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# Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column

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## HIGHLIGHTS

- Dynamic behaviour of the column was described by S-shaped breakthrough curves.
- Several models were applied to simulate the continuous biosorption.
- Thomas and Dose Response models suitable for breakthrough prediction.
- Desorption study indicated that metal-loaded modified MMBB could be eluted by HCl.
- Applicability of biosorbent was tested using semi-simulated wastewater.

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## ABSTRACT

A continuous fixed-bed study was carried out utilising a breakthrough biosorbent, specifically multi-metal binding biosorbent (MMBB) for removing cadmium, copper, lead and zinc. The effect of operating conditions, i.e. influent flow rate, metal concentration and bed depth was investigated at pH 5.5 ± 0.1 for a synthetic wastewater sample. Results confirmed that the total amount of metal adsorption declined with increasing influent flow rate and also rose when each metal concentration also increased. The maximum biosorption capacities of 38.25, 63.37, 108.12 and 35.23 mg/g for Cd, Cu, Pb and Zn, respectively, were achieved at 31 cm bed height, 10 mL/min flow rate and 20 mg/L initial concentration. The Thomas model better described the whole dynamic behaviour of the column rather than the Dose Response and Yoon–Nelson models. Finally, desorption studies indicated that metal-loaded biosorbent could be used after three consecutive sorption, desorption and regeneration cycles by applying a semi-simulated real wastewater.



## 1. Introduction

As a consequence of global industrialisation and extensive use of machines in many industries, heavy metal pollution of the environment has now become a chronic worldwide problem and major threat to human health. Heavy metal ions such as cadmium, lead, zinc, nickel, copper, mercury and chromium or their compounds are now recognised as serious toxic pollutants due to their non-biodegradability and constant presence in the food chain.

In recent decades, the annual global release of heavy metal reached 22,000 tons (metric tons) for cadmium, 939,000 tons for copper, 783,000 tons for lead and 1,350,000 tons for zinc (Ansari et al., 2014). Therefore, it is very urgent to treat industrial wastewater effluents, before they are discharged into the environment. It is essential that such action is in accordance with effective health and environmental regulations developed for various bodies of water (Shanmugaprakash and Sivakumar, 2015; Kalavathy and Miranda, 2010). To remediate heavy metal polluted effluents, a wide range of physicochemical/biological treatment technologies

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are currently employed in various industries (e.g. chemical precipitation, extraction, ion-exchange, filtration, reverse osmosis, membrane bioreactor and electrochemical techniques). Nonetheless, these existing 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 (Montazer-Rahmati et al., 2011; Aksu et al., 2007). Recently, attention has focused on cheap agro-industrial wastes and by-products such as biosorbents (Bhatnagar et al., 2015; Bhatnagar and Sillanpaa, 2010). Although numerous studies on biosorption of heavy metals in batch systems have been published, in order to evaluate the feasibility of biosorption processes for real world applications, continuous biosorption studies in packed bed columns would be more useful (Bhatnagar et al., 2015). Additionally, a large volume of wastewater can be continuously treated using a defined quantity of adsorbent in the column. Reuse of biosorbent is also possible which makes the treatment process cheaper and more sustainable (Aksu et al., 2007).

This study's main aim was to examine chemically modified multi-metal binding biosorbent (MMBB) in a packed bed column. Its biosorptive potential for removing heavy metals in batch system has been documented in previous studies (Abdolali et al., 2016, 2015). In the present work, the influences of bed height, flow rate and initial concentration on packed bed reactors performance have been investigated and the possibility of regeneration and reuse studied. To evaluate the ability and applicability of MMBB in a real life situation, the MMBB packed-bed column was applied to a real wastewater. Moreover, Thomas, Dose Response and Bed Depth Service Time (BDST) models were applied for experimental data to simulate the breakthrough curves and to find the column capacity in order to predict the scale-up of a unit plant.

## 2. Material and methods

### 2.1. Synthetic water and real wastewater

The synthetic 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). Concerning the removal of any inaccuracies in metal concentration, all stock solutions with metal concentrations of 3000 mg/L were examined by MP-AES to correct their concentration for use in experiments with the required amounts.

The real wastewater employed in this study was the primary effluent, downstream of the Malabar WWTP sedimentation tanks collected from Sydney WaterPlant, NSW, Australia. Prior to the adsorption test, the sewage was settled for 24 h, filtered using a 150 μm sieve, and used for column adsorption tests without any pH alterations. The concentrations of Cd, Cu, Pb and Zn and major quality parameters of the solutions before and after passing through the column were determined according to standard procedures. Since the concentrations of Cd, Cu, Pb and Zn were very low, an appropriate amount of metallic nitrate salts were added to provide the desired initial concentrations for each metal ion which was 20 mg/L. It is necessary to mention that this concentration was applied firstly as to be close to those values from industrial electroplating processes (Long et al., 2014; Bulgariu and Bulgariu, 2016) and secondly, in order to compare the breakthrough curves obtained from synthetic solution with the ones of the semi-simulated real wastewater in similar conditions.

### 2.2. Preparation of adsorbents

The biosorbent was a combination of tea waste (TW), maple leaves (ML) and mandarin peel (MP) with weight ratio of 3, 2 and 1, respectively. These biosorbents displayed better biosorptive capacity for cadmium, copper, lead and zinc among a group of low-cost and very available lignocellulosic wastes and by-products. According to previous studies (Abdolali et al., 2015, 2016), all biosorbents were dried separately in oven (Labec Laboratory Equipment Pty Ltd., Australia) over night. Having ground, sieved (RETSCH AS-200, Germany) and then kept in desiccator prior to use. For chemical modification, pretreatment with the mixture of 250 mL NaOH (0.5 M) and 250 mL $CaCl_2$ (1.5 M) solutions in 500 mL ethanol showed better performance. 10 g of each biosorbent was soaked in 1 L of mentioned mixture thoroughly shaken (150 rpm) for 24 h at room temperature of 23 °C. 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.

### 2.3. Continuous biosorption experiments

The continuous sorption of Cd(II), Cu(II), Pb(II) and Zn(II)by MMBB was done in a mini glass column100 cm long and an inner radius of 22 mm. 5, 10, 15 g of biosorbent (particle size distribution = 425–600 μm) mixture were uniformly packed into the column with respective bed height of 9.5, 21 and 31 cm. A disk with a 150 μm pore was constructed on the bottom of the glass column to support the biosorbent and also prevent any loss. The column was first filled with glass beads (~5 cm) at the bottom. It was then packed with 2 g glass wool (about 2 cm), modified MMBB, 2 g of glass wool and this was followed by another layer of glass beads (~5 cm) for an even liquid flow across the column's cross-sectional area. The glass wool prevented venting of MMBB accompanied by effluent. The column was packed with a defined amount of MMBB (5, 10, 15 g) to achieve the desired bed height. Once the columns were filled, the biosorbent beds were fully immersed by distilled water, and then the bed was left to swell to ensure complete air bubbles expulsion. Following this the column was compacted by gravity. The fixed bed's packing was kept at a constant density. To ensure consistent packing porosity, the column was packed at varied bed heights using a constant bulk density of MMBB which was determined from the packing bulk density in a 0.5 m high column.

Column leaching experiments were conducted at room temperature, and the leaching rate was maintained at 10, 20 and 30 mL/min. In other word, the superficial velocity (v) also called hydraulic loading rate (HLR) was kept at 1.578 $m^3/m^2.h$, 3.156 $m^3/m^2.h$ and 4.734 $m^3/m^2.h$. The metal solutions were fed into the top of the column from a 20 L storage tank using a mechanical pump. The feed solution containing various heavy metal concentrations (10, 20, 30 mg/L) passed through the column in a downward direction at different flow rates (10, 20, and 30 mL/min) or HLR of 1.578 $m^3/m^2.h$, 3.156 $m^3/m^2.h$ and 4.734 $m^3/m^2.h$.

The top of the column was connected to a peristaltic pump (Masterflex® Console Drive, Model No. 77521-47, Cole-Parmer Instrument Company) using a silicone tube to obtain a constant steady downward flow. These experimental parameter values were selected to be as close as possible to those derived from industrial electroplating processes which have been used by other researchers. A stream of synthetic or semi-simulated real wastewater was pumped through the column. 10 mL samples were collected at predefined time intervals to: firstly, assess the residual concentration of metals; and secondly, determine the retained amount of heavy metal by Microwave Plasma-Atomic Emission Spectrometer, MP-AES (Agilent Technologies, USA). In order to ensure the formation