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Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: Batch and column studies

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Abstract

This study involved the investigation of enhancement of chromium biosorption capacity of dead *Aspergillus niger* fungal biomass by pretreatment and its use in a column mode. Cetyl trimethyl ammonium bromide (CTAB) pretreatment exhibited maximum chromium removal. An initial factorial design of experiments showed that factors such as pH of the solution, temperature and biomass mass were important. The kinetics of biosorption of chromium was found to follow Ho pseudo-second order reaction. Isotherm studies conducted at 5 ± 2, 15 ± 2, 22 ± 2, and $30 \pm 2\,^{\circ}C$ provided maximum biosorption capacities of 14.5, 15.2, 10.6, and 11.6 mg/g, respectively. The Freundlich isotherm model was found to describe biosorption. Thermodynamic studies indicated that the biosorption reaction was spontaneous and exothermic in nature. Reusability of biomass was examined by the desorption studies, in which NaOH eluted 90% chromium. Data from a column study using CTAB pretreated biomass immobilized in polysulfone matrix followed Yan's model and the adsorption capacity of the biomass was found to be less than the adsorption capacity obtained in the batch study. Fourier transform infrared spectroscopy analysis indicated that in addition to various functional groups present on the cell wall, the contribution of amino groups towards the biosorption process was evident.

Keywords: Sorption; Chromium; Fungal biomass; Isotherms; Kinetics

1. Introduction

Biosorption is an emerging and attractive technology which involves sorption of dissolved substances by a biomaterial. It is a potential technique for the removal of heavy metals from solutions and recovery of precious metals [1]. It is a metabolism-independent process and thus can be performed by both living and dead cells [2]. The process has gained importance due to its advantages over conventional separation techniques such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and activated carbon adsorption, which are used to remove toxic metals from waste streams. These advantages are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [3,4]. Pioneering research in this field has led to the identification of a number of effective biosorbents. Microorganisms including bacteria, fungi, and yeasts are found to be capable of efficiently accumulating heavy metals [5]. Fungi (*Aspergillus*, *Mucor*, *Rhizopus*, and *Pencillium* species) and yeast (*Saccharomyces* species) have shown excellent metal sequestering abilities for heavy metals such as Cu, Zn, Cd, Pb, Fe, Ni, Ag, Th, Ra, and U [6].

A number of chromium compounds have great economic importance and are used extensively in chemical, metallurgical and refractory industries. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to both humans and animals [7]. This has led to the concern over the environmental effects of chromium present in surface water and groundwater. Studies on biosorption of chromium by live and dead microorganisms have recently gained momentum. Several algal species such as *Ecklonia*, *Spriogyra*, *Synechocystis*, *Scenedesmus obliquus*, and *Chlorella vulgaris* [8–10], bacterial species such as *Bacillus* [4], and yeast *Saccharomyces cerevisiae* [11] have been studied for their Cr(VI) biosorption capacity. Dead biomass of fungus *Mucor hiemalis* [12], *Neurospara crassa* [13], *Rhizopus arrhizus* [14,15], and

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Rhizopus nigricans [16] have also shown promise in accumulating chromium.

Chromium removal using *Aspergillus niger* fungal biomass has been investigated by some researchers [17–19]. Park et al. [20] reported that the removal efficiency of total chromium decreased in the following order for biosorbent used in the study: *S. cerevisiae* ($44.2 \pm 1.8\%$) > *P. chrysogenum* ($40.3 \pm 0.3\%$) > *A. niger* ($29.3 \pm 3.0\%$) > *R. oryzae* ($23.5 \pm 0.3\%$). Fungus *A. niger* is reported to have less affinity to Cr(VI) compared to other fungal biomass, *R. nigricans*, *R. arrhizus*, and *A. oryzae* [17]. Fungi of *Mucorales* family (*Mucor rouxii* or *R. arrhizus*) were found to possess more chitosan than *A. niger* [2]. However, pretreating the *A. niger* biomass to improve the biosorption capacity, and the use of immobilized pretreated *A. niger* biomass in a column for chromium removal have not yet been investigated. Pretreatment of fungal biomass has been found to improve the biosorption capacity of fungal biomass for other metals [6]. There is a potential for the use of the pretreated fungal biomass for sorption of chromium from industrial wastewaters. The development of pretreated fungal biomass is technically feasible because the techniques required for development are relatively simple and technologically viable. Therefore, this present work focuses on these aspects of chromium biosorption by *A. niger* biomass.

2. Materials and methods

2.1. Biomass preparation and pretreatment

A laboratory strain of *A. niger* (ATCC #11414) was routinely maintained on Bacto® potato dextrose agar. For experimental purposes, *A. niger* was inoculated into a liquid medium comprising (in g/L) the following: Difco® dextrose, 20; Bacto® peptone, 10; Bacto® yeast extract, 3, in deionized water with pH adjusted to 5.0 by 1.0N HCl. The cultures were grown in an aerobic condition at room temperature ($22 \pm 2\,^{\circ}C$) with 100 mL of the liquid medium in 250 mL conical flasks on a rotary shaker agitated at 125 rpm. All culture work was conducted aseptically. The fungi grew as pellicles and were harvested after 4 days of growth by filtering the growth media through a 150 μm sieve. The harvested fungal pellicles were washed with generous amounts of deionized water and autoclaved for 30 min at 121 °C and 103 kPa. The autoclaved biomass was allowed to cool down, hand-pressed, and dried in an oven at 60 °C for 24 h. This dried autoclaved biomass was ground to a powder and used directly in metal biosorption experiments or pretreated with various chemicals. Five grams of powdered autoclaved biomass was agitated for 24 h in 500 mL of each of the following chemicals: acid (0.1N H_2SO_4); alkali (0.01N NaOH); acetone (50%, v/v); formaldehyde (10%, v/v); cetyl trimethyl ammonium bromide (CTAB) (5%, w/v); polyethylemine (PEI) (1%, w/v); and 3-(2-amino ethyl amino) propyl trimethoxy silane (APTS) (3%, v/v). The resulting biomass was filtered, washed thoroughly with at least a few litres of deionized water and then dried at 40 °C for 24 h. After drying, the pretreated biomasses were ground into a powder and biomass particles passing through 425 μm sieve were used in biosorption experiments.

2.2. Chromium solution and analysis

Stock chromium solution of 1000 mg/L was prepared by dissolving 2.828 g of potassium dichromate in 1 L of deionized water. The working chromium solution of 10 mg/L was prepared by diluting the stock chromium solution. The total chromium concentration in the solution was determined by atomic absorption spectroscopy using a Varian AA10 atomic absorption spectrometer [21].

2.3. Batch biosorption studies

All batch biosorption experiments were conducted in 250 mL Erlenmeyer flasks with 100 mL metal solution. Sodium acetate buffer (pH 4.0 and 5.0), potassium phosphate buffer (pH 6.0–8.0), 0.1N NaOH, and 0.1N HCl solutions were used to adjust and maintain the pH of the metal solutions. Buffer solutions were not used at lower pH values (2.0 and 3.0), as negligible pH drift occurred below 2.5 [22]. Metal solutions were vacuum-filtered through 0.45 μm polycarbonate filters after biosorption experiments. A control with no biomass was also set up for each run. All experiments were conducted in duplicate and the mean values were used in the analysis of data.

2.3.1. Effect of pretreatment

To study the effect of pretreatment on *A. niger* biomass, each pretreated and autoclaved biomass of 0.2 g was shaken in a metal solution of pH 2.0 for 12 h at 175 rpm on a mechanical platform shaker at room temperature ($22 \pm 2\,^{\circ}C$).

2.3.2. Factorial design of experiments

A two level full factorial design ($2^4 = 16$ runs) was chosen, with the total number of runs with replicates being 32. High and low level values of factors such as pH (2.0 and 8.0), temperature (5 ± 2 and $30 \pm 2\,^{\circ}C$), agitation speed (100 and 200 rpm), and mass of the adsorbent (0.1 and 1 g) were varied for each experimental setup. The samples were shaken for a fixed time period of 12 h on a mechanical platform shaker. Temperature was maintained at desired values using a temperature-controlled storage unit, where the experiments were conducted. The analysis of results was performed by the statistical and graphical analysis software MINITAB® Release 14 [23], developed by Minitab Inc., USA.

2.3.3. Effect of pH

The effect of pH on the biosorption of chromium was investigated by contacting the best pretreated biomass (0.2 g) in the pH range of 2.0–8.0, with increments of 1. The pH was kept constant during the study. The samples were shaken 12 h at 175 rpm at room temperature ($22 \pm 2\,^{\circ}C$).

2.3.4. Kinetics of sorption

In order to determine the equilibrium time, the sorption mixture was agitated at 175 rpm at the optimum pH. Samples were collected at very short intervals for the first 1 h and every hour for 12 h after that. Data from the kinetic studies were fitted to the Lagergren and Ho models to examine the biosorption kinet-