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Application of a by-product of *Lentinus edodes* to the bioremediation of chromate contaminated water

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Abstract

The agricultural by-product of *Lentinus edodes* was used as a novel biosorbent for bioremediation of chromate contaminated waste water in the simulated experimental conditions. The contact time, particle size, biosorbent dosage and optimum pH range were investigated to optimize the sorption condition. The biosorption by the biomass was strongly affected by pH. At pH 1.0–2.5, all hexavalent chromium was diminished, either removed by the biosorbent or reduced to less toxic trivalent chromium even in very high concentration of 1000 mg/L. The adsorbed hexavalent chromium and reduced trivalent chromium were both linearly dependent on the initial chromium concentration. Most uptake of Cr occurred at pH around 4. The maximum uptake of chromium was 21.5 mg/g when simulated with Langmuir model, which showed the potential biosorption capacity of this biomaterial. The change of oxidation–reduction potential (ORP) during biosorption process revealed strong reduction ability of this biosorbent. Comparing analysis from Fourier transform infrared spectrums indicated that nitrogen oxide and carboxyl groups were increased after biosorption. The energy-dispersive X-ray microanalyzer revealed the mechanism of cation exchange during biosorption.

Keywords: Bioremediation; Waste water; Chromium; Agricultural by-product

1. Introduction

Soluble hexavalent chromium among heavy metals are extremely toxic and exhibit carcinogenic effects on biological systems due to their strong oxidizing nature among heavy metals [1]. The industrial waste water from electroplating, pigment, metal cleaning, leather processing and mining is the main source causing water pollution. Many strategies are investigated to remove chromium from solutions such as chemical reduction, electrochemical treatment, ion exchange, etc. [2–4]. But obvious disadvantages, such as high energy requirements, incomplete metal removal, high quantity of toxic waste sludge and inhibit the application of the conventional strategies [4].

Bioremediation is an alternative method that has emerged in recent years to treat the waste water instead of the traditional processes. Plants, hydrophytes or microorganisms attract more attention of researchers to exploit the new field to protect the finite resources. The applications of microorganisms, such as bacteria [1,5–7], fungi [2,8], algae [9,10], dead microbial biomass [11] and other biomaterials [4,12,13], are the hot topics in this research realm. The prominent advantages are the selectivity of heavy metal from solutions and the high removing efficiency in low metal concentration [14]. But time consuming process and growing cost of appropriate biomass are the main drawbacks of the biosorption with living biomass. So research interest has turned to the dead biomass which is abundant at low cost.

The removal of heavy metals by plant tissues or by biomass by-products from agricultural, industrial or pharmaceutical industry has been proved with high efficiency and very low cost [3,15]. Cone biomass of *Thuja orientalis* can efficiently adsorb copper(II) from aqueous solutions [16]. Cone biomass of *Pinus sylvestris* has biosorption ability for chromium(VI) [4]. The rice milling by-product—rice husks, can be also used to treat the heavy metal containing solutions including Cd(II), Pb(II), Al(III), Cu(II) and Zn(II) [17]. These biomaterials are

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of little commercial value and tested good as substitutes for the expensive chemical drugs and live biomass.

These dead biomaterials usually are of low content of heavy metals and large quantity of adsorption sites [17,18,11]. Functional groups for ion exchange such as hydroxyl, carboxyl and phosphate groups are often found from Fourier transform infrared spectrum [17–19]. N-ligand of glucose or chitin in cell wall is of strong complex ability to form coordinated metal complex.

A kind of agricultural biomass by-product—*Lentinus edodes*, is proved to be very efficient to remove Pb(II), Cd(II) and Cr(III) from simulated waste water under experimental condition [19]. This kind of biomaterial is obtained in large quantities from the biggest solid-state-fermentation industry in the world [20]. About five times of the solid residue is brought about compared with the production of fungi. Not only much space is occupied but also some useful materials are wasted. Plentiful of functional groups in chitin, cellulose and mycelium are efficient to complex heavy metal ions [21].

The aim of this study was to investigate the biosorption potential of chromium(VI) and to characterize the biosorbent of the by-product biomass of *L. edodes*. The adsorption capacity of the biosorbent was evaluated by studying the equilibrium adsorption isotherms of Cr(VI) in batch experiment mode. The effect of factors, such as particle size, dose of biosorbent, pH, oxidation–reduction potential and initial concentration, was examined. Fourier transform infrared spectrum and the energy-dispersive X-ray microanalyzer were employed to understand the biosorption mechanism.

2. Materials and methods

2.1. Biosorbent preparation

The by-product biomass of *L. edodes* was kindly presented by the Hunan Academy of Agricultural Sciences, Hunan Province in China. The biomass was oven-dried at 80 °C for 24 h after preliminary crumbing by hand. Then powder biomass, with different particle sizes, was obtained by using a sample mill (Foss Tecator, Sweden) through copper sieves. The ground biomaterial was water washed, redried and stored in polyethylene bottles in vacuum dryer and used as biosorbent in the following experiments.

2.2. Preparation of the dichromate containing solution

A stock solution containing 1000 mg/L chromium was prepared by dissolving potassium dichromate with deionised distilled water. Other different concentrations of chromium solutions were obtained by suitable dilution from the stock solution. The deionised distilled water was used throughout the experiment from a hyperfiltration pure water system (Labconco, Water Pro Plus, USA).

Final concentration of Cr(VI) was determined by a spectrophotometer at a wavelength of 540 nm using the complexing agent of 1,5-diphenylcarbazide in acid medium. The total Cr was determined with the flame atomic absorption spectrometry (FAAS) (AA700, Perkin-Elmer, USA). The reduced Cr(III) was calculated by the difference between the total Cr and Cr(VI) in the solution after filtration.

2.3. Contact time

To determine the contact time required for the adsorption equilibrium experiments, the adsorption dynamics was examined first. The initial concentration of chromium was 100 mg/L, and 20 g/L dose of biosorbent was added to the flask containing 200 mL of chromium solution. Then the flask was agitated on the incubator at 25 °C. Samples were intermittently removed from the flask in order to analyze the chromium remaining in solution. The total volume of samples withdrawn did not exceed 2% of the initial volume (200 mL) for each sampling. All experiments were done in triplicate throughout the study.

2.4. Particle size

Different particle sizes of biosorbent, 2 mm, 1 mm and 450 μm, were used to examine the effect of the granularity to the biosorption. One hundred milligrams per liter chromium solution was added to the biomaterial at the dosage of 20 g/L in an incubator at 25 °C for 24 h. Then the concentration of chromium in the filtered solution was determined.

2.5. Dosage of the biomaterial

To evaluate the optimum dosage of the biomaterial, different mass of the biomaterial were used to adsorb chromium in solution. Biomaterials with weight of 0.125 g, 0.250 g, 0.500 g and 0.75 g were added to 25 mL 100 mg/L chromium, respectively, after enough contacting for 24 h (determined by previous experiment). The filtrate was used to measure the content of Cr(VI) and total Cr with the method mentioned above. pH had not been adjusted.

2.6. Effect of pH and oxidation–reduction potential

One hundred milligrams per liter chromium solution and 20 g/L biomass dosage were utilized in the experiments. Different volumes of acid (0.5 mol/L H_2SO_4) or alkali (1 mol/L NaOH) were added to adjust the pH of the mixture and agitated in the same method as before. In the scheduled interval, the pH and the oxidation–reduction potential (ORP) of the solutions were examined with a pH electrode (E-201-C) and an ORP electrode (ORP-412, mV). The final concentration of Cr(VI) and total Cr were examined with the same methods.

2.7. Initial concentration of chromium

A series of Cr(VI) solution ranging from 20 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L and 1000 mg/L were prepared to determine the equilibrium isotherms following the addition of the biosorbent. The acid or alkali was added to maintain the best adsorption pH condition as determined above. The mixtures were agitated in the same incubator at 25 °C for 24 h.