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Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies

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HIGHLIGHTS

- A novel multi-metal binding biosorbent (MMBB) was prepared and characterized.
- Carbonyl and carboxylate groups are involved in metal binding of MMBB.
- Desorption and regeneration have been evaluated.
- The obtained results recommend this MMBB as potentially low-cost biosorbent.

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ABSTRACT

This work attends to preparation and characterization of a novel multi-metal binding biosorbent after chemical modification and desorption studies. Biomass is a combination of tea waste, maple leaves and mandarin peels with a certain proportion to adsorb cadmium, copper, lead and zinc ions from aqueous solutions. The mechanism involved in metal removal was investigated by SEM, SEM/EDS and FTIR. SEM/EDS showed the presence of different chemicals and adsorbed heavy metal ions on the surface of biosorbent. FTIR of both unmodified and modified biosorbents revealed the important role of carboxylate groups in heavy metal biosorption. Desorption using different eluents and 0.1 M HCl showed the best desorption performance. The effectiveness of regeneration step by 1 M $CaCl_2$ on five successive cycles of sorption and desorption displays this multi-metal binding biosorbent (MMBB) can effectively be utilized as an adsorbent to remove heavy metal ions from aqueous solutions in five cycles of sorption/desorption/regeneration.

1. Introduction

Heavy metal ions are one of the most toxic aquatic pollution discharging from various industries. They are very harmful for all plants, animals and human life due to their high environmental mobility in soil and water and also strong tendency for bioaccumulation in the living tissues through food chain (Akar et al., 2012). In order to remediate polluted water and wastewater streams, a wide range of physicochemical/biological treatment technologies are employed in industry (e.g. chemical precipitation, extraction, ion-exchange, filtration, reverse osmosis, membrane bioreactor and electrochemical techniques). Nonetheless, these methods are not effective enough in low concentrations and might be very expensive as a result of high chemical reagent and energy requirements, as well as the disposal problem of toxic secondary sludge (Abdolali et al., 2014a; Montazer-Rahmati et al., 2011; Gupta et al., 2009).

Recently, the attention has been addressed towards cheap agro-industrial wastes and by-products as biosorbents. Therefore, introducing a properly eco-friendly and cost effective technology for wastewater treatment has provoked many researchers into this matter (Abdolali et al., 2014b; Hossain et al., 2014; Tang et al., 2013; Ding et al., 2013; Ronda et al., 2013; Kumar et al., 2012; Hossain et al., 2012; Gadd, 2009; Gurgel and Gil, 2009; Volesky, 2007).

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The metal binding takes place as a passive mechanism based on the chemical properties of surface functional groups. The mechanisms involved in metal bioaccumulation are complicated; therefore the interpretation is very difficult. Usually these mechanisms are related to electrostatic interaction, surface complexation, ion-exchange, and precipitation, which can occur individually or in combination (Oliveira et al., 2014). Moreover, pretreatment of adsorbents improves physical and chemical properties of biosorbent, increases the adsorption capacity and prevents organic leaching, while chemical modification makes some improvements on surface active sites, liberates new adsorption sites and enhances mechanical stability and protonation (Yargıç et al., 2014; Anastopoulos et al., 2013; Velazquez-Jimenez et al., 2013).

However, the major disadvantage of biosorption is producing huge amount of solid biomass or aqueous solutions with high concentration of heavy metals to environment. To tackle the problem attributing to solid biomass, applying proper desorbing and regenerating agent would be effective. Desorption can be carried out by proton exchange using mineral and organic acids such as HCl, HNO_3, H_2SO_4 and acid acetic, by exchange with other ions like applying $CaCl_2$ or by chelating agents (for example EDTA). An efficient eluant is one that desorbs the metal completely without any damaging the biomass structure and functionality to be able to reuse (Mata et al., 2009).

All of the previous attempts have been made to study the agro-industrial wastes and by-products individually. The present work is therefore novel as it uses the combination of selected agro-industrial multi-metal binding biosorbents for removal of cadmium, copper, lead and zinc ions from aqueous solutions. The purpose of blending different lignocellulosic materials is to have all potentials of biosorbents for heavy metal uptake. Also these wastes were selected because of the good results reported in other literatures for heavy metal removal. Additionally, they are properly available in Australia and also all over the world.

This work mainly explored characterization of this new biosorbent to find the principal surface functional groups and possible biosorption mechanisms involved in the biosorption in terms of chemical modification and desorbing agents using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS). Desorption studies were carried out in terms of eluent type, concentration and contact time of desorption process. The effect of regeneration step by $CaCl_2$ was taken into consideration as well.

2. Methods

2.1. Preparation of heavy-metal-containing effluent

The stock solutions containing Cd, Cu, Pb and Zn were prepared by dissolving cadmium, copper, lead and zinc nitrate salt, $Cd(NO_3)_2{\cdot}4H_2O$, $Cu_3(NO)_2{\cdot}3H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ in Milli-Q water. All the reagents used for analysis were of analytical reagent grade from Scharlau (Spain) and Chem-Supply Pty Ltd (Australia). The metal concentration was analyzed by Microwave Plasma-Atomic Emission Spectrometer, MP-AES, (Agilent Technologies, USA).

2.2. Preparation of adsorbents

The biosorbent was a combination of tea waste (TW), maple leaves (ML) and mandarin peel (MP). These biosorbent displayed better biosorptive capacity for cadmium, copper, lead and zinc among a group of low-cost and very available lignocellulosic wastes and by-products. Maple leaves (ML) was collected in Sydney area. Tea (TW) and mandarin (MP) were bought from a local market and after using the useful parts were washed by tap water and then by distilled water to remove any dirt, color or impurity. All biosorbents were dried in oven (Labec Laboratory Equipment Pty Ltd., Australia) over night. Having crushed, ground and sieved (RETSCH AS-200, Germany) to the particle size of <75, 75–150, 150–300 and >300 μm, the natural biosorbents were kept in desiccator prior to use. Biosorbent was physical modified by heating (50–150 °C in a drying oven for 24 h) and boiling (100 g biosorbent in 150 mL water). For chemical modification, HCl (1 M), NaOH (1 M), HNO_3 (1 M), H_2SO_4 (1 M), $CaCl_2$ (1 M), formaldehyde (1%) and mixture of NaOH (0.5 M) and $CaCl_2$ (1.5 M) in ethanol were used as the modification agents. 10 g of each biosorbent was soaked in 1 L of each solution and thoroughly shaken (150 rpm) for 24 h at room temperature. Pretreatment with the mixture of 250 mL NaOH (0.5 M) and 250 mL $CaCl_2$ (1.5 M) solutions in 500 mL ethanol was same as other chemicals hereinabove. Afterwards, all materials were filtered and rinsed several times with distilled water to remove any free chemicals until the neutral pH to be obtained and dried in oven over night. All biosorbents were kept in a desiccator prior to use in future experiments.

2.3. Biosorption studies

The tests were performed with synthetic multi-metal stock solution with concentration of 3000 mg/L for each metal, prepared by dilution in Milli-Q water. Solution pH was adjusted with 1 M HCl and NaOH solutions.

A known weight of adsorbent (5 g/L) was added to a series of 200 mL Erlenmeyer flasks containing 50 mL of metal solution on a shaker (Ratek, Australia) at room temperature and 150 rpm. After equilibration, to separate the biomasses from solutions, the solutions were filtered and final concentration of metal was measured using MP-AES. All the experiments were carried out in duplicates.

The experimental conditions of Cd(II), Cu(II), Pb(II) and Zn(II) applied for current study were pH 5.5 ± 0.1, room temperature, biosorbent dose of 5 g/L and biosorbent particle size of 75–150 μm.

2.4. Desorption studies

Desorption study was carried out in a similar way to the biosorption studies. After adsorption step, metal-loaded biosorbent (5 g/L) was filtered, dried, weighed and shaken with 50 mL of desorbing agents in 250 mL Erlenmeyer flasks at 150 rpm on an orbital shaker. The suspension of metal-loaded MMBB and eluent was centrifuged and the supernatant was filtered and analyzed for metal ions desorbed.

In order to evaluate the regeneration properties of 1 M $CaCl_2$, desorption experiments were performed with and without regeneration step in five consecutive sorption/desorption cycles with modified MMBB.

2.5. Characterization of adsorbents by FTIR and SEM/EDS

To determine the functional groups involved in biosorption of Cd(II), Cu(II), Pb(II) and Zn(II) onto MMBB, a comparison between the Fourier Transform Infrared Spectroscopy (FTIR) before and after meal loading was done using SHIMADZU FTIR 8400S (Kyoto, Japan). Metal-loaded biosorbent were filtered and dried in the oven. The small amount of samples was place in the FTIR chamber on the KBr plates for analyzing the functional groups involving in biosorbent process by comparing with unused multi-metal biosorbent.