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Novel biomaterials from citric acid fermentation as biosorbents for removal of metals from waste chromated copper arsenate wood leachates

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ABSTRACT

The paper discusses the potential of different waste biomaterials for biosorption. Waste biomaterials after citric acid fermentation and chitosan extraction using *Aspergillus niger* were evaluated for biosorption of toxic metals (Cu, Cr and As) from leachates of chromated copper arsenate woods. The different waste BMs, such as fungal biomass (living and dead), alkali insoluble material and acid and alkali insoluble material were used in this study. The effect of different parameters, such as biosorbent concentration, metal concentration and contact time were investigated. The fitness of biosorption data for Freundlich and Langmuir adsorption models was investigated through batch adsorption technique. Among the adsorption isotherm tested, Langmuir isotherm gave the best fit with correlation coefficients (R^2) value ranging from 0.89 to 0.97; 0.96–0.99 and 0.76–0.95 for As, Cr and Cu, respectively using solid state fermented biomass. Similarly, the significant removal of metals (>60% in leachate 2) from waste CCA wood leachate was achieved with the different BMs. Therefore, this study demonstrates the potential of CA fermentation derived waste BMs for biosorption of toxic metals from waste waters.

1. Introduction

The most widely used formulation for wood preservation since 1970's is chromated copper arsenate (CCA). According to American Wood Preservation Agency, CCA type C is the most commonly used CCA formulation, and is comprised of 19% copper (II) oxide (CuO_2), 50% chromium (VI) oxide (CrO_3) and 31% arsenic (V) oxide (As_2O_5). The complexion mechanism of CCA into the wood is carried out by the reduction of chromate (Bull, 2001) that leads to the formation of Cr (III)/As (V) cluster, Cr (III) and Cu (II) complex with the wood components as well as hydroxide compounds (Bull, 2001; Nico et al., 2004). Arsenic and hexavalent chromium are highly toxic to the living organisms including humans. Various studies have revealed that leaching of metals results from in-service CCA treated woods (Stilwell and Graetz, 2001; Solo-Gabriele et al., 2003; Townsend et al., 2003; Khan et al., 2006a, 2006b). The discarded CCA-treated wood contains high metal concentrations (Cooper et al., 2001). Therefore, discarded CCA-treated woods pose serious environmental and health challenges to flora and fauna. The chemicals used for wood preservation are highly toxic to the organisms and they may be harmful, if discharged in to the environment. However, as governmental organizations have described treated wood material as non-hazardous waste, it is frequently dumped into landfills where it is susceptible to metal-leaching and dispersion (Jambeck et al., 2007). The quantity of metals leached from CCA-treated wood can generally exceed the toxicity guidelines meant for hazardous waste identification (Townsend et al., 2004). Various other studies also demonstrated the potential of arsenic release from CCA-treated wood wastes in construction and demolition landfills or municipal landfills (Khan et al., 2006a, 2006b; Cooper et al., 2001; Townsend et al., 2004; Jambeck et al., 2007). Considering currently in-service CCA-treated wood and expected service life-time, about 2.5 million m^3 of CCA-treated

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wood waste would be generated in Canada by 2020 and over 9 million m^3 in USA by 2015 (Cooper, 2003). In view of the huge quantity of generated waste wood, it is imperative to develop new ecologically safe management and recycling strategies to avoid the accumulation of discarded CCA wood wastes in landfill sites. Various conventional physical and chemical techniques for removal of chromium ions from effluents, such as reverse osmosis, ion exchange, reduction, precipitation, adsorption, solvent extraction, and lime coagulation are preferred choice (Bai and Abraham, 2001; Selvi et al., 2001). However, these techniques are highly expensive, ineffective at lower metal concentrations, and environmentally hostile as they generate a large amount of toxic sludge, which has to be disposed in further steps.

Over the decades, biosorption has emerged as an alternative green technology to the existing conventional physico-chemical methods for removal of heavy metals. It eliminates the need for huge sludge handling and utilizes biomaterials (BMs) that are cheaper and readily available. Different type of BMs, such as fungal, bacterial, yeast, moss, aquatic plants and algal biomass have been investigated with the aim of developing efficient and cheap metal-removing biosorbents (Niu et al., 1993; Chang et al., 1997; Fang et al., 2006). Biosorption of Cr (III) and Cr (VI) from aqueous solutions have been carried out using *R. nigricans* (Bai and Abraham, 2001). However, no information is available on the use of waste biomass resulting from citric acid (CA) fermentation and chitosan (CTS) extraction from waste fungal mycelium as a biosorbent for the removal of toxic metals from waste CCA woods. Fungal biomass is produced in huge quantities by various biotechnological and pharmaceutical industries. Fungal cell walls contain chitin along with other components. The utilization of chitin rich fungal biomass for its transformation to important biopolymer, CTS offers numerous economic and environmental benefits. The remaining waste biomass after treatment of fungal mycelium with dilute alkali and acids for CTS extraction is a kind of activated BMs. It provides a cost effective solution for biosorption of toxic metals from waste CCA woods. Moreover, fungal biomass has numerous advantages over traditional sorbents, such as regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed, higher efficiency in dilute effluents and have large surface area to volume ratio. The fungal biomass possesses high metal binding capacities due to the presence of polysaccharides, proteins or lipids present on the surface of their cell walls. The cell walls contain some functional groups, such as amino, hydroxyl, carboxyl and sulfate, which can act as binding sites for metals. The non-viable form has been proposed as potential biosorbents as they are essentially dead materials and require no nutrition to maintain the biomass.

The main aim of the present investigation is to develop a cost-effective and ecologically safe process for biosorbents for treatment of CCA wood leachates. The objectives are: 1) screening of different BMs resulting from CA fermentation and CTS extraction process as potential biosorbents for removal of metals from aqueous solution spiked with As, Cr and Cu under different conditions; 2) kinetics of metals removal using selected biosorbents to establish the mechanism and; 3) real world applications of selected biosorbents along with few commercial biopolymers (chitin, CTS and CA) for removal of metals from discarded CCA wood leachates.

2. Materials and methods

2.1. Chemicals

All the chemicals used for ICP were of trace metal grade. Stock metal solutions, As_2O_3, CrO_3, and Cu_2O (Sigma Aldrich) having concentration of 1000 ppm were prepared in 4% HNO_3. Final metal solutions after biosorption were made to 2% (v/v) HNO_3. Chitin and CTS low molecular weight chitosans (LMWC) [MW 190–310 kDa, degree of deacetylation (DD) 82%, and viscosity 522 cps] and medium molecular weight chitosan (MMWC) [MW 310–375 kDa, DD 77%, and viscosity 1120 cps] were purchased from Sigma Aldrich, CTS high molecular weight chitosan (HMWC) [MW of 600–800 kDa, DD >90%, and viscosity 200–500 cps] and CA were purchased from Fischer Scientific, Quebec, Canada.

2.2. Fungal citric acid fermentation through solid-state fermentation and submerged fermentation and CTS extraction

The solid-state CA fermentation by *A. niger* using apple pomace (AP) as a substrate and solid support was carried out in a 12-L rotating drum type bioreactor, Terrafor (Infors HT, Switzerland) (Dhillon et al., 2013a). Similarly, submerged fermentation (SmF) of AP ultrafiltration sludge (APS) was performed in a 7.5 l capacity fermenter with 4.5 l working volume (Labfors, HT Bottmingen, Switzerland) (Dhillon et al., 2013b). The waste *A. niger* mycelium resulting from CA production from previous studies was used for CTS extraction (Dhillon et al., 2013c). In case of solid-state fermentation (SSF), the whole fermented AP after CA extraction was used for CTS extraction, as it was not possible to separate mycelium from AP. The flowchart for CA fermentation and sequential CTS extraction is described in Supplementary Fig. 1. The waste byproducts resulting during CA fermentation and CTS extraction from waste fungal mycelium were used as biosorbents for removal of metals from CCA wood leachates. BMs having live fungal biomass were used as such without drying. BMs with dead fungal biomass were prepared by autoclaving the biomass and oven drying it (BMs during CTS extraction process, such as AIM and acid and AAIM were prepared according to the protocol described in Supplementary Fig. 1). AIM and AAIM were dried till constant weight at 45 ± 1 °C in hot air oven. All the BMs will be referred as biosorbents in following sections for clarity.

2.3. Characterization of BMs by scanning electron microscopy (SEM)

Different biosorbents, such as waste fungal mycelium resulting from SSF and SMF, AIM and AAIM fractions obtained during CTS extraction were characterized using SEM (Model: Carl Zeiss EVO® 50 smart SEM system) (Arief et al., 2008). Preparation of samples for SEM monographs was performed by mounting the powdered samples on aluminum stubs and coated with gold using a SPI™ sputter coater module to increase conductivity and thus to minimize sample charge up. The biosorbents were examined by a SEM with a working distance (WD) 20 mm, secondary electrode 1 (SE 1) detector and EHT 10 kV.

Different biosorbents used for removal of metals from aqueous solutions spiked with different metals are given in Table 1. The removal performance of metals (As Cr and Cu) by different biosorbents was determined by measuring the residual concentrations of metals over time. Batch experiments were carried out in Erlenmeyer flasks. The metal solutions were prepared by dissolving the exact quantities of analytical quality CrO_3 (Aldrich Chemical Company), As_2O_3 (Sigma-Aldrich) and Cu_2O (MAT) in ultrapure water. Each solution was acidified with concentrated HNO_3 (Martin et al., 1994).

Initially, screening of biosorbents (2.5 g/l) was performed using metal solution (50 mg/l of each metal) in an Erlenmeyer flask and incubated at 25 ± 1 °C and 175 rpm for 24 h. The samples were vacuum filtered through a Whatman (Fischer) filter paper having pore diameter of 0.45 μm. The filtrate was collected in tubes of 50 ml and was made to 2% HNO_3 and ICP analysis was carried out

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