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Comparative study of Cd(II) biosorption on cultivated *Agaricus bisporus* and wild *Lactarius piperatus* based biocomposites. Linear and nonlinear equilibrium modelling and kinetics

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ABSTRACT

Biosorption of Cd(II) ions from aqueous solutions onto immobilized fruit bodies of cultivated *Agaricus bisporus* and wild *Lactarius piperatus* was investigated in batch system. The biosorbent was characterized using FTIR analysis. Cd(II) removal process was studied using as biosorbent *A. bisporus* and *L. piperatus* immobilized in calcium alginate (biocomposite). The influences of stirring rate, biomass quantity, initial metal ion concentration, contact time and pH were studied. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models (linear regression) and the model parameters were evaluated. A nonlinear optimization algorithm (CMA-ES) applied on ten isotherm models was also used to describe the biosorption process. The optimization algorithm tested showed that nonlinear regression analysis has better performances, with Sips model describing biosorption process the best. Experimental data were also used to study biosorption kinetics using pseudo-first-, pseudo-second-order, intra-particle and film diffusion models. The results showed that the biosorption process of both macrofungus studied, followed well pseudo second-order kinetics. From the experimental data we can concluded that wild *L. piperatus* showed higher removal efficiency on Cd(II) ions compared to the cultivated *A. bisporus*.

1. Introduction

Industrial activities produce every year large amounts of wastewaters containing different types of organic (*e.g.* dyes) and inorganic (*e.g.* heavy metals) toxic pollutants, which are discharged directly or indirectly in the environment. Due to their non-degradable form, heavy metals represent a threat for human health as well for aquatic organisms.

Cadmium is widely present in wastewater from industrial sources such as: electroplating, mining, batteries, paint pigments, iron and steel manufacturing, *etc.* [1]. Chronic exposure to elevated level of cadmium cause renal dysfunction, hypertension, hepatic injury, blood damage and can disrupt protein metabolism [2]. Several conventional methods were developed and tested over the years to remove toxic heavy metals (*e.g.* cadmium) from wastewaters including chemical precipitation, membrane separation, ion-exchange or electrochemical treatment [3]. These conventional methods have some disadvantages such as: high operational cost and high specific consumption of reagents and energy. Therefore, sciences focused on easily available agricultural and biological origin materials or by-products as biosorbents. The main advantages of these biomaterials are their reusability, high efficiency and low operational cost. In recent years, numerous studies have showed that both cultivated and wild fruit bodies of mushrooms can accumulate high amounts of heavy metals. Heavy metals biosorption by different materials was previously reported, on biomasses such as: red algae [4], moss [5], lichen [6], yeast biomass [7], tea waste [8] and various type of sawdust [9,10]. These materials proved to be both green and eco-friendly materials. Several mushroom biomasses, *Lentinus edodes* [11], *Amanita rubescens* [12], *Pleurotus platypus*, *Agaricus bisporus* [13], *Pycnoporus sanguineus* [14], *Lactarius scrobiculatus* [15] were studied for the removal of cadmium ions from wastewaters. All of these fungal biomasses showed high biosorption capacities and could be considered as alternative biosorbents for wastewater treatment containing cadmium ions. Natural polymers such as alginate, chitosan, polyvinyl alcohol (PVA) have been mostly used as matrix for the immobilization of the biomass. The immobilization matrix is suitable for practical use in biosorption due to mechanical and chemical stability. Furthermore these polymer supports could also enhance cells surface and adsorptive capacity of the biosorbents for the removal of heavy metals [16].

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The aim of this work was to make a comparison between the potential use of cultivated *A. bisporus* and wild *L. piperatus* based biocomposites for removal of Cd(II) ions from aqueous solutions. The influences of process parameters such as stirring rate, biomass quantity, initial metal ion concentration, contact time and pH were studied. Linear and nonlinear regression (CMA-ES algorithm) was used to describe the biosorption process. Ten isotherm models were tested to determine the best fit with experimental data. The biosorption kinetic data were analyzed in terms of pseudo-first-, pseudo-second-order, intra-particle and film diffusion models.

2. Material and methods

2.1. Preparation of biomass

Fruit bodies of cultivated *A. bisporus* were purchased from a local mushroom farm in Nuşfalău, Sălaj County, Romania. A special substrate for cultivation is produced from nitrogen-amended cereal straw which is taken through an aerobic solid-state fermentation, or composting, that replaces easily available carbon and nitrogen compounds with humic-rich complexes. This highly selective medium is then pasteurized and inoculated with *A. bisporus* mycelium. Fruit bodies of *L. piperatus* biomass were collected from a local woodland area near Cluj-Napoca, Cluj County, Romania. Before use, samples were washed several times with distilled water to remove dirt and surface impurities, and dried at 70 °C for 24 h. Dried samples were grinded and sieved; <0.2 mm fraction was further used in all experiments. The sieved biomass was then stored in an airtight box before its utilization.

2.2. Chemicals

Na-alginate was purchased from Fluka, United Kingdom. The stock solution, 1 g/L of Cd(II) was prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ (Merck, Germany) in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in 45–265 mg/L range. HCl (0.1 M) and NaOH (0.1 M) volumetric solutions (Sigma–Aldrich, USA) were used to adjust the solution pH. All chemicals used were of analytical grade.

2.3. Biomass immobilization

The cross-linking procedure with Na-alginate described in literature [17] was used for biomass immobilization in order to obtain the biocomposite. 0.5–2 g of biomass was suspended in 40 ml distilled water. This suspension was next blended with 1 g Na-alginate. The mixture was then dropped into a 0.2 M $CaCl_2$ solution, using a peristaltic pump and a 1.2 mm needle. The immobilized beads with a diameter of 4 mm were cured and stored in this solution at 4 °C to enhance their mechanical stability. Then, the obtained beads were rinsed several times with distilled water in order to remove excess of calcium ions and stored at 4 °C prior to use.

2.4. Biomass characterization

Fresh and loaded (separated from cadmium after adsorption) beads were dried at 50 °C and prepared for FTIR analysis (1.2 mg of finely grounded biomass particles in 300 mg KBr, Merck, Germany). Infrared spectra were obtained using a JASCO 615 FTIR spectrometer (Jasco, Japan), 500–3500 cm^{-1}, resolution 2 cm^{-1} and data were processed with ORIGIN PRO 8.5 software.

2.5. Biosorption studies

The biosorption of Cd(II) ions onto biocomposite beads was investigated in batch system. Biocomposite beads were contacted with 100 mL aqueous solution of Cd(II) ions for 240 min (until equilibrium was reached). In order to establish the evolution of the removal process, samples of 100 μL were collected at different time intervals. The effect of stirring rate (700–300–100 rpm), biomass quantity (0.5–2.5 g), initial Cd(II) concentration (45–265 mg/L) and initial pH (2.75–8.5) were studied. Concentration of metal in the aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia) on samples previously filtered using a 45 μm cellulose filter.

In order to evaluate the amount of cadmium retained per unit mass of biosorbent (biocomposite), the adsorption capacity and removal efficiency (percentage removal) were calculated. Experimental data were used to determine the equilibrium time, equilibrium concentrations, amounts adsorbed at equilibrium, optimum initial pH and the quantity of biomass for maximum efficiency. Also the experimental data were used to establish isotherm (linear and nonlinear regression) and kinetics models. All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectral analysis is an important tool to obtain valuable information about functional groups in biosorbents, which are responsible for biosorption of heavy metals. In the present study the FTIR spectra of *A. bisporus* and *L. piperatus* based biocomposites as fresh and loaded (before and after biosorption) samples were studied, in order to determine the main changes in functional groups. The complex nature of these two materials is evidenced by spectra from Figs. 1 and 2. A significant change can be mentioned, for the broad and strong band in the case of *A. bisporus* spectrum (Fig. 1), at 3410 cm^{-1}, which indicates the presence of bond hydroxyl groups (–OH) or amine (–NH) groups, which was shifted to 3439 cm^{-1} ($\Delta\upsilon = 29\ cm^{-1}$) after biosorption of Cd(II) ions. In Fig. 2 the *L. piperatus* spectrum is presented. The peak at 3421 cm^{-1}, corresponding to hydroxyl groups from unloaded biocomposite, was shifted to 3426 cm^{-1} after metal loading. The bands observed at 2926 and 2853 cm^{-1} (Fig. 1, *A. bisporus*) and at 2918 and 2849 cm^{-1}

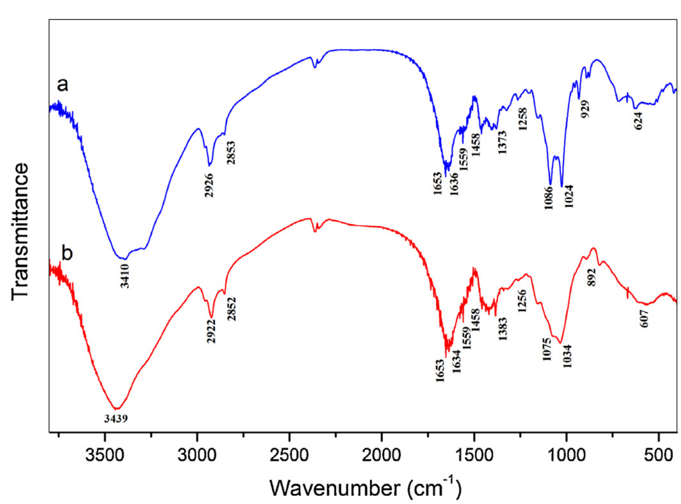

Fig. 1. FTIR spectra of the *A. bisporus* based biocomposite before (a) and after Cd(II) (b) biosorption.