Elsevier required licence: © <2017>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

ACCEPTED MANUSCRIPT

Application of a breakthrough biosorbent for removing heavy metalsfrom synthetic and real wastewaters in a lab–scale continuous fixed–bed column

Atefeh Abdolali[a], Huu Hao Ngo[a,*], Wenshan Guo[a], John. L. Zhou[a], Jian Zhang[b], Shuang Liang[b], Soon W. Chang[c], Dinh Duc Nguyen[c], Yi Liu[d]

[a] *Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Broadway, NSW 2007, Australia*

[b]*Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science & Engineering, Shandong University, Jinan 250100, PR China*

[c]*Department of Environmental Energy & Engineering, Kyonggi University, 442−760, Korea*

[d]*Shanghai Advanced Research Institute, Chinese Academy of Science, Haike Road, Pudong, Shanghai, P. R. China*

* Corresponding author: School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), P.O. Box 123, Broadway, NSW 2007, Australia. Tel.: +61 2 9514 2745; Fax: +61 2 9514 2633. *E−mail address:* ngohuuhao121@gmail.com

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

ACCEPTED MANUSCRIPT

be used after three consecutive sorption, desorption and regeneration cycles by applying a semi–simulated real wastewater.

Keywords: Breakthrough curve, Fixed–bed column, Heavy metal, Lignocellulosic waste, Modelling

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 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

ACCEPTED MANUSCRIPT

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; Abdolali et al., 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, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu_3(NO)_2 \cdot 3H_2O$,

ACCEPTED MANUSCRIPT

$Pb(NO_3)_2$ 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 3000mg/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

ACCEPTED MANUSCRIPT

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 (0.5M) and 250 mL $CaCl_2$ (1.5M) solutions in 500mL ethanol showed better performance. 10 g of each biosorbent was soaked in 1 L of mentioned mixture thoroughly shaken (150 rpm) for 24 hr at room temperature of 23^{o}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 31cm. 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 (~5cm) 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

ACCEPTED MANUSCRIPT

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 of a complete breakthrough curve, each experiment was run for approximately 10 hr. The samples were taken at 15 min intervals in the first 4 hr and then at 30min intervals for the rest of the experiment.

One of the most important factors in measuring the feasibility of a biosorbent in a real and practical application is the performance of biosorption process in a continuous fixed

ACCEPTED MANUSCRIPT

bed column. In fact, the results from batch studies only present the biosorption equilibrium and kinetics (Shanmugaprakash and Sivakumar, 2015).Therefore, in order to predict the performance of MMBB to remove Cd(II), Cu(II), Pb(II) and Zn(II) ions in the continuous mode, the experiments were carried out in a continuous reactor. The performance of the fixedbedcolumn was studied by varying the efficiency of the flow rate, influent concentration and bed height.

Based on the results obtained from batch studies (Abdolali et al., 2015), metal adsorption onto modified MMBB was strongly pH dependent and the optimum pH value was observed at 5.5±0.1. Thus in the continuous mode experiments, the pH value of the synthetic solution was adjusted to 5.5±0.1. The municipal wastewater collected from Sydney Water was not contaminated by Cd, Cu, Pb and Zn, and therefore an appropriate amountof metallic nitrate salts were added to provide the desired initial concentrations of 20 mg/L of each metal ion. The pH of this semi−simulated real wastewater was 5.9±0.1, and no change in pH value was required for the actual application of modified MMBB in a fixedbed column.

2.4 Continuous desorption experiments

The desorption study in batch experiments showed that 0.1 M HCl (5g/L) was the best desorption agent (Abdolali et al., 2015). Prior to conducting the desorption test, the metal−loaded fixed−bed column was thoroughly washed with a large amount of distilled water for 30 min (20 mL/min) to eliminate unbound heavy metal ions. After each desorption cycle by passing 0.1 M HCl (10 mg/L), the column was washed with distilled water for 30 min (20 mL/min) in order to eliminate the rest of the acid placed in the bed. Then 1 M $CaCl_2$ solution with flow rate of 10 mL/min passed through the column to regenerate the used biosorbent. The column was followed by rinsing again

ACCEPTED MANUSCRIPT

using distilled water for 30 min (20 mL/min) and then run for another biosorption cycle (10 mL/min).

2.5 Calculations

The column capacity, q_c (mg), for a given inlet concentration and flow rate is equal to the area under the plot of the adsorbed metal concentration, where C_i and C_e (mg/L) are the influent and effluent metal ion concentrations, respectively, versus time (min) and is calculated as follows (Martín–Lara et al., 2016):

$$C_{ads} = C_i - C_e \quad (1)$$

$$q_c = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t} C_{ads}\, dt \quad (2)$$

where Q is the flow rate (mL/min), A is the area under the breakthrough curve and t (min) could be t_{total}, t_{sat} or t_b that represent the total flow time, the saturation or exhaustion time (C_e/C_i=90%), or the breakthrough time (C_e/C_i=10%), respectively (for more calculations, see *Supplementary Material A*).

The elution efficiency (%E) can be obtained by dividing the amount of metal desorbed by the amount of metal adsorbed in the previous biosorption stage and the amount of metal remaining on the biosorbent following desorption. As a result, the efficiency removing metal ions was determined for each cycle using the following equations:

$$q_{total,d} = \frac{Q}{1000}\int_{t=0}^{t=t} C_e\, dt \quad (3)$$

$$q_{e,d} = \frac{q_{total,d}}{M} \quad (4)$$

$$\%E = \frac{q_{e,d}}{q_i + q_{e,d}} \times 100 \quad (5)$$

where $q_{e,d}$ is g of desorbed metal per g of adsorbent and M is the total mass of the biosorbent in the column. In the first cycle the adsorbent is free of heavy metal ions (q_i=0), but in the consecutive cycles q_i (mg/g) is different from zero, as the desorbing

ACCEPTED MANUSCRIPT

agent was not completely efficient. Hence, some heavy metal ions were retainedat the adsorbent binding sites (Martín–Lara et al.,2016).

2.6 Fixed bed biosorption process analysis and modelling

In continuous biosorption systems, the concentration profiles in the liquid and adsorbent phases vary in both space and time. The mathematical and quantitative modelling approaches are applied for design and optimization of fixed–bed columns. Consequently, from the perspective of process modelling, the dynamic behaviour of a fixed–bed column can be described in terms of the effluent concentration–time profile, i.e. the breakthrough curves (Chu, 2004). Several models have been applied to predict the breakthrough performance, calculate the column kinetic constants and evaluate the fixed–bed columns' adsorption capacity (Cruz–Olivares et al., 2013).

Thomas model (Th)

$$\frac{C}{C_i} = \frac{1}{1+\exp\left[\left(\frac{k_{Th}}{Q}\right)(q_{Th}M - C_i Q t)\right]} \quad (6)$$

where k_{Th} is the Thomas rate constant (mL/ mg min) and q_{Th} is the maximum adsorption capacity for heavy metal ions (mg/g).

Dose Response model (DR)

$$\frac{C}{C_i} = 1 - \frac{1}{1+\left(\frac{C_i Q t}{q_{D-R} M}\right)^a} \quad (7)$$

where a is a constant and q_{D-R} is the maximum adsorption capacity for heavy metal ions (mg/g) calculated by the Dose Response model.

Yoon–Nelson model (YN)

$$\frac{C}{C_i} = \frac{\exp\left(k_{Y-N} t - k_{Y-N}\tau\right)}{1+\exp\left(k_{Y-N} t - k_{Y-N}\tau\right)} \quad (8)$$

where k_{Y-N} is the Yoon–Nelson proportionality constant (1/min) and τ is the time required for retaining 50% of the initial adsorbate (min).

ACCEPTED MANUSCRIPT

Bed Depth Service Time (BDST) model

$$\frac{C}{C_i} = \frac{1}{1+\exp\left[k_{BDST}C_i\left(\frac{N_{BDST}}{C_i v}L - t\right)\right]} \quad (9)$$

where N_{BDST} is the biosorption capacity (mg/L), v is the linear flow velocity of metal solution through the bed (cm/h), k_{BDST} is the adsorption rate constant that describes the mass transfer from the liquid to the solid phase (L/mg h), and L is the bed height (cm).

3. Results and discussion

The breakthrough curve showed the relative concentrations (C_t/C_i) on the y−axis versus time (t in min) on the x−axis. The column studies were conducted at the optimum pH value of 5.5±0.1 (from theprevious batch system studies (Abdolali et al., 2016; Abdolali et al., 2015) for synthetic solutions to be representative of environmentally relevant conditions. The pH value of real wastewater did not change after adding the heavy metal salts because it was 5.9±0.1 and above the optimal pH. All the breakthrough curves followed the typical S−shape curve for column operation as the ratio of the effluent concentration at time t (C_t) to the influent concentration (C_i) versus time or throughput volume.The breakthrough curve's shape is determined by the shape of the equilibrium isotherm and any individual transport process can change it (Long et al., 2014). The most efficient adsorption performance will be obtained when the shape of the breakthrough curve is as sharp as possible (Chu, 2004). Results show that the adsorption of each metal ion onto the biomass surface strongly depended on the flow rate (Acheampong et al., 2013; Cruz−Olivares et al., 2013; Aksu et al., 2007). Initially each metal ion was rapidly adsorbed on the biomass due to the high availability of active sites. In consequence, the metal ions were captured around or inside the cells; meanwhile the effluent from the bottom of the bed was almost free of solute. As the

ACCEPTED MANUSCRIPT

solution continued to flow, due to the gradual occupancy of the available active sites, the uptake became less effective and, accordingly, the outlet concentration started to increase until the saturation point was reached or at least until the outlet concentration was 90% of inlet concentration.

3.1 Effect of flow rate

The breakthrough curves at three different flow rates (10, 20 and 30 mL/min; HLR of 1.578 $m^3/m^2.h$, 3.156 $m^3/m^2.h$ and 4.734 $m^3/m^2.h$) are shown in Figure 1. The bed height was constant at 21 cm and the initial metal concentration at 20 mg/L. An increase in the flow rate reduced the volume of effluent treated before the bed became saturated and decreased the service time of the bed and vice versa. The slower flow rate provides more residence time for mass transfer into the pores, subsequently allowing metals ions to access more active sites within the adsorbent.Consequently better adsorption capacity was achieved. Increasing the flow rate increased the steepness of the breakthrough curves. Also, the breakpoint time as well as saturation occurred faster with a higher flow rate. In other words, by increasing the flow rate the external film diffusion mass transfer resistance decreases, culminating in fast saturation and early breakthrough time. Moreover, with a decrease in linear flow rate, the intra−particle diffusion becomes more effective due to longer residence time. An increase in the contact time between metal−containing solution and the biosorbent in a packed−bed column at lower influent flow rates explained this result. The best performance was obtained at the lowest flow rate. Generally, the column's removal efficiency fell when the flow rate increased, and the mass transfer zone decreased when the flow rate ebbed (Riazi et al., 2016). The biosorption capacity in a flow rate of 10 mL/min was 23.72, 43.32, 54.53 and 19.36 mg/g for Cd, Cu, Pb and Zn, respectively, which was higher than the other two flow

ACCEPTED MANUSCRIPT

rates of 20 and 30 mL/min.These findings agree with those documented in another study (Acheampong et al., 2013).

Figure 1

3.2 Effect of bed depth

Figure 2 presents the breakthrough curves of Cd(II), Cu(II), Pb(II) and Zn(II) biosorption onto MMBB obtained at various bed depths with a metal concentration of 20 mg/L and a constant flow rate of 10 mL/min (HLR of 1.578 $m^3/m^2.h$). Three bed depths of 9.5, 21 and 31 cm, corresponding to 5, 10 and 15 g dry weight of MMBB, respectively, were investigated. The breakthrough curves (Figure 2) indicate that the breakthrough time and exhaustion (or saturation) time increased remarkably with an increase in bed depth from 9.5 to 31 cm. Breakthrough occurred at 77, 48, 32 and 45 min for 9.5 cm and 172, 180, 150 and 105 min for 31 cm bed height within Cd, Cu, Pb and Zn biosorption, respectively. A similar raising pattern can be obtainedfor saturation time. This was attributed to the more adsorbent−specific surface and more available metal binding sites at higher bed height, which meant that consequently the total adsorbed metal ions increased. Moreover, an increase in the bed depth resulted in a wide mass transfer zone, which made the breakthrough curves moderately steeper. In fact when the bed depth increased, the diffusion mass transfer predominated in comparison with the axial dispersion phenomenon. For that reason, an enormous increase in the breakthrough time was observed. As Riazi et al. (2016) and Acheampong et al. (2013) reported for better performance of a fixed−bed column, the biosorbent's higher bed height would be more desirable if more active binding sites are to be provided.

Figure 2

3.3 Effect of inlet metal concentration

ACCEPTED MANUSCRIPT

The effect of initial concentration on the breakthrough curves is shown in Figure 3, using a bed depth of 21 cm at a flow rate of 10 mL/min (HLR of 1.578 m3/m^2.h). The breakthrough curves of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} were obtained from variations in the metal concentrationin the column influent with time. As can be seen in Figure 3 the shape and gradient of the breakthrough curves changed significantly with an increase in metal concentration. The higher influent metal concentration resulted in the faster breakthrough and saturation and as a consequence the sharper breakthrough curves shifted to the left. This earlier exhaustion might be a result of two things: firstly, greater concentration gradient; and secondly, smaller mass transfer resistance at a higher metal concentration. The breakthrough times were 281.6, 279.2, 171.0 and 221.6 min for Cd, Cu, Pb and Zn, respectively, using an influent metal concentration of 10 mg/L. When the influent metal concentration was increased to 30 mg/L, breakthrough took place in about 127.5, 158.3, 94.1 and 125 min for Cd, Cu, Pb and Zn, respectively.

As presumed, an increase in inlet metal concentration (10 to 30 mg/L) gave an earlier saturation time from 510 to 225, 420 to 250, 277.5 to 165 and 430 to 195 for Cd, Cu, Pb and Zn, respectively. These results demonstrated that the diffusion process of metal removal is highly concentration dependent (Bennani et al., 2015). Due to higher influent concentrations, higher driving force for mass transfer and larger concentration gradient was expected. In addition, a decrease in the diffusion coefficient or mass transfer coefficient led to a lower concentration gradient and a slower mass transport of heavy metal ions from the film layer to the adsorbent's surface. These results confirmed that the change of initial concentration as a driving force affects the saturation rate, breakthrough time and adsorption zone length (Chen et al., 2012;Baral et al., 2009; Aksu et al., 2007).The dynamic adsorption capacities of cadmium, copper, lead and zinc

ACCEPTED MANUSCRIPT

raised from 13.04, 28.90, 32.73 and 11.73mg/g to 35.96, 47.51, 81.92 and 33.05mg/g, respectively, by elevating the inlet metal concentration from 10 to 30 mg/L.

Figure 3

3.4 Breakthrough curve modelling

Table 1 lists the calculated parameters of Thomas, Yoon–Nelson and Dose Response models derived from the experimental data when initial influent concentration, flow rate and bed depth were varied. The best results for adsorption capacity were obtained at a flow rate of 10 mL/min (HLR of 1.578 m3/m^2.h) and height of the bed of 31 cm. All parameters and the models' correlation coefficient values were generated by MATLAB nonlinear curve fitting tools. The correlation coefficient values indicate a proper agreement between the experimental and column data generated using the models (Table 1). From Table 1, for Thomas and Dose Response models the values of the calculated adsorption capacity increased as initial concentration rose.This is because at a higher concentration, mass transfer is enhanced due to themass gradient's higher driving force, and led to an improvement in the adsorption capacity. Where external and internal mass diffusion steps are not the limiting steps, Thomas and Dose Response models are suitable for describing the adsorption processes (Cruz–Olivares et al., 2013).Moreover, the values of maximum biosorption capacities calculated from fitting the experimental data to Thomas and Dose Response models were also very similar.The results showed that the Yoon–Nelson model less adequately matches the experimental data (the values of R^2). The time required to reach 50% of the retention decreaseswhen the inlet concentration increased, due to rapid saturation in the higher concentration.

Table 1

ACCEPTED MANUSCRIPT

3.4.1 Comparative study

From Table 1, the highest metal adsorption capacities of modified MMBB at the exhaustion times were 38.25, 63.37, 108.12 and 35.23 mg/g for Cd, Cu, Pb and Zn, respectively. The maximum biosorption capacity values were achieved for a bed height of 31 cm, flow rate of 10 mL/min (HLR of 1.578 m3/m^2.hn) and initial metal concentration of 20 mg/L, particle size of 425−600 μm, and influent pH of 5.5. Biosorption capacity of Pb was the highest in comparison to those of other metals due to better affinity towards biosorbents. This phenomenon can be confirmed by calculating the Langmuir parameter of b_L representing this attraction. In addition, thermodynamic study revealed that except for zinc, calculated ΔS° values for cadmium, copper and lead were positive, reflecting the increased randomness at the solid/solution interface during sorption. It also indicates an affinity of the sorbent towards Cd, Cu and Pb ions (Abdolali et al., 2016; Abdolali et al., 2015). Biosorption capacities of some biosorbents with reference to Cd(II), Cu(II), Pb(II) and Zn(II) removal in a packed−bed column study are summarised in Table 2. As observed, the biosorption capacity of modified MMBB is comparable with the reported biosorption capacities. It is, however, too difficult to conclude which adsorbent performed better since experimental operating conditions were completely different.

Table 2

3.4.2 Scale−up study

The BDST model was derived from the equation described by Adams−Bohart, but was modified by Hutchins (Izquierdo et al., 2010). It is one of the most widely used models that describes heavy metal adsorption in a fixed−bed column. BDST is a simple model able to predict the relationship between the depth and service time in terms of metal

ACCEPTED MANUSCRIPT

concentration and biosorption parameters. The model is based on physically measuring the capacity of the bed at different breakthrough values, i.e. 10%, 30%, 60% and 90%. It ignores the intra−particle mass transfer resistance and neglects the external film resistance. As a result, the adsorbate is directly adsorbed onto the biosorbent surface. According to the BET analysis MMBB has a specific surface area of 1.3 m^2/g with an average pore diameter of 5.55 nm. The atomic radius of cadmium, copper, lead and zinc is 0.230, 0.140, 0.202 and 0.139 nm, respectively. Then the sorption process can take place on the surface and inside the pores. Iso−concentration lines for removing Cd, Cu, Pb and Zn ions in a fixed bed at C_t/C_i= 10%, 30%, 60% and 90% were determined (see *Supplementary Material B*). As presented in Table 3, a consistent increase in slopes and a subsequent increase in the corresponding dynamic sorption capacity, N_{BDST}, were observed for C_t/C_i ratios of 10–90%. Apart from this the rate constant, k_{BDST}, outlined the rate of solute transfer from the fluid phase to the solid phase. The k_{BDST} value declined at higher C_t/C_i ratio due to progressive binding sites saturation during heavy metal removal. Moreover, at 50% breakthrough, C_t/C_i=2, therefore reducing the logarithmic term of the BDST equation to zero with a good correlation coefficient, suggested the BDST model's conformity with the sorption of Cd, Cu, Pb and Zn by modified MMBB. The critical bed depth, $L_{critical}$, is calculated by setting t=0 and C_t=C_b. The critical bed depths of Cd, Cu, Pb and Zn adsorption were 8.64, 1.90, 3.21 and 7.43 cm, respectively. This value presents the minimum theoretical bed height of the adsorbent in a packed−bed column which is sufficient such that the effluent concentration at t=0 will not exceed the breakthrough concentration, C_b. In addition the calculated depth of the adsorption zone for all metals was about 19 cm and the Empty Bed Contact Time (EBCT) was 8.0 min. The data obtained from laboratory is used as

ACCEPTED MANUSCRIPT

the basis for designing a pilot scale and full or industrial scale adsorption column (see *Supplementary Material B*). One of the most important design parameters is bed depth for a specific adsorption service time.

Table 3

3.5 Applicability of modified MMBB packed–bed column in treating a real wastewater

The purpose of the biosorption process is to remove pollutants from industrial wastewater effluents which regularly contain other anions and cations rather than specified heavy metal ions. For this reason, continuous biosorption process experiments were also done under identical experimental conditions utilising a semi–simulated wastewater as the column feed. All the laboratory experiments were conducted in accordance with national and institutional guidelines for the protection of human subjects and animal welfare.

As mentioned before, the real wastewater used in this study was the primary effluent, downstream of the Malabar WWTP sedimentation tanks collected from Sydney Water Plant 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 municipal wastewater composition was determined as follows: pH 7.37±0.1, salinity 0.45‰, turbidity 83.5 NTUs, electrical conductivity 863 μS/cm,total dissolved solids (TDS) 567 mg/L, total suspended solids (TSS) 97 mg/L, ammonium 62 mg/L, nitrate 3.45 mg/L, orthophosphate 5.4 mg/L, total organic carbon (TOC) 21.55 mg/L, chemical oxygen demand (COD) 246 mg/L, chloride 118.32 mg/L, calcium 28.62 mg/L, magnesium 9.67 mg/L, iron 0.29 mg/L, copper 0.2 mg/L, lead 0.35 mg/L,

ACCEPTED MANUSCRIPT

manganese 0.05 mg/L, nickel 0.03 mg/L. Furthermore the zinc and cadmium were undetectable. Obviouslythe concentration of heavy metals was negligible in municipal wastewater. Hence an appropriate amount of metallic nitrate salts was added to provide the desired initial concentrations of 20 mg/L of each metal ion. 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.

The results presented in Figure4 indicate that the modified MMBB packed−bed column removed more than 90% of Cd(II), Cu(II), Pb(II) and Zn(II) ions from 3227, 2617, 1714 and 2019 mL municipal wastewater in 322, 261, 171 and 201 minutes, respectively. From Figure 4, the breakthrough time and the dynamic biosorption capacity of cadmium, copper, lead and zinc eliminated from the municipal wastewater were quite similar to those from the synthetic solution. Moreover, by using a column packed with only 10 g of modified MMBB, the levels of copper, lead and zinc concentrations in the effluent were within the recommended standard discharge limit of heavy metal ions (about 5, 10 and 10 mg/L, respectively). Cadmium has been identified as the major heavy metal of concern which needs to be remedied using another treatment method. As a result of successful metal removal by modified MMBB column, the effect of co−existing ions in the municipal wastewater on the continuous adsorption process could be negligible. It is also proven that modified MMBB can remove heavy metal ions from real municipal wastewater in the dynamic adsorption system.However, if behaviour in batch reactors is compared to performance in a fixed bed column utilising the same operating conditions, biosorption capacities of copper and lead are higher when the biosorption process is carried out in a fixed bed column. According to Gupta et al. (2004), because a large concentration gradient continuously presents at the

ACCEPTED MANUSCRIPT

interface zone as the metal solution passes through the column, a higher column capacity can be obtained whereas the concentration gradient decreases with time in batch experiments.

Figure 4

3.6 Continuous sorption and desorption experiments

Regeneration of metal–loaded adsorbent, subsequent reuse of the biosorbent and recovery of adsorbate (if possible) would make the wastewater treatment process economically feasible, reasonable and sustainable (Jain et al., 2013; Naddafi et al., 2007). The main factors for choosing suitable eluents and regenerating agents are the type of biosorbent and the biosorption mechanism (Bhatnagar et al., 2015).

In batch studies, desorption of Cd, Cu, Pb and Zn ions was evaluated by applying different desorbing agents and the best eluent was hydrochloric acid The results showed that 0.1 M HCl effectively desorbed 96.33%, 99.93%, 76.26% and 91.93%, respectively, for cadmium, copper, lead and zinc. The spent adsorbent was regenerated by 1 M $CaCl_2$. Calcium chloride can increase the stability and reusability of MMBB and repairing the damage caused by the desorbing agents. It can also remove the excess protons after each elution and thereby provide new binding sites. This observed mechanical stability and stiffness of the modified MMBB make it suitable for fixed bed column applications (Abdolali et al., 2015). Thus the reusability of modified MMBB for removing heavy metal from real wastewater was conducted using 0.1 M HCl (10 mL/min) within three successive cycles of alternating sorption and desorption in a continuous system, supplemented by a solution of cadmium, copper, lead and zinc. The influent concentration of each metal was adjusted to 20 mg/L for each metal.

ACCEPTED MANUSCRIPT

The desorption of Cd(II), Cu(II), Pb(II) and Zn(II) from loaded modified MMBB took place rapidly. Actually, the breakthrough curves of these three cycles showed notangiblechange for three adsorption times especially in the first three cycles. A negligible loss in bed height and mass of modified MMBB was observed after three cycles, and the obtained results for biosorption and desorption are presented in *Supplementary Material B*. For the first adsorption step, the breakthrough of Cd(II), Cu(II), Pb(II) and Zn(II) was 82.4, 75, 51.6 and 83.8 min, while the exhaustion taking place was 423, 261.7, 171.4 and 201.7 min, also respectively. For the third time, the breakthrough time achieved was 55, 56.2, 42.3 and 53.6 min and exhaustion time occurred at 270, 231, 157.5 and 186.4 min. After three cycles of sorption, desorption and regeneration, there was a modest decline in the metal uptake at the exhaustion times which were 49.94, 50.76, 56.38 and 53.87% for Cd, Cu, Pb and Zn, respectively. It means the regenerated modified MMBB was still able to remove heavy metal ions even after the third cycle with moderately similar removal efficiency (Table 4). Nonetheless a decrease in the total amount of heavy metal removal was probably due to possible biosorbent damage.

Table 4 also shows that some heavy metal ions are irreversibly bound to the surface of modified MMBB. The desorption efficiency amounts decreased when the number of cycles rose from 48.08, 47.61, 57.37 and 45.88% in the first cycle to 22.80, 23.69, 34.44 and 23.80% in the third cycle for Cd, Cu, Pb and Zn. Biosorption and desorption efficiency progressively decreased, as the biosorption and desorption cycles continued as reported by Bulgariu and Bulgariu (2016).

Figure 5 indicates the desorption curves obtained for Cd, Cu, Pb and Zn. These unsymmetrical–shaped desorption curves are very similar. The initial metal

ACCEPTED MANUSCRIPT

concentration increase is followed by a flatter reduction in that within the first 30 min, the maximum concentration peak was achieved for all heavy metal ions in the first 10 min. The advantage of applying acidic eluent with a higher desorption rate was reported by Martín–Lara et al. (2016). Moreover, from these desorption profiles, the maximum concentration peak, C_p (mg/L), in which the eluted metal concentration reached to its maximum value at the time of t_p (min) can be measured. The peak information provides a clue to the elution rate.

Figure 5 and Table 4

4. Conclusions

Although all of the predictive models explained the dynamic behaviour of the breakthrough curves fairly well, the Thomas model strongly correlated the experimental data, as deduced from the statistical calculated parameters (i.e. R^2>0.99). Furthermore, the BDST model was utilised successfully for the evaluation of the column's performance. The results obtained from column regeneration demonstrated that reusing the modified MMBB is feasible. This study also indicated that modified MMBB could serve as a viable low–cost potential biosorbent for the removal of Cd(II), Cu(II), Pb(II) and Zn(II) ions from aqueous solution in a continuous column mode.

References

1. Abdolali, A., Ngo, H.H., Guo, W.S., Lu, S., Chen, S.S., Nguyen, N.C., Zhang, X., Wang, J., Wu, Y., 2016. A breakthrough biosorbent in removing heavy metals: equilibrium, kinetic, thermodynamic and mechanism analyses in a lab–scale study. Sci. Total Environ. 542, 603–611.
2. Abdolali, A., Ngo, H.H., Guo, W.S., Zhou, J.L., Du, B., Wei, Q., Wang, X.C., Nguyen, P.D., 2015. Characterization of a multi–metal binding biosorbent:

ACCEPTED MANUSCRIPT

chemical modification and desorption studies. Bioresour. Technol. 193, 477–487.

3. Acheampong, M.A., Pakshirajan, K., Annachhatre, A.P., Lens P.N.L., 2013. Removal of Cu(II) by biosorption onto coconut shell in fixed–bed column systems J. Ind. Eng. Chem.19, 841–848.
4. Aksu, Z., Çağatay, Ş.Ş., Gönen F., 2007. Continuous fixed bed biosorption of reactive dyes by dried *Rhizopusarrhizus*: Determination of column capacity. J. Hazard.Mater.143,362–371.
5. Ansari, A.A., Gill, S.S., Gill, R., Lanza, G.R., Newman, L., 2014. Phytoremediation: Management of Environmental Contaminants, Springer.
6. Baral, S.S., Das, N., Ramulu, T.S., Sahoo, S.K., Das, S.N., Chaudhury, G.R., 2009. Removal of Cr(VI) by thermally activated weed *Salviniacucullata* in a fixed–bed column.J. Hazard. Mater. 161, 1427–1435.
7. Bennani, K.A., Mounir, B., Hachkar, M., Bakasse, M., Yaacoubi, A., 2015. Adsorption of cationic dyes onto Moroccan clay: Application for industrial wastewater treatment, J. Mater. Environ. Sci. 6, 2483–2500.
8. Bhatnagar, A., Sillanpää, M., Witek–Krowiak, A., 2015. Agricultural waste peels as versatile biomass for water purification – A review. Chem. Eng. J.270, 244–271.
9. Bhatnagar, A., Sillanpaa, M., 2010. Utilization of agro–industrial and municipal waste materials as potential adsorbents for water treatment—a review, Chem. Eng. J. 157, 277–296.

ACCEPTED MANUSCRIPT

10. Bulgariu, D., Bulgariu L., 2016. Potential use of alkaline treated algae waste biomass as sustainable biosorbent for clean recovery of cadmium(II) from aqueous media: batch and column studies. J. Clean Prod. 112, 4525–533.
11. Chen, S.,Yue,Q., Gao, B., Li, Q.,Xu, X., Fu, K., 2012. Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed–bed column study. Bioresour. Technol.113, 114–120.
12. Chao, H.P., Chang, C.C., Nieva, A., 2014.Biosorption of heavy metals on Citrus maxima peel, passion fruit shell, and sugarcane bagasse in a fixed–bed column. J. Ind. Eng. Chem. 20, 3408–3414.
13. Chu, K.H., 2004. Improved fixed bed models for metal biosorption. Chem. Eng. J. 97, 233–239.
14. Cruz–Olivares, J., Pérez–Alonso, C., Barrera–Díaz, C., Ureña–Nuñez, F., Chaparro–Mercado, M.C., Bilyeu, B., 2013. Modelling of lead (II) biosorption by residue of allspice in a fixed–bed column. Chem. Eng. J. 228, 21–27.
15. Gupta, V.K., Imran, Ali S., Saini, V.K., 2004. Removal of rhodamine B, fast green, andmethylene blue from wastewater using red mud, an aluminum industry waste. Ind. Eng. Chem. Res. 43, 1740–1747.
16. Izquierdo, M., Gabaldón, C., Marzal, P., Álvare–Hornos F.J., 2010, Modelling of copper fixed–bed biosorption from wastewater by *Posidoniaoceanica.* Bioresour. Technol. 101, 510–517.
17. Jain, M., Garg, V.K., Kadirvelu, K., 2013. Cadmium(II) sorption and desorption in a fixed bed column using sunflower waste carbon calcium–alginate beads. Bioresour. Technol. 129, 242–248.

ACCEPTED MANUSCRIPT

18. Kalavathy, M.H., Miranda, L.R., 2010. *Moring aoleifera*−A solid phase extractant for the removal of copper, nickel and zinc from aqueous solutions. Chem. Eng. J.158, 188–199.

19. Long, Y., Lei, D., Ni, J., Ren, Z., Chen, C., Xu H., 2014. Packed bed column studies on lead(II) removal from industrial wastewater by modified *Agaricusbisporus*. Bioresour. Technol. 152, 457–463.

20. Martín−Lara, M.A., Blázquez, G., Calero, M., Almendros, A.I., Ronda, A., 2016. Binary biosorption of copper and lead onto pine cone shell in batch reactors and in fixed bed columns. Int. J. Miner. Process. 148, 72–82.

21. Montazer−Rahmati, M.M., Rabbani, P., Abdolali, A., Keshtkar, A.R., 2011. Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae. J. Hazard. Mater. 185, 401–407.

22. Muhamad, H., Doan, H., Lohi, A., 2010. Batch and continuous fixed−bed column biosorption of Cd^{2+} and Cu^{2}+. Chem. Eng. J. 158, 369–377.

23. Naddafi, K.,Nabizadeh, R., Saeedi, R., Mahvi, A.H.,Vaezi, F.,Yaghmaeian,K., Ghasri, A., Nazmara, S.,2007.Biosorption of lead(II) and cadmium(II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column.J. Hazard. Mater.147, 785–791.

24. Riazi, M., Keshtkar, A.R., Moosavian, M.A., 2016. Biosorption of Th(IV) in a fixed−bed column by Ca−pretreated *Cystoseiraindica*. J. Env. Chem. Eng. 4, 1890–1898.

25. Shanmugaprakash, M., Sivakumar, V., 2015. Batch and fixed−bed column studies for biosorption of Zn(II) ions onto pongamia oil cake

ACCEPTED MANUSCRIPT

(*Pongamiapinnata*) from biodiesel oil extraction. J. Environ. Manage. 164,161–170.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Figure Caption:

Figure 1 Effect of influent flow rate on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MMBB (pH 5.5±0.1, bed heights = 21 cm, influent metal concentration = 20 mg/L, particle size =425-600 μm, room temperature = 23^{o}C)

Figure 2 Effect of bed height (MMBB weight= 5, 10 and 15 gr) on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MMBB (pH 5.5±0.1, influent flow rate = 10 mL/min or HLR = 1.578 m^3/m^2.h , influent metal concentration = 20 mg/L, particle size = 425-600 μm, room temperature = 23^{o}C)

Figure 3 Effect of influent metal concentration on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MBB (pH 5.5±0.1, bed heights = 21 cm, influent flow rate = 10 L/min or HLR = 1.578 m^3/m^2.h, particle size = 425-600 μm, room temperature = 23^{o}C)

Figure 4 Breakthrough curves of Cd, Cu, Pb and Zn adsorption onto modified MMBB from synthetic and semi-simulated municipal wastewater (bed heights = 21 cm, influent flow rate = 10 mL/min or HLR =1.578 m^3/m^2.h, influent each metal concentration = 20 mg/L, particle size = 425-600 μm, room temperature = 23^{o}C)

Figure 5 Desorption kinetic of Cd, Cu, Pb and Zn adsorbed on modified MMBB (10 g , desorption solution = 0.1 M HCl, flow rate = 10 mL/min or HLR = 1.578 m^3/m^2.h)

ACCEPTED MANUSCRIPT

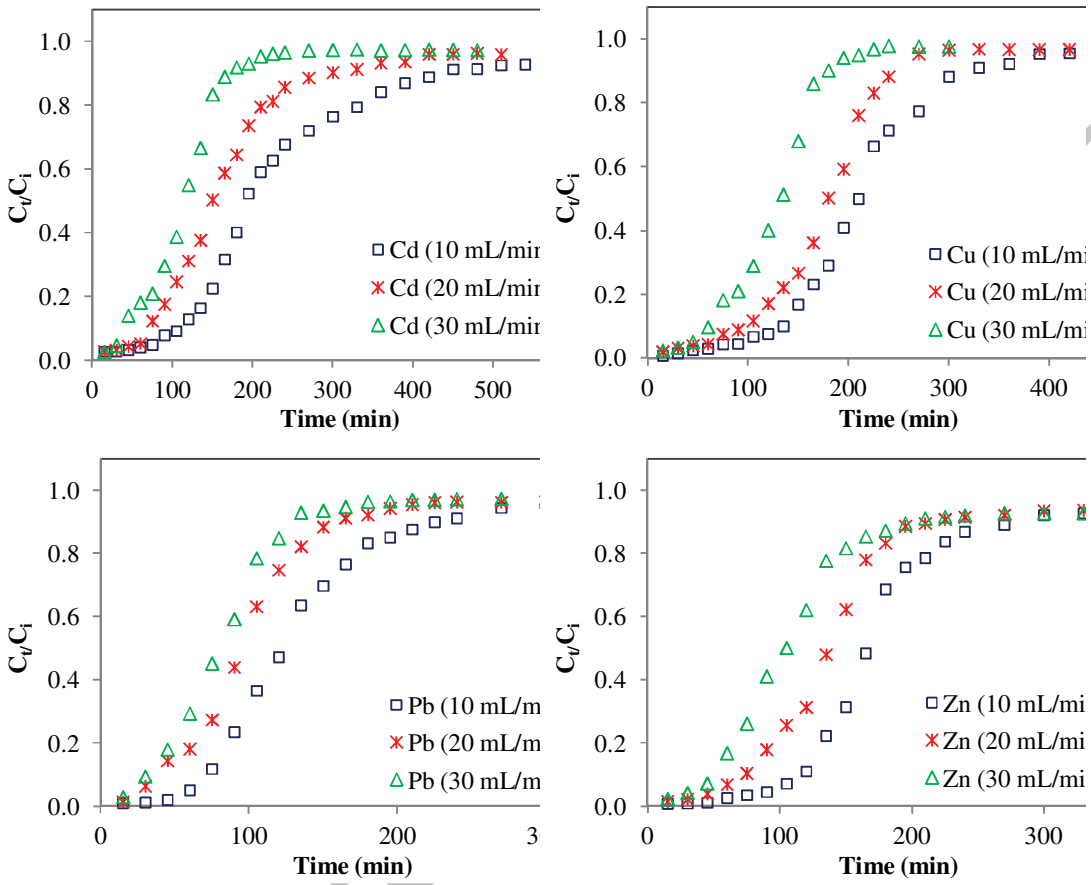
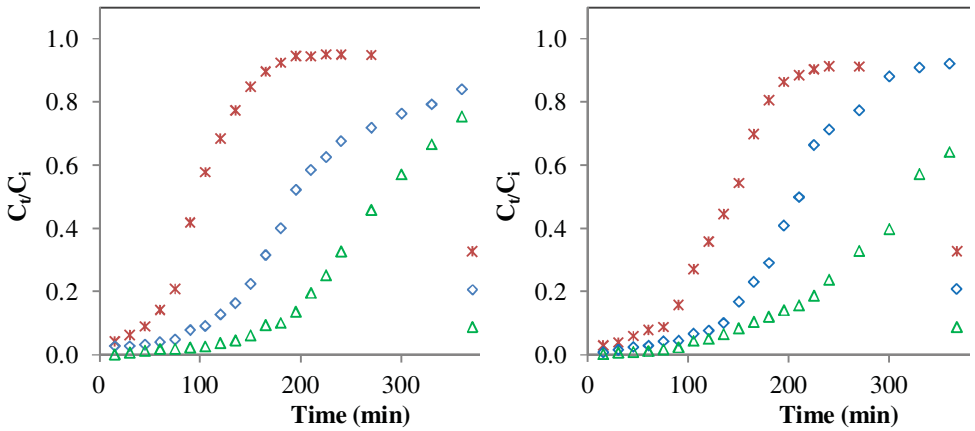


Figure 1 Effect of influent flow rate on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MMBB (pH 5.5±0.1, bed heights = 21 cm, influent metal concentration = 20 mg/L, particle size =425-600 µm, room temperature = 23°C)



ACCEPTED MANUSCRIPT

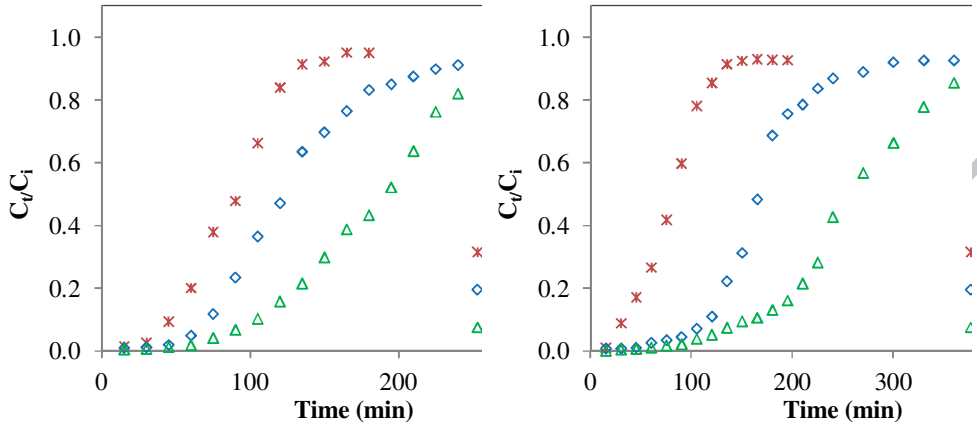
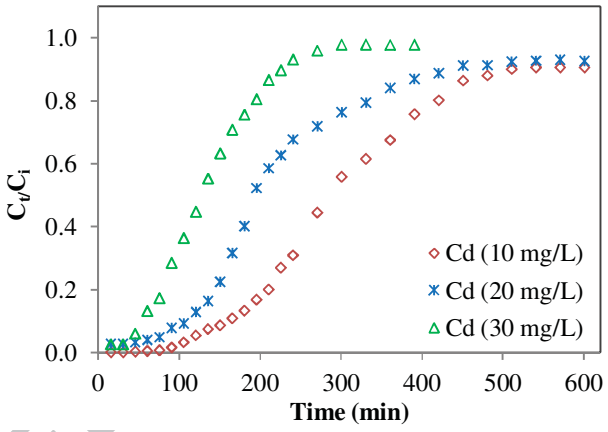
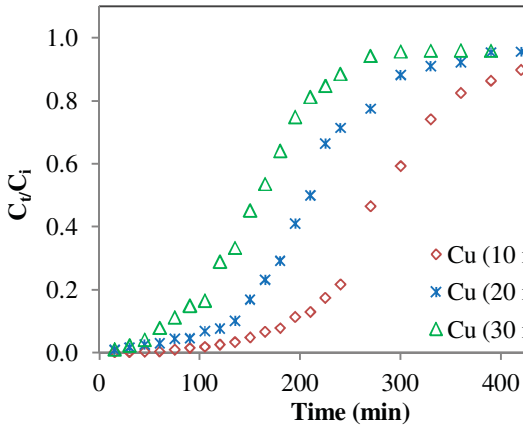
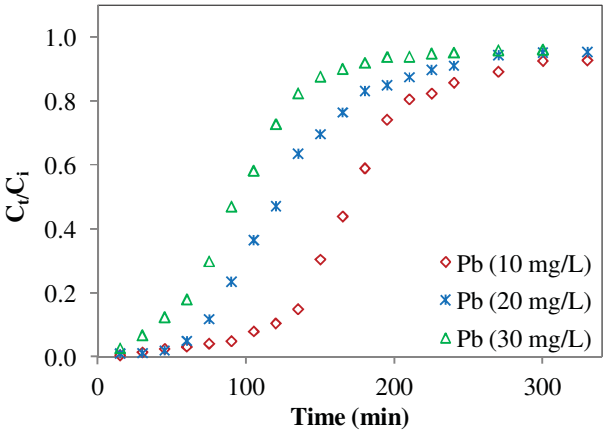
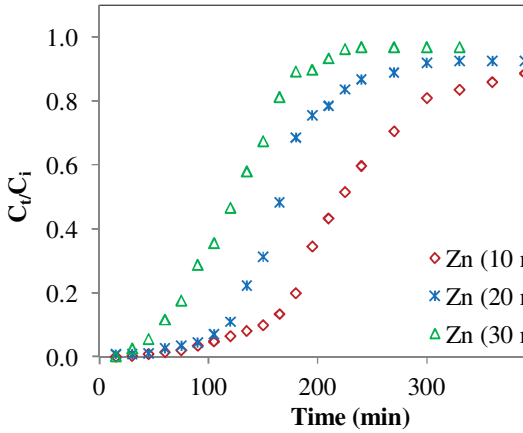


Figure 2 Effect of bed height (MMBB weight= 5, 10 and 15 gr) on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MMBB (pH 5.5±0.1, influent flow rate = 10 mL/min or HLR = 1.578 $m^3/m^2.h$, influent metal concentration = 20 mg/L, particle size = 425-600 µm, room temperature = 23°C)









ACCEPTED MANUSCRIPT

Figure 3 Effect of influent metal concentration on the breakthrough curve of Cd, Cu, Pb and Zn adsorption onto modified MBB (pH 5.5±0.1, bed heights = 21 cm, influent flow rate = 10 L/min or HLR = 1.578 m^3/m^2.h, particle size = 425-600 µm, room temperature = 23°C)

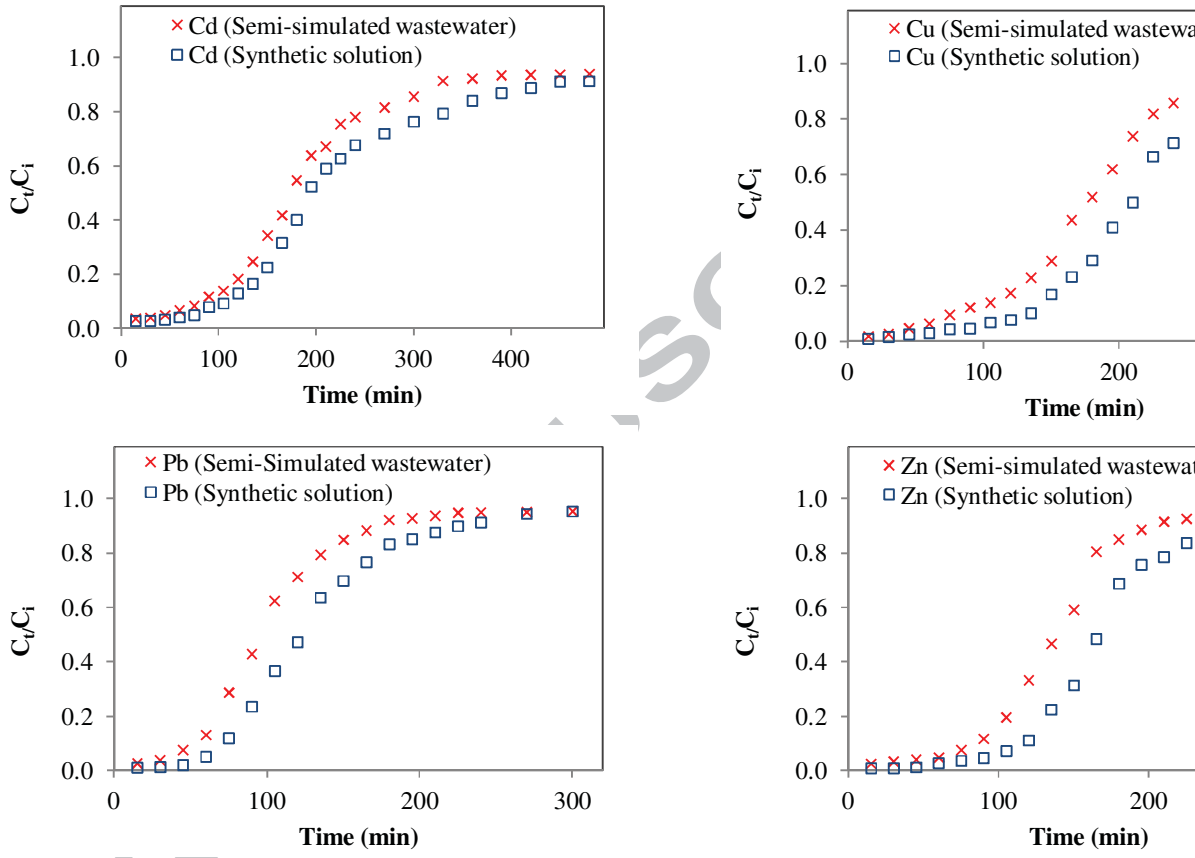


Figure 4 Breakthrough curves of Cd, Cu, Pb and Zn adsorption onto modified MMBB from synthetic and semi-simulated municipal wastewater (bed heights = 21 cm, influent flow rate = 10 mL/min or HLR = 1.578 m^3/m^2.h, influent each metal concentration = 20 mg/L, particle size = 425-600 µm, room temperature = 23°C)

ACCEPTED MANUSCRIPT

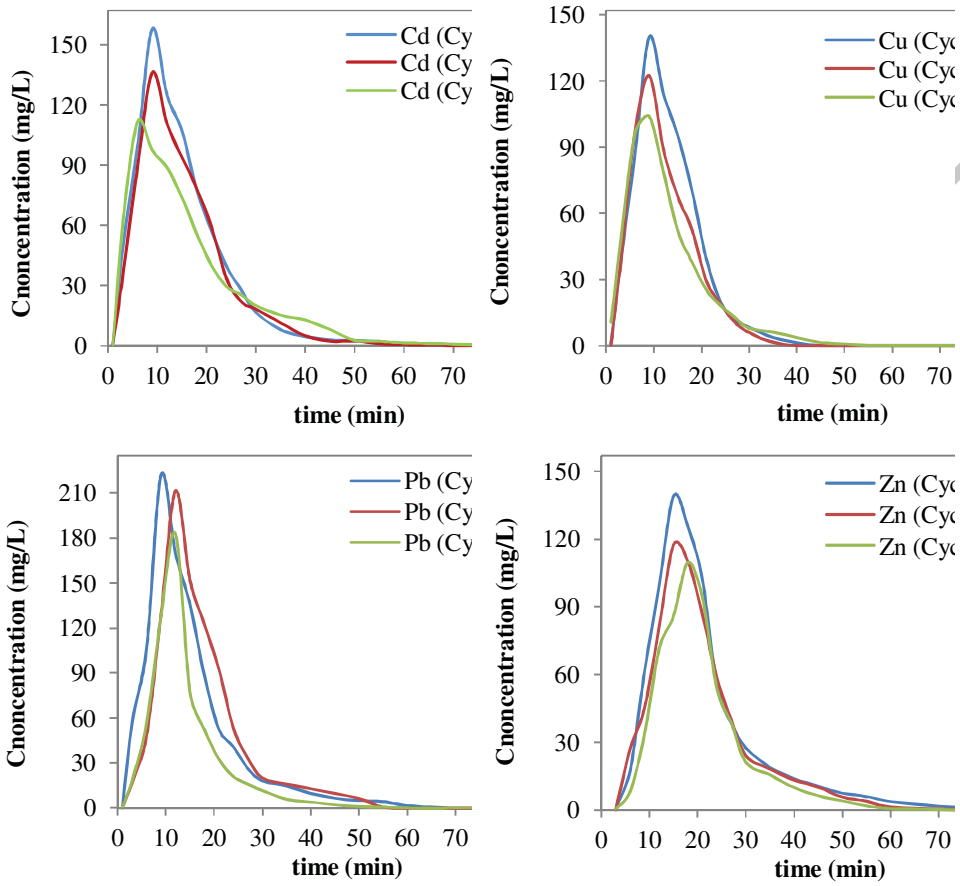


Figure 5 Desorption kinetic of Cd, Cu, Pb and Zn adsorbed on modified MMBB (10 g , desorption solution = 0.1 M HCl, flow rate = 10 mL/min or HLR = 1.578 $m^3/m^2.h$)

ACCEPTED

ACCEPTED MANUSCRIPT

Table 1 Thomas, Yoon-Nelson and Dose Response model constants for Cd, Cu, Pb and Zn adsorption onto modified MMBB column (pH 5.5±0.1, particle size = 425-600 μm, room temperature)

Table 2 Dynamic adsorption capacity of cadmium, copper, lead and zinc onto different adsorbents

Table 3 Parameters predicted from the BDST model for biosorption of Cd, Cu, Pb and Zn on MMBB (5, 10 and 15 g or 9.5, 21 and 31 cm) in a fixed-bed column

Table 4 Desorption parameters for three cycles of biosorption and desorption cycles with semi-simulated municipal wastewater

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 1 Thomas, Yoon-Nelson and Dose Response model constants for Cd, Cu, Pb and Zn adsorption onto modified MMBB column (pH 5.5±0.1, particle size = 425-600 µm, room temperature)

Metal	Conditions				Thomas			Yoon-Nelson			Dose Response		
	Q	Bed height	C_i	q	k_{Th}	q_{Th}	R^2	k_{Y-N}	τ	R^2	a	q_{D-R}	R^2
Cd	10	21	20	23.72	0.485	23.66	0.991	0.016	210.7	0.971	3.128	23.53	0.989
	20	21	20	12.43	0.572	12.36	0.998	0.023	155.2	0.987	3.271	11.95	0.991
	30	21	20	4.55	0.768	4.52	0.994	0.034	127.8	0.993	4.393	4.46	0.988
	10	21	10	13.04	1.358	13.03	0.999	0.027	282.4	0.986	3.768	12.81	0.988
	10	21	30	35.96	0.483	35.93	0.996	0.025	130.9	0.996	3.265	34.74	0.985
	10	9.5	20	14.10	1.921	14.03	0.992	0.038	101.6	0.987	3.941	13.61	0.984
	10	31	20	38.25	0.238	38.07	0.994	0.029	283.2	0.990	4.575	37.76	0.989
Cu	10	21	20	43.32	0.615	43.18	0.994	0.025	210.6	0.991	4.962	42.43	0.991
	20	21	20	24.30	0.751	24.23	0.996	0.029	178.6	0.992	5.334	24.03	0.990
	30	21	20	14.42	1.191	14.38	0.995	0.036	128.0	0.994	5.328	14.14	0.989
	10	21	10	28.90	2.123	28.88	0.999	0.033	279.5	0.985	5.656	28.38	0.993
	10	21	30	47.51	0.879	47.46	0.997	0.026	158.2	0.997	4.081	46.99	0.993
	10	9.5	20	28.25	1.525	28.03	0.992	0.034	142.7	0.985	4.222	27.26	0.990
	10	31	20	63.37	0.773	63.14	0.991	0.038	321.7	0.988	4.668	63.27	0.992
Pb	10	21	20	54.53	0.749	54.48	0.996	0.032	126.1	0.985	3.739	54.25	0.995

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Metal	Conditions				Thomas			Yoon-Nelson			Dose Response		
	Q	Bed height	C_i	q	k_{Th}	q_{Th}	R^2	$k_{Y\text{-}N}$	τ	R^2	a	$q_{D\text{-}R}$	R^2
	20	21	20	27.74	0.988	27.64	0.993	0.039	95.9	0.989	3.686	26.91	0.991
	30	21	20	12.67	1.549	12.54	0.994	0.045	79.9	0.993	3.543	11.78	0.991
	10	21	10	32.73	0.871	32.61	0.995	0.032	174.1	0.986	5.722	32.41	0.992
	10	21	30	81.92	0.168	81.87	0.992	0.037	196.2	0.991	5.799	81.19	0.990
	10	9.5	20	19.02	2.36	17.88	0.992	0.047	89.4	0.984	4.074	17.84	0.992
	10	31	20	108.12	0.295	107.27	0.991	0.026	186.3	0.990	4.418	103.64	0.989
Zn	10	21	20	19.36	0.542	19.18	0.993	0.033	178.6	0.982	5.572	19.24	0.987
	20	21	20	10.95	0.855	10.89	0.998	0.034	136.7	0.986	4.431	10.33	0.988
	30	21	20	3.68	1.710	3.50	0.993	0.032	105.9	0.972	3.134	3.60	0.987
	10	21	10	11.73	1.684	11.56	0.993	0.035	218.6	0.984	4.401	11.54	0.991
	10	21	30	33.05	0.068	32.93	0.997	0.032	123.1	0.987	3.905	32.47	0.992
	10	9.5	20	16.32	2.263	16.25	0.997	0.045	81.23	0.985	3.492	15.55	0.989
	10	31	20	35.23	0.153	35.15	0.995	0.041	256.3	0.989	5.132	34.79	0.987

Notation: bed depth (cm); Q, flow rate (mL/min); C_i, influent metal concentration (mg/L); q, adsorption capacity (mg/g); k_{Th}, Thomas model rate constant (mL/mg min), q_{Th}, Thomas sorption capacity (mg/g); $k_{Y\text{-}N}$, Yoon-Nelson model rate constant (1/min); τ, the time required for 50% breakthrough (min), a is a constant and $q_{D\text{-}R}$ is Dose Response model adsorption capacity of heavy metal ions (mg/g)

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 2 Dynamic adsorption capacity of cadmium, copper, lead and zinc onto different adsorbents

Adsorbent/adsorbate	Ci (mg/L)	Bed depth (cm)	Q (mL/min)	q_{Th} (mg/g)	q_{exp} (mg/g)	Reference
Pongamia oil cake /Zn	100	15	5	49.7	84.2	Shanmugaprakash and Sivakumar, 2015
Citrus Maxima peel/Cd	300	2	3	144	-	Chao et al., 2014
Citrus Maxima peel/Cu	300	2	3	98.1	-	Chao et al., 2014
Citrus Maxima peel/Pb	300	2	3	173	-	Chao et al., 2014
Passion fruit shell/Cd	300	2	3	55.8	-	Chao et al., 2014
Passion fruit shell /Cu	300	2	3	36.3	-	Chao et al., 2014
Passion fruit shell /Pb	300	2	3	59.4	-	Chao et al., 2014
Sugarcane bagasse/Cd	300	2	3	26.7	-	Chao et al., 2014
Sugarcane bagasse /Cu	300	2	3	22.2	-	Chao et al., 2014
Sugarcane bagasse /Pb	300	2	3	31.8	-	Chao et al., 2014
Agaricus bisporus/Pb	35	2	3	67.7	67	Long et al., 2014
Allspice residue/ Pb	15	15	20	14.3	16.2	Cruz-Olivares et al., 2013
Allspice residue/ Pb	25	15	20	13.4	15.9	Cruz-Olivares et al., 2013
Sunflower waste/Cd	10	30	1	-	23.6	Jain et al., 2013
Coconut shell/Cu	10	20	10	53.5	7.2	Acheampong et al., 2013
Wheat straw/Cd	100	50	300	12.13	16.9	Muhamad et al., 2010

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 3 Parameters predicted from the BDST model for biosorption of Cd, Cu, Pb and Zn on MMBB (5, 10 and 15 g or 9.5, 21 and 31 cm) in a fixed-bed column

Metal	Breakpoint (%)	Slope (hr/cm)	Intercept (hr)	N_{BDST} (mg/L)	K_{BDST} (L/mg h)	MTZ (cm)	$L_{critical}$ (cm)	R^2
Cd	10	0.073	0.631	51.63	0.167	6.23	8.64	0.992
	30	0.09	0.676	63.65	0.060	12.44		0.995
	60	0.102	1.359	72.14	0.014	18.92		0.991
Cu	10	0.102	-0.194	74.39	0.528	6.74	1.90	0.998
	30	0.118	0.229	86.06	0.172	14.19		0.999
	60	0.153	0.072	111.59	0.262	19.06		0.994
Pb	10	0.091	-0.292	66.99	0.347	7.19	3.21	0.992
	30	0.126	0.17	92.75	0.230	13.19		0.999
	60	0.147	0.077	108.21	0.243	18.82		0.999
Zn	10	0.046	0.342	32.00	0.314	6.22	7.43	0.993
	30	0.063	0.525	43.83	0.079	12.84		0.998
	60	0.079	0.923	54.96	0.021	18.66		0.998

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 4 Desorption parameters for three cycles of biosorption and desorption cycles with semi-simulated municipal wastewater

Metal	Cycle	t_b (min)	t_{sat} (min)	q_i (mg/g)	q_c(mg/g)	$q_{e,d}$ (mg/g)	%R	%E	t_p (min)	C_p (mg/L)	CF_p
Cd	1	82.4	423	0	9.58	4.61	47.90	48.08	9	157.94	8.08
	2	65	322.7	4.97	9.82	4.13	49.12	27.94	9	129.16	6.61
	3	55	270	5.69	9.90	3.57	49.94	22.80	7	111.35	5.70
Cu	1	75	261.7	0	9.66	4.60	48.30	47.61	9	139.82	7.05
	2	60	235	5.06	9.94	4.08	49.69	27.22	10	124.33	6.27
	3	56.2	231	5.85	10.15	3.79	50.76	23.69	9	117.6	5.93
Pb	1	51.6	171.4	0	11.21	6.43	56.04	57.37	8	223.40	10.99
	2	48	166.2	4.78	11.23	5.98	56.14	37.38	12	211.42	10.40
	3	42.3	157.5	5.24	11.28	5.69	56.38	34.44	11	182.67	8.99
Zn	1	83.8	201.7	0	10.44	4.79	52.20	45.88	15	139.07	6.63
	2	63.7	195	5.65	10.70	4.38	53.50	26.79	14	117.61	5.61
	3	53.6	186.4	6.32	10.77	4.07	53.87	23.80	18	109.82	5.23

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

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.

ACCEPTED MANUSCRIPT