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A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study

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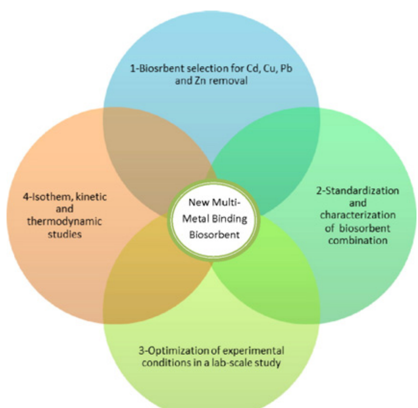
HIGHLIGHTS

- A novel multi-metal binding biosorbent (MMBB) was studied.
- The biosorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} on MMBB was evaluated.
- Hydroxyl, carbonyl and amine groups are involved in metal binding of MMBB.
- Equilibrium data were presented and the best fitting models were identified.
- The obtained results recommend this MMBB as potentially low-cost biosorbent.

GRAPHICAL ABSTRACT



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ABSTRACT

A breakthrough biosorbent namely multi-metal binding biosorbent (MMBB) made from a combination of tea wastes, maple leaves and mandarin peels, was prepared to evaluate their biosorptive potential for removal of Cd(II), Cu(II), Pb(II) and Zn(II) from multi-metal aqueous solutions. FTIR and SEM were conducted, before and after biosorption, to explore the intensity and position of the available functional groups and changes in adsorbent surface morphology. Carboxylic, hydroxyl and amine groups were found to be the principal functional groups for the sorption of metals. MMBB exhibited best performance at pH 5.5 with maximum sorption capacities of 31.73, 41.06, 76.25 and 26.63 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. Pseudo-first and pseudo-second-order models represented the kinetic experimental data in different initial metal concentrations very well. Among two-parameter adsorption isotherm models, the Langmuir equation gave a better fit of the equilibrium data. For Cu(II) and Zn(II), the Khan isotherm describes better biosorption conditions while for Cd(II) and Pb(II), the Sips model was found to provide the best correlation of the biosorption equilibrium data. The calculated thermodynamic parameters indicated feasible, spontaneous and exothermic biosorption process. Overall, this novel MMBB can effectively be utilized as an adsorbent to remove heavy metal ions from aqueous solutions.

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1. Introduction

Heavy metals are discharged to aquatic environments from various industries such as paper, textile, plastic, ceramic and cement manufacturing, mining and electronics plating. These poorly biodegradable pollutants are harmful for all plants, animals and human life due to high environmental mobility in soil and water and also a strong tendency for bioaccumulation in the living tissues along the food chain (Vargas-García et al., 2012; Akar et al., 2012; Bulut and Tez, 2007). In order to remediate polluted water and wastewater streams, a wide range of treatment technologies are employed in industry (e.g. chemical precipitation, extraction, ion exchange, filtration, reverse osmosis, membrane bioreactor and electrochemical techniques) (Santos et al., 2015; Abdolali et al., 2014a; Montazer-Rahmati et al., 2011; Fu and Wang, 2011). 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 (Bulut and Tez, 2007; Sud et al., 2008).

Therefore, introducing a properly eco-friendly and cost effective technology for wastewater treatment has provoked many researchers into this matter in recent decades (Abdolali et al., 2014b; Tang et al., 2013; Fu et al., 2013; Kumar et al., 2012; Hossain et al., 2012; Witek-Krowiak et al., 2011; Gadd, 2009; Volesky, 2007; Šćiban et al., 2007) to use cheap agro-industrial wastes and by-products as biosorbents. Some of these materials include sawdust and wood waste (Wahab et al., 2010; Bulut and Tez, 2007; Šćiban et al., 2007), sugarcane bagasse (Homagai et al., 2010; Martín-Lara et al., 2010; Khoramzadeh et al., 2013),fruit rind, pulp and seeds (Martín-Lara et al., 2010; Liu et al., 2012; Pehlivan et al., 2012; Schiewer and Patil, 2008), wheat or barley straw, rice husk, hull and straw (Asadi et al., 2008), and olive pomace and stone (Blázquez et al., 2010; Blázquez et al., 2009; Fiol et al., 2006).

All of the previous attempts have been made to study the agro-industrial wastes and by-products individually. The novelty of the present work is using combination of selected agro-industrial multi-metal binding biosorbents for removal of cadmium, copper, lead and zinc ions from synthetic aqueous multi-metal solutions. The significant difference between previous studies and current work is gaining the advantages and also using the biosorptive potentials of various biosorbents in a combination. The purpose of blending different lignocellulosic materials is having all potentials of biosorbents for heavy metal uptake (Abdolali et al., 2014a; Martín-Lara et al., 2010; Martín-Lara et al., 2010). Also these wastes were selected because of the good results reported in other literatures for heavy metal removal (Abdolali et al., 2014a; Feng et al., 2011; Amarasinghe and Williams, 2007). Additionally, they are properly available in Australia and also all over the world.

Firstly, the adsorption studies were carried out to select the best combination of different biosorbents, as mentioned hereinabove. Then the experiments were continued to compare the effect of different contact times, pH, initial metal concentration, temperature, and biosorbent dose and particle size on biosorptive potential of selected combination. The results were mainly evaluated by two popular kinetic models of pseudo-first-order and pseudo-second-order correlations and three two-parameter and three three-parameter adsorption models (Langmuir, Freundlich, Dubinin–Radushkevich, Khan, Sips and Redlich–Peterson). In addition, thermodynamic parameters were determined for the sorption of all metal ions to explain the process feasibility.

2. Material and methods

2.1. Preparation of adsorbents and heavy metal-containing effluent

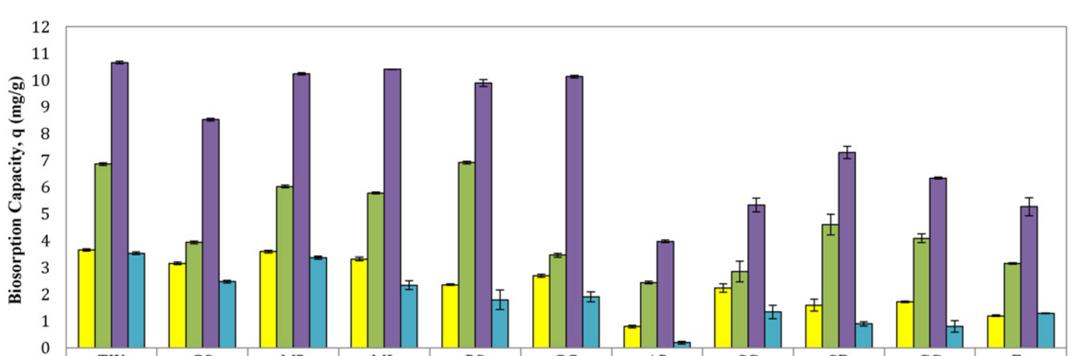
The stock solutions containing Cd, Cu, Pb and Zn were prepared by dissolving cadmium, copper, lead and zinc nitrate salt, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu_3(NO)_2 \cdot 3H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ in Milli-Q water. All the reagents used for analysis were of analytical reagent grade 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).

The biosorbents were applied in metal removal process for selecting the best ones in term of biosorption capacity sawdust (SD), sugarcane (SC), corncob (CC), tea waste (TW), apple peel (AP), grape stalk (GS), palm tree skin (PS), eucalyptus leaves (EU), mandarin peel (MP), maple leaves (ML) and garden grass (GG). All biosorbents were collected from Sydney area or local markets. After using or removing their useable parts, they were washed by tap and distilled water to remove any dirt, color or impurity and then dried in the oven (Labec Laboratory Equipment Pty Ltd., Australia) at 105 °C overnight. Having ground and sieved (RETSCH AS-200, Germany) to different sizes (<75 μm, 75–150 μm, 150–300 μm and >300 μm), the natural biosorbents were kept in a desiccator prior to use in future experiments.

2.2. Biosorption studies in batch system

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 the flasks were shaken at



	TW	GS	MP	ML	PS	GG	AP	SC	SD	CC	Eu
Cd	3.65	3.17	3.59	3.33	2.37	2.70	0.80	2.24	1.60	1.72	1.20
Cu	6.86	3.93	6.02	5.78	6.92	3.46	2.45	2.86	4.60	4.08	3.16
Pb	10.66	8.53	10.24	10.41	9.89	10.13	3.97	5.33	7.30	6.34	5.27
Zn	3.52	2.48	3.37	2.35	1.80	1.91	0.20	1.35	0.90	0.81	1.30

Fig. 1. Biosorption capacity of different agro-industrial wastes and by-products.