Competitive adsorption of metals on cabbage waste from multi-metal solutions


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

bStrategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

*Corresponding author at: School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW 2007, Australia. Tel.: +61-2-9514-2745/1693; Fax: +61-2-9514-2633. E-mail address: h.ngo@uts.edu.au

Abstract

This study assessed the adsorption capacity of the agro-waste ‘cabbage’ as a biosorbent in single, binary, ternary and quaternary sorption systems with Cu(II), Pb(II), Zn(II) and Cd(II) ions. Dried and ground powder of cabbage waste (CW) was used for the sorption of metals ions. Carboxylic, hydroxyl, and amine groups in cabbage waste were found to be the key functional groups for metal sorption. The adsorption isotherms obtained could be well fitted to both the mono- and multi-metal models. In the competitive adsorption systems, cabbage waste adsorbed larger amount of Pb(II) than the other three metals. However, the presence of the competing ions suppressed the sorption of the target metal ions. Except the case of binary system of Cd(II)-Zn(II) and Cd(II)-Cu(II), there was a linear inverse dependency between the sorption capacities and number of different types of competitive metal ions.

Keywords: Cabbage waste, competitive adsorption, biosorption, multi-metals, isotherm model, antagonism mechanismµ
1. Introduction

Untreated and uncontrolled discharge of heavy metal containing wastewaters into the natural environment could be toxic to humans, animals, plants, and to urban ecosystems (Ahmad et al., 2010; Pamukoglu and Kargi, 2006). Cu(II), Pb(II), Cd(II) and Zn(II) are used in various
remove heavy metals from wastewater with high solute loadings and even at dilute concentrations (<100 mg/L) (Popuri et al., 2009). Among the adsorbents, activated carbon is commonly used as a commercial adsorbent for removing heavy metals from wastewater. However, this is still an expensive material, requiring costly regeneration. This has prompted the search for an inexpensive yet effective alternative adsorbent.

Removal of heavy metals by biosorption is a relatively new and an emerging technology in the...
explain the binding characteristics of metallic cations during biosorption (Karthikeyan et al., 2007).

First time by this investigation, cabbage-biosorbent is used to determine the biosorption in single, binary, ternary and quaternary solutions while establishing the applicable isotherm model and antagonism mechanism.

2. Materials and methods

2.1 Materials

Cabbage wastes were collected from Campsie Fruits World (Campsie, NSW, Australia). Copper (II) nitrate [Cu(NO$_3$)$_2$, 99.0%], cadmium(II) nitrate [Cd(NO$_3$)$_2$, 98.0%], lead(II) nitrate [Pb(NO$_3$)$_2$, 99.0%], and zinc(II) nitrate [Zn(NO$_3$)$_2$·6H$_2$O] were purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade chemicals were used as received.

2.2 Methods

2.2.1 Preparation of biosorbent and characterisation

The cabbage waste was cut into small pieces and washed twice with tap and then distilled water. After air drying, cabbage was dried further at 105 °C for 24 h. Subsequently, the dried cabbage was ground into powder (75-300 µm) and kept in air-tight containers for experiments. A BET surface area of cabbage waste was measured by Micrometric Gemini 2360, UK. The functional groups on thus prepared biosorbent were determined by an FTIR instrument (SHIMADZU FTIR 8400S, Kyoto, Japan). For the FTIR analysis, the testing pellet comprised 1% (w/w) of the biosorbent in KBr. The surface morphology of cabbage was scanned with a scanning electron microscope (SEM) instrument (JEOL, JSM-35CF, UK).
2.2.2 Metals solutions and measurement

A stock solution of Pb(II), Cd(II), Cu(II) and Zn(II) were obtained by dissolving the exact quantity of Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Cu(NO$_3$)$_2$ and Zn(NO$_3$)$_2$·6H$_2$O in Milli-Q water. The test solutions containing single ions were prepared by diluting 1000 mg/L of stock solutions of metal ions to the desired concentrations. The ranges of concentrations of both metal ions prepared from stock solutions varied between 1 mg/L to 500 mg/L.

For the investigation with binary metal solutions, the desired combinations of Cu(II)-Pb(II), Pb(II)-Cd(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions were obtained by diluting 1000 mg/L of stock solutions of metal ions and mixed them in the test medium. Before mixing the biosorbent, the pH of each test solution was adjusted to the required value with 0.1 N H$_2$SO$_4$/NaOH. Similarly, the ternary solutions of Pb(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Cd(II), Cu(II)-Pb(II)-Zn(II) and Cu(II)-Cd(II)-Zn(II) were quaternary solution of Cu(II)-Pb(II)-Cd(II)-Zn(II) was prepared with required dilutions from the stock solutions.

The concentrations of heavy metal ions in solution were determined by Atomic Adsorption Spectroscopy (AAS) (Contra®AA 300, Analytikjena, Germany) after samples were filtered with Whatman™ GF/C-47mm φ circle filters (GE Healthcare, Buckinghamshire, UK).

2.3 Adsorption experiments

2.3.1 Effect of pH
shaken at 120 rpm for 120 min at room temperature (20 °C). These experiments were conducted in three replicates.

2.3.2 Adsorption isotherm

Adsorption isotherm experiments were studied at eight concentrations ranging from 1 to 500 mg. These experiments were described under Section 2.3.2.

2.3.2.1 Single, binary, ternary and quaternary adsorption equilibrium isotherms

The Langmuir model is not only used for prediction of adsorption but is the best model for adsorption monolayer adsorption onto biosorption. This model is used for metals adsorption onto different systems. The equilibrium data for a single metal adsorption can be normally interpreted by the Langmuir isotherms (Langmuir, 1918), which is represented mathematically as follows:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(1)

where:

- \( q_e \) is the equilibrium adsorption capacity (mg/g) at equilibrium concentration, \( C_e \) (mg/L),
- \( K_L \) is the isotherm parameter and \( q_m \), maximum adsorption capacity (mg/g).

Langmuir isotherm can be modified to multi-metals isotherm by introducing some interaction factors (Padilla-Ortega et al., 2013; Srivastava et al., 2008):

\[ q_{e,i} = \frac{q_{m,i} K_{L,i} (C_{e,i})}{1 + \sum_{j=1}^{N} K_{L,j} (C_{e,j})} \]  

(2)

where:

- \( q_{e,i} \) is the equilibrium adsorption capacity for metal i (mg/g) at equilibrium concentration, \( C_{e,i} \) (mg/L),
- \( q_{m,i} \) is the maximum adsorption capacity for metal i (mg/g),
- \( K_{L,i} \) is the isotherm parameter for metal i.

Page 6 of 22
For Pb(II):
\[
q_{e,Pb} = \frac{q_{m,Pb} K_{L,Pb} C_{e,Pb}}{1 + K_{L,Pb} C_{e,Pb}}
\]  
(3)

For Cd(II):
\[
q_{e,Cd} = \frac{q_{m,Cd} K_{L,Cd} C_{e,Cd}}{1 + K_{L,Cd} C_{e,Cd}}
\]  
(4)

For Cu(II):
\[
q_{e,Cu} = \frac{q_{m,Cu} K_{L,Cu} C_{e,Cu}}{1 + K_{L,Cu} C_{e,Cu}}
\]  
(5)

And for Zn(II):
\[
q_{e,Zn} = \frac{q_{m,Zn} K_{L,Zn} C_{e,Zn}}{1 + K_{L,Zn} C_{e,Zn}}
\]  
(6)

(ii) Binary metal adsorption system

\[
q_{e,Pb} = \frac{q_{m,Pb} K_{L,Pb} (C_{Pb})}{1 + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd}}
\]  
(7)

For Cd (II):
\[
q_{e,Cd} = \frac{q_{m,Cd} K_{L,Cd} (C_{Cd})}{1 + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd}}
\]  
(8)

Similarly, the equation (2) can be transformed for the binary solution of Cu(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) adsorption systems.
(iii) Ternary metal adsorption system

\[ q_{e,Cu} = \frac{q_{m,Cu} K_{L,Cu}(C_{Cu})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd}} \] (9)

for Pb(II):

\[ q_{e,Pb} = \frac{q_{m,Pb} K_{L,Pb}(C_{Pb})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd}} \] (10)

and for Cd(II):

\[ q_{e,Cd} = \frac{q_{m,Cd} K_{L,Cd}(C_{Cd})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd}} \] (11)

Similarly, the equation (2) can be rewritten for Pb(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Zn(II) and Cu(II)-Cd(II)-Zn(II) adsorption systems.

(iv) Quaternary metal adsorption system

\[ q_{e,Cu} = \frac{q_{m,Cu} K_{L,Cu}(C_{Cu})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd} + K_{L,Zn} C_{e,Zn}} \] (12)

For Pb(II):

\[ q_{e,Pb} = \frac{q_{m,Pb} K_{L,Pb}(C_{Pb})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd} + K_{L,Zn} C_{e,Zn}} \] (13)
For Cd(II): 

$$q_{e,Cd} = \frac{q_{m,Cd} K_{L,Cd} (C_{Cd})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd} + K_{L,Zn} C_{e,Zn}}$$  \(14\)

And for Zn(II): 

$$q_{e,Zn} = \frac{q_{m,Zn} K_{L,Zn} (C_{Zn})}{1 + K_{L,Cu} C_{e,Cu} + K_{L,Pb} C_{e,Pb} + K_{L,Cd} C_{e,Cd} + K_{L,Zn} C_{e,Zn}}$$  \(15\)

2.4 Data analysis and validation

The isotherm data were modelled with a modelling technique of Excel Spreadsheet and MATLAB. Data fitting was assessed by the magnitude of $R^2$, RMSE and $\chi^2$ error functions. The percent reduction in adsorption capacities in the competitive systems (binary, ternary and quaternary) were calculated by the following expression:

$$\% \text{ reduced} = \left( \frac{q_m \text{ from single metal system} - q_m \text{ from multi - metal system}}{q_m \text{ from single metal system}} \right) \times 100$$

3. Results and discussion

3.1 Characterization of biosorbent with FTIR and SEM

The surface structures of biosorbents produced from cabbage waste was analysed by an SEM. Generally, the micrographs revealed that it contained asymmetrical particles. In lower magnification (1KX), the heterogeneous structures were noticed. It was observed that the surface of the particles was built with uneven, asymmetric steps and pores. It is believed that irregular shapes of particles have more internal binding or uptakes places and eventually absorb more metals (Ricordel et al., 2001). The BET surface area of cabbage-biosorbent was 1.027 m²/g, which is lower than conventional biosorbents available in literature (Hossain et al., 2013).

A biosorbent may consist of complex organic and inorganic materials such as proteins, lipids, carbohydrate polymers and sometimes metals. Chemisorptions and ions exchange mostly
depends on the available functional groups in a particular biosorbent and eventually metal adsorption depend on it. Carbon-oxygen and carbon bonds are the attracting and stimulating bonds of metals adsorption (Ricordel et al., 2001). From FTIR spectra of the biosorbent, the following major functional groups were noticed: O-H stretch-free hydroxyl for alcohols/phenols (3624.54 cm\(^{-1}\)), O-H stretch for carboxylic acids (between 3300-2500 cm\(^{-1}\)), C-N stretch for aliphatic amines (1024.25 cm\(^{-1}\)), C-O stretch for alcohols/carboxylic acids/esters/ethers (between 1320-1000 cm\(^{-1}\)), =C-H bend for alkanes (between 1000-650 cm\(^{-1}\)) and C-H “OOH” for aromatics (817.85 cm\(^{-1}\)). Among the functional groups, hydroxyl, amines and carboxyl groups could bind heavy metal ions with adsorbent (Kongsuwan et al., 2009; Sheng et al., 2004).

### 3.2 Effect of pH

The pH of 2 and 9.5 (Fig. 1). The negative charge of any biosorbent (in aqueous solution) can be correlated with metal adsorption and it varies with water pH depending on the isoelectric pH of the biosorbent. In general, the adsorption capacity of the biosorbent may increase with an increase in pH under some limited conditions such as constant temperature and out of range of metal precipitate pH (Conrad and Bruun Hansen, 2007). Fig. 1 shows that the adsorption increased with an increasing of pH from 2.2 to 7.0. Cu(II) adsorption by cabbage increased from 1.126 to 1.375 mg/g with a 1.22-fold increase when the pH of the solution was increased from 2.0 to 6.0. The adsorption capacity of Cd(II) at pH 2.0 and 6.0 corresponded to 0.811 mg/g and 1.101 mg/g, respectively, indicating a 1.35-fold increase at the elevated pH. The amount of Pb(II) adsorbed was found to be 1.616 and 1.977 mg/g at pH 2.0 and 6.0, respectively (a 1.22-fold increment). Similarly, a 1.10-fold increase was observed for Zn(II) removals and it was 0.936 to 0.999 mg/g for the pH of 2.0 and 7.0. Similar results have been also reported in literature (Conrad and Bruun Hansen, 2007; Demirbas, 2008; Hossain et al., 2008).
al., 2012). It was observed that the Cu(II), Cd(II), Zn(II) and Pb(II) metals precipitates as a
form of Cu(OH)$_2$, Cd(OH)$_2$, Zn(OH)$_2$ and Pb(OH)$_2$ beyond a pH of 7. Hence, to avoid metal
precipitation the remaining experiments were conducted between 6.0 and 6.5 pH.

**Fig. 1**

### 3.3 Adsorption isotherm

#### 3.3.1 Single metal adsorption

Langmuir model is applicable for monolayer adsorption onto a surface containing a finite
number of identical sites (Aksu, 2005). This model was used to describe experimental data
from adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions onto cabbage. The sorption data were
fitted to the non-linear form of Langmuir isotherm model (Eq. 1) and parameters are evaluated
In this study, apart from Cd(II), diverse relationship between the adsorption capacity and the ionic radius (Cu = 73, Zn = 74, Cd = 95 and Pb = 77.5 nm) (Kusvuran et al., 2012) was observed. Higher ionic radii of heavy metals generally led to higher maximum adsorption capacities. For example, because the ionic radius of Pb(II) is larger than that of Cu(II), the maximum adsorption capacities of cabbage were higher in case of Pb(II) than Cu(II) (Table 1). Table 1 also reveals a higher maximum adsorption capacity for Cd(II) as its ionic radius is...
16.660 mg/g for Pb(II), Cu(II), Pb(II), Pb(II), Cd(II) and Cu(II) ions in binary sorption of
Pb(II)-Cd(II), Cu(II)-Zn(II), Cu(II)-Pb(II), Pb(II)-Zn(II), Cd(II)-Zn(II) and Cd(II)-Cu(II)
systems, respectively. The results indicate that the adsorption capacity for Pb(II) was higher
than that of Cd(II), Cu(II) and Zn(II) as Pb(II) could bind with more varieties of functional
groups (Kongsuwan et al., 2009). The maximum adsorption capacities of Cd(II), Zn(II), Cu(II)
and Pb(II) obtained from binary metals sorption were less than those obtained from the single
metal system (Table 1).

### 3.3.3 Adsorption behaviour in ternary solutions

Wastewaters may contain more than one metal ion and therefore, the examination of multiple
metal interactions simultaneously is very important for accurate representation of adsorption
data (Hammaini et al., 2003). The competitive adsorption among the Cu(II), Pb(II), Cd(II) and
Zn(II) in the ternary systems of Cd(II)-Pb(II)-Cu(II), Cd(II)-Pb(II)-Zn(II), Cu(II)-Cd(II)-Zn(II)
and Cu(II)-Pb(II)-Zn(II) were conducted in batch systems between 1 to 200 mg/L of initial
concentration. It was experimented for 3 hours at 120 rpm and room temperature. The
adsorption parameters of ternary systems is tabulated in Table 3. The experimental data were
well fitted with the ternary adsorption model (Eq. 9-11) as evident by the R2 values exceeding
0.99. (Tables 1, 2 and 3). The adsorption capacities of cabbage were found to be 12.264, 8.785
and 40.963 mg/g for Cd(II)-Cu(II)-Pb(II) system, 7.587, 1.828 and 50.216 mg/g for Cd(II)-
Zn(II)-Pb(II) system, 4.965, 7.584 and 5.844 mg/g for Cd(II)-Cu(II)-Zn(II) system, and 8.194,
6.380 and 22.803 mg/g for Cu(II)-Zn(II)-Pb(II) system of ternary-metal interactions,
respectively (Table 3). The findings could be explained by the fact that the ionic charge, ionic
radius, and electrochemical potential affect adsorption capacity of biosorbent in the multi-metal
ion sorption system (Yakup Arıca et al., 2004) while adsorption capacity decreases in the
multi-metal adsorption system with respect to single metal adsorption capacity (Padilla-Ortega
et al., 2013).
Table 3

3.3.4 Adsorption behaviour in quaternary solutions

The calculated parameters from the quaternion Langmuir isotherms are summarised in Table 4. This isotherm model successfully fitted the competitive adsorption of Cu(II)-Pb(II)-Cd(II)-Zn(II) onto the biosorbent prepared from cabbage.

Table 4

The experimental adsorption capacities of Cu(II), Pb(II), Cd(II) and Zn(II) from the four metals system [Cu(II)-Pb(II)-Cd(II)-Zn(II)] were compared to the molar uptake values of Cu(II), Pb(II), Cd(II) and Zn(II) predicted with the quaternary Langmuir isotherm (Eqs. 12-15). The Langmuir isotherm accurately estimated the adsorption capacities for all four metal uptakes as evident by the superimposing predicted lines and the experimental plots. However, it overestimated the molar uptake of Zn(II) and showed the similar adsorption capacity (10.170 mg/g) with single metal systems (Table 1). The other three uptakes for metals Cu(II), Pb(II) and Cd(II) are underestimated as the magnitude of the adsorption capacities (2.415 mg/g, 15.085 mg/g and 8.697 mg/g) are lower than the single metals system.

The values of the parameter $K_L$ of the Langmuir isotherm provides indication of the affinity of the biosorbent for the systems with two, three or four metal ions in the test solution: greater the value of these parameters, lesser is the affinity for a metal ion. The values of $K_{L-Cu}$, $K_{L-Pb}$, $K_{L-Zn}$ and $K_{L-Cd}$ are higher in the case of the binary, ternary and quaternary system than the value of $K_L$ derived for the single metal system using the Langmuir sorption isotherm for single-metal (Tables 1, 2, 3 and 5). This means that the affinity of cabbage biosorbent for metal ions was reduced in multi-metals metal system.

3.3.5 Competitive adsorption in multi-metal systems
It is evident from available literature (Christophi and Axe, 2000; Leyva-Ramos et al., 2001) that the multi-metal Langmuir model provides a reasonable fit to the multi-metals adsorption data as long as the $q_m$ values for each metal calculated from single-metal Langmuir isotherm are similar to each other. However, the prediction for $q_m$ values from all binary, ternary and quaternion system are lower than single metals system (Kumar et al., 2008), evidencing competitive sorption of the metals. In this regard, the 3D surface plots of Cu(II)-Zn(II), Pb(II)-Cd(II), Cd(II)-Zn(II), Cu(II)-Cd(II) and Pb(II)-Cu(II) are prepared for the binary systems (Figures 2 and 3). The area plot for ternary system [Cd(II)-Pb(II)-Cu(II), Cd(II)-Pb(II)-Zn(II), Cu(II)-Cd(II)-Zn(II) and Cu(II)-Pb(II)-Zn(II)] is shown in Figure 4 and the spider diagram for the quaternary system [Cd(II)-Pb(II)-Cu(II)-Zn(II)] is given in Figure 5.

**Fig. 2**

Fig. 2(A) shows the effect of the presence of Zn(II) on the capacity of the cabbage for adsorbing Cu(II). The competitive surface of Cu(II) adsorption indicates that the presence of Zn(II) reduced drastically the uptake of Cu(II) adsorbed on the cabbage. A moderate reduction of the uptake of Cu(II) can be noted as compared to the single metal systems (from 10.315 to 7.140 mg/g). On the other hand, the effect of the presence of Cu(II) on the capacity for adsorbing Zn(II) is shown in Fig.2(B). The effect is stronger and reduced to half of the uptake of Zn(II) (from 8.970 to 4.760 mg/g) though the surface of adsorption is perfectly slanting evenly (Padilla-Ortega et al., 2013). In the Pb(II)-Cd(II) system the effects of Pb(II) and Cd(II) ions on the uptake of Cd(II) and Pb(II) on to the cabbage are plotted in Fig.2(C) and Fig.2(D), respectively. The Pb(II) uptake was reduced to 43.907 mg/g in binary system from 60.568 mg/g in single metals. Similarly, the reduction of the adsorption capacity for Cd(II) is changed significantly (from 20.565 to 18.582 mg/g). These metals significantly interfered in the adsorption of each other, as evidenced by the uneven surface of adsorption in 3D graphs (Fig.2).
Similarly, the partial aggression on the adsorption of Cd(II) and Zn(II) in Cd(II)-Zn(II), Cu(II) and Cd(II) in Cu(II)-Cd(II), and; Pb(II) and Cu(II) in Pb(II)-Cu(II) binary system are plotted in 3D graph of Fig.3. As can be seen in Fig.3, strong interference existed between the metals but the dominance of Pb(II) and Cd(II) uptake did not change by their counter pairs of metals (Apiratikul and Pavasant, 2006). High affinity of cabbage toward the Pb(II) and Cd(II) ions are internal causes (functional groups) for the significant adsorption of those metals. For instance, in Cd(II)-Zn(II) system Cd(II) uptake (18.030 mg/g), and in Pb(II)-Cu(II) system Pb(II) (60.311 mg/g) uptake were more than their pairs of Zn(II) and Cu(II) (Tables 1 and 2). Fig.3 (A, C, and E) shows that the adsorption surfaces are more even than counter metals. However, a significant change was found in Cu(II)-Cd(II) system where Cu(II) uptake increased (from 10.315 mg/g in single metal system to 20.660 mg/g in binary system) in the presence of Cd(II) ions. It is also noticeable that Zn(II) adsorption slightly increased in binary system (11.053 mg/g) with the presence of Cd(II) ions. It might be due to the fact that the presences of Cd(II) ions enhance the uptake of Cu(II) and Zn(II) with considering of minor change of its own uptake (Papageorgiou et al., 2009).

**Fig. 3**

The results of the competitive adsorption of ternary system of Cu(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Zn(II), Cu(II)-Pb(II)-Cd(II) and Cd(II)-Pb(II)-Zn(II) onto cabbage are demonstrated in the surface plot of Fig.4 (a, b, c and d). It is revealed that the Pb(II) ions presented a higher affinity for the binding sites of the cabbage than the Cu(II), Cd(II) and Zn(II) ions. In other words, the cabbage was much more selective towards Pb(II) than to other three metals in the competitive adsorption. The Pb(II) ions presented strong resistancne against (i) the adsorption of Cu(II) and Cd(II) ions in Cu(II)-Pb(II)-Cd(II), against of Cd(II) and Zn(II) ions in Cd(II)-Pb(II)-Zn(II) system; (ii) against of Cu(II) and Zn(II) in Cu(II)-Pb(II)-Zn(II) system whereas the Cu(II) and Cd(II) ions, Cd(II) and Zn(II) ions; and (iii) Cu(II) and Zn(II) ions exhibited light resistance against the adsorption of Pb(II) (Apiratikul and Pavasant, 2006; Padilla-Ortega...
et al., 2013). This behaviour could not be predicted from the single metal adsorption system. It is also found from Fig. 4 (b, c and d) that Pb(II) ions took higher physical surface area than

The higher ionic radius and molecular weight for Pb(II) were responsible for

Thus, the most binding sites of cabbage are occupied

Fig. 4

The real wastewater is the mixture of several metal matrices and interference/competition is the common among the metals and others organic and inorganic components (Raize et al., 2004). To understand the interference in a real wastewater more closely, a quaternary system of Pb-Cu(II)-Zn(II)-Cd(II) metal solution between 1 to 25 mg/L were prepared and batch isotherm experiments were conducted. The data were analysed with Langmuir quaternary system (Eq.12 to 15) and tabulated in Table 4. To visualise the interference among the four metals, a spider diagram was constructed (Fig.5). From Fig.5, a clear picture of competition was observed. The strongest interference created by the Pb(II) ions is evidenced by it occupying the highest spiral surface of the spider plot (Apiratikul and Pavasant, 2006; Raize et al., 2004). Cu(II) ions followed the Pb(II) ions in terms of the creation of interference to other metal sorption although the maximum uptake capacity for Cu(II) was the lowest (2.415 mg/g) among the four-metals (Table 4). Cd(II) and Zn(II) ions demonstrated similar adsorption on cabbage though their prediction from single and binary systems was different (Padilla-Ortega et al., 2013).

Fig. 5

The extent of adsorption of the most dominant metal ion i.e., Pb(II) ion reduced to 28.33%, 1.6% and 29.91% for the binary systems; 33%, 18% and 62.78% for the ternary systems; and 75.37% for the quaternion system. The biosorbent demonstrated the second highest adsorption
capacity for Cd(II) ions; however, it dropped to 16%, 18.50% and 26.4% for binary, 44.56%,
Acknowledgment

This research was supported by Research Theme of Sustainable Water: Wastewater Treatment and Reuse Technologies, Centre for Technology in Water and Wastewater (CTWW), School of Civil and Environmental Engineering, University of Technology, Sydney (UTS) and UTS International Postgraduate Research Scholarship.

References


Prasad, M., Saxena, S. 2004. Sorption mechanism of some divalent metal ions onto low-
Industrial & Engineering Chemistry Research, 43(6), 1512-1522.

Prasad, M., Xu, H.-Y., Saxena, S. 2008. Multi-component sorption of Pb(II), Cu(II) and
¥
©
—cost mineral adsorbent. Journal of Hazardous Materials, 154(1–3), 221-

Raize, O., Argaman, Y., Yannai, S. 2004. Mechanisms of biosorption of different heavy

onto peanut husks carbon: characterization, kinetic study and modeling. Separation and


Srivastava, V.C., Mall, I.D., Mishra, I.M. 2008. Removal of cadmium(II) and zinc(II) metal
ions from binary aqueous solution by rice husk ash. Colloids and Surfaces A:
Physicochemical and Engineering Aspects, 312(2–3), 172-184.

from aqueous solution by dried biomass of macrophytes. Bioresource Technology, 99(6),
1932-1938.

Microbiology, 3(1), 17-24.

Yakup Arıca, M., Bayramoğlu, G., Yılmaz, M., Bektaş, S., Genç, Ö. 2004. Biosorption of
Hg
2+, Cd
2+, and Zn
2+ by Ca-alginate and immobilized wood-rotting fungus Funalia trogii.

2+ and Cu
2+
by EDTAD-
List of Caption and Tables

**Table 1**
The Langmuir monolayer adsorption constant for the adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions on cabbage biosorbent at room temperature, 5g/L adsorbent dose, 2 hours, 120 rpm and pH:6.0-6.5.

**Table 2**
Calculated parameters from Langmuir model for binary adsorption of Pb(II)-Cd(II), Cd(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions on cabbage waste.

**Table 3**
Ternary adsorption parameters calculated from Langmuir model for Cu(II), Cd(II), Cu(II) and Zn(II) adsorption

**Table 4**
Isotherm parameters of Langmuir model of fourary metals [Cd(II)-Cu(II)-Zn(II)-Pb(II)] adsorption
Table 1
The Langmuir monolayer adsorption constant for the adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions on cabbage biosorbent at room temperature, 5 g/L adsorbent dose, 2 hours, 120 rpm and pH:6.0-6.5.

<table>
<thead>
<tr>
<th>Langmuir isotherm model</th>
<th>Equilibrium parameters</th>
<th>Cu(II) adsorption</th>
<th>Pb(II) adsorption</th>
<th>Zn(II) adsorption</th>
<th>Cd(II) adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$</td>
<td>$q_m$ (mg/g)</td>
<td>12.955±0.45</td>
<td>61.267±0.85</td>
<td>10.890±0.72</td>
<td>22.123±0.67</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>10.315±0.32</td>
<td>60.568±0.38</td>
<td>8.970±0.56</td>
<td>20.568±0.23</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/g)</td>
<td>0.022</td>
<td>0.021</td>
<td>0.019</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.991</td>
<td>0.996</td>
<td>0.997</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.383</td>
<td>8.219</td>
<td>0.189</td>
<td>8.219</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.081</td>
<td>2.555</td>
<td>0.357</td>
<td>2.554</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.21-0.92</td>
<td>0.27-0.98</td>
<td>0.18-0.95</td>
<td>0.28-0.99</td>
</tr>
</tbody>
</table>
Table 2
Calculated parameters from Langmuir model for binary adsorption of Pb(II)-Cd(II), Cu(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions on cabbage waste.

<table>
<thead>
<tr>
<th>Pb(II)-Cd(II)</th>
<th>Cu(II)-Zn(II)</th>
<th>Cu(II)-Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pb(II)-Zn(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Pb(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Pb = 42.942±0.88$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Pb = 0.036±0.006$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Zn = -0.050±0.035$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2 = 0.997$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Zn(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Zn = 9.460±0.92$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Zn = 0.036±0.012$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Cu = -0.050±0.005$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2 = 0.997$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cd(II)-Zn(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Cd(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Cd = 18.030±0.78$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Cd = 0.060±0.005$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Zn = -0.044±0.0019$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2 = 0.999$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Zn(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Zn = 11.053±0.34$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Zn = 0.060±0.004$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Cu = -0.044±0.001$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2 = 0.998$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cd(II)-Cu(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Cd(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Cd = 16.280±0.95$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Cd = 0.041±0.002$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Cu = -0.0306±0.001$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2 = 0.999$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Cu(II):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m,Cu = 16.660±0.81$ mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L,Cu = 0.041±0.003$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_S,Cu = -0.0306±0.001$ L/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R2 = 0.999$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3
Ternary adsorption parameters calculated from Langmuir model for Pb(II), Cd(II), Cu(II) and Zn(II) adsorption

<table>
<thead>
<tr>
<th></th>
<th>Cd(I)·Pb(II)·Cu(I)</th>
<th>Cd(I)·Pb(II)·Zn(I)</th>
<th>Cu(I)·Cd(II)·Zn(I)</th>
<th>Cu(I)·Pb(II)·Zn(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(I)·Pb(II)·Cu(I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(I)·Pb(II)·Zn(I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(I)·Cd(II)·Zn(I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(I)·Pb(II)·Zn(I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4
Isotherm parameters of Langmuir model of quaternion metal [Cd(II)-Cu(II)-Zn(II)-Pb(II)] adsorption system

<table>
<thead>
<tr>
<th></th>
<th>For Cd(II)</th>
<th>For Cu(II)</th>
<th>For Zn(II)</th>
<th>For Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{m-Cd}$</td>
<td>8.697±1.53 mg/g</td>
<td>2.415±0.82 mg/g</td>
<td>10.170±1.77 mg/g</td>
<td>15.085±0.78 mg/g</td>
</tr>
<tr>
<td>$K_{L-Cu}$</td>
<td>0.0034±0.001 L/g</td>
<td>-0.039±0.004 L/g</td>
<td>-0.063±0.007 L/g</td>
<td>-0.052±0.007 L/g</td>
</tr>
<tr>
<td>$K_{L-Cd}$</td>
<td>0.050±0.006 L/g</td>
<td>0.038±0.007 L/g</td>
<td>0.004±0.001 L/g</td>
<td>0.055±0.002 L/g</td>
</tr>
<tr>
<td>$K_{L-Zn}$</td>
<td>-0.014±0.006 L/g</td>
<td>-0.022±0.0003 L/g</td>
<td>0.029±0.005 L/g</td>
<td>-0.034±0.004 L/g</td>
</tr>
<tr>
<td>$K_{L-Pb}$</td>
<td>-0.015±0.008 L/g</td>
<td>0.029±0.0016 L/g</td>
<td>0.038±0.007 L/g</td>
<td>0.038±0.001 L/g</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
<td>0.998</td>
<td>0.999</td>
<td>0.998</td>
</tr>
</tbody>
</table>
**List of Captions and Figures**

**Fig.1.** Effect of pH on Cd(II), Cu(II), Zn(II) and Pb(II) adsorptions ($C_0 = 10$ mg/L; dose = 0.5 g/100 ml).

**Fig.2.** Antagonism among the metals for Cu(II)-Zn(II) (A&B) and Pb(II)-Cd(II) (C&D) binary system.

**Fig.3.** Antagonism among the metals for Cd(II)-Zn(II) (A&B), Cu(II)-Cd(II) (C&D) and Pb(II)-Cu(II) (E&F) binary system.

**Fig.4.** Occupied physical surface area of metals in terms of capacity for ternary metals adsorption system onto cabbage.

**Fig.5.** Engaged area in terms of capacity of metals in spider diagram for quaternary metals adsorption onto cabbage.
Fig. 1. Effect of pH on Cd(II), Cu(II), Zn(II) and Pb(II) adsorptions (C₀ = 10 mg/L; adsorbent dose = 5g/L). Error bars show the standard deviation of three replicate experiments.
Fig 2. Antagonism among the metals for Cu(II)-Zn(II) (A&B) and Pb(II)-Cd(II) (C&D) binary system
Fig. 3. Antagonism among the metals for Cd(II)-Zn(II) (A&B), Cu(II)-Cd(II) (C&D) and Pb(II)-Cu(II) (E&F) binary system.
Fig. 4. Occupied physical surface area of metals in terms of capacity for ternary metals adsorption system onto cabbage.

Fig. 5. Engaged area in terms of capacity of metals in spider diagram for quaternary metals adsorption onto cabbage.
Highlights

- Modified Langmuir model described well the multi-metal adsorption system.
- Adsorbent from cabbage waste is effective for Pb(II) and Cd(II) adsorption.
- High interference among the metals was observed in a multi-metal system.
- Adsorption capacity was suppressed by the presence of other metal ions.
- The highest reduced in adsorption capacities were found for Pb(II), Zn(II) and Cd(II).