphthalene-1,5-disulfonate of 55% commercially available purity level. The stock solution of the dye was prepared in distilled water, and working solutions were obtained by appropriate dilution.

Sodium chloride and sulphate, anionic surfactant–sodium dodecyl sulphate, hydrochloric acid and sodium hydroxide were purchased as research-grade chemicals (Avantor Performance Materials, Poland).

2.2. Preparation and evaluation of multifunctional chitin/lignin biosorbent

Multifunctional chitin/lignin sorbent was prepared according to the procedure described previously by Klapiszewski et al. [24] and Wysokowski et al. [25]. Chitin and lignin were combined using mechanical milling of these materials with simultaneous homogenization in a centrifugal ball mill (Fritsch, Germany). The weight ratio of precursors (chitin:lignin) was 1:1 in the presence of 100 mL of 15% hydrogen peroxide. The final product was dried at 105 °C for 12 h and passed through 100 μm size sieve, thus increasing its uniformity.

The multifunctional chitin/lignin biosorbent used as a dye adsorbent was subjected to thorough physicochemical analysis. Based on the obtained data, the brief physicochemical characteristics of the biosorbent are listed in Table 1.

The elemental composition was determined using the Vario El Cube system (Elementar Analysen systeme GmbH, Germany). The formed material consists mainly of carbon (43.8%). The presence of nitrogen is connected with the precursor used for preparation of the final material which was chitin (poly(β-(1-4)-*N*-acetyl-D-glucosamine). A small amount of sulfur comes from lignin.

In order to characterize the parameters of the porous structure, nitrogen adsorption/desorption isotherms, surface area, pore volume, average pore size and particle size distribution an ASAP 2020 (Accelerated Surface Area and Porosimetry) instrument (Micromeritics Instrument Co., USA) was used.

Images of the biosorbent were taken using the scanning electron microscope (SEM, Zeiss EVO40, Germany). Analyzing the SEM images (Table 1) of the prepared material, there can be observed a fibrous form of chitin of multishaped structure. However, lignin occurs in the form of single irregular molecules.

The FT-IR analysis of chitin/lignin biosorbent before and after sorption of C.I. Direct Blue 71 was made using the Vertex 70 spectrophotometer (Bruker, Germany). The biosorbent was analyzed as a tablet (ca. 250 mg of anhydrous KBr mixed with 1.5 mg of the sample). Spectra were recorded over 4000–400 cm^{-1} range with a resolution of 0.5 cm^{-1}.

In order to calculate the zeta potential of the chitin/lignin biosorbent, the electrophoretic mobility was measured using the Zetasizer Nano ZS instrument (Malvern Instruments Ltd., UK) equipped with an autotitrator. Measurements were performed at 25 °C. Simultaneously changes in the conductivity and pH values of the suspension were observed. Prior to the measurement, the apparatus was calibrated by determining the zeta potential of a latex suspension and measuring the pH of buffer solutions with the pH values of 4 and 9.

The potentiometric titration method was applied to measure the surface charge density of the chitin/lignin biosorbent using the Mettler Toledo T5 titrator (Metler Toledo Ltd., Switzerland). Titration was made in the pH range 3–10. In the first stage 0.1 g of the sample was dispersed in 50 mL of 0.001 M sodium chloride. Then the system was automatically titrated with both an acid (0.2 M hydrochloric acid) and a base (0.2 M sodium hydroxide). An analogous procedure was applied for the system not containing the biosorbent but only the basic electrolyte.

2.3. Batch adsorption experiments

Briefly, 0.25 g of the chitin/lignin composite was agitated with 25 mL of dye solution using a laboratory shaker Elpin Plus (type 357, Poland) with the agitation speed 180 rpm. After different time intervals (1–240 min or 24 h) the aqueous and chitin/lignin phases