

Biosorption of Lead(II), Copper(II) and Cadmium(II) in Single - and Multi-metal Systems by Aerobic Granule Sludge by Fixed-Bed Column and Batch Sorption

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Abstract: Heavy metals are present in nature and industrial wastewater. Due to their mobility in natural water ecosystems and toxicity, the presence of heavy metals in surface water and ground water has become a major inorganic contamination problem. Discharge and treatment of industrial wastewater containing heavy metals are important issues in environmental protection. If unrecognized or inappropriately treated, heavy-metal toxicity can result in serious hazards. The present work describes our study on the biosorption Lead (II), copper (II) and cadmium (II) ions onto aerobic granular sludge from single component and multi systems. Results showed that aerobic granules as a novel effective biosorbent for Pb^{2+} , Cu^{2+} and Cd^{2+} ions removal. The metal removal capacity of aerobic biomass were six times higher than that of activated carbon, especially the cadmium removal capacity of aerobic biomass was very high. The biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from multi metals system were studied in equilibrium systems and in both batch sorption experiment and continuous flow column. The single-metal sorption uptake capacity of the aerobic granules for Pb^{2+} was slightly inhibited by the presence of Cd^{2+} only 17.9 % and by the presence of Cu^{2+} ion by 25.6 %. The affinitive order of aerobic granular sludge for the three metal ions was established as: $Pb^{2+} > Cu^{2+} > Cd^{2+}$. Factors such as hydration effects and electronegative ions may contribute to the competitive sorption results.

Keywords: Aerobic granule, biosorption, competitive sorption, Cd (II), Pb(II), Cu(II).

1. Introduction

The application of aerobic granular sludge has been regarded as one of the promising processes in wastewater treatment, and was developed for treating high-strength

wastewaters containing organics, nitrogen, phosphorus, toxic substances and xenobiotics (Adav et al., 2008). Several review papers were published in the last 5 years, and they covered almost every aspect of aerobic granulation (Liu, Tay, 2004; Adav et al., 2008; Kreuk, 2007). Compared to conventional activated sludge, aerobic granular sludge has the advantages of

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excellent settle ability, dense and porosity microbial structure, suggesting that it could satisfy the basic requirements for biosorbents for heavy removal. Unlike anaerobic granulation technology which needs a long cultivation period, aerobic granular sludge could be rapidly cultivated using activated sludge as seed in sequencing batch reactors (SBRs), with a wide variety of feed substrate, including glucose, acetate, ethanol, phenol, synthetic wastewater and real wastewater (Adav et al., 2008). In a batch system, it could not only be used for pollution control, but also be used as biosorbent for heavy-metal ion removal from industrial wastewater streams with a high sorption capacity.

Heavy metal wastewater has become a global environmental concern due to serious health threaten to humans and ecosystems (Srivastava et al., 2008; Karvelas et al., 2003). Lead (II), Copper (II) and Cadmium (II) ions were supposed to be the main heavy-metal ions in the wastewater of the battery factory. In my country, the battery factory, every year discharges a lot of amounts of wastewater; it means that discharged a significant quantity of Lead (II), Copper (II) and Cadmium (II) ions into aquatic ecosystems. As a result, removal and recovery of heavy metals from industry wastewater before biological treatment have gained significant attention in recent years to protect the environment.

Recent studies have focused on the biosorption process as an alternative method to remove toxic metals from wastewater due to its advantages such as low cost, short operation time, and reuse ability of the biomaterial (Yao et al., 2009; Volesky, 2007; Wang, 2006). Numerous studies have reported the biosorption of heavy-metal ions onto aerobic granular sludge. Those studies were aimed to determine

the mono metal ion biosorption capacity and equilibrium isotherms (Liu Y et al., 2003; Zhang et al., 2005; Nancharaiah et al., 2006b; Yao et al., 2009). Other studies were aimed to determine the metal ion biosorption mechanism (Nancharaiah et al., 2006b; Xu, Liu, 2008; Yao et al., 2009). Sun et al., 2008 study about binary metal adsorption, competitive adsorption.

Heavy metal removal capacity by dead biomass was always lower than live biomass. However, the use of non-viable biomass offers the following advantages over viable cells. The metal removal system is not subject to toxicity limitations, no requirements for growth media and nutrients. The biosorbed metal ions can be easily desorbed and biomass that can be reused, much simpler process control. The biomass can be stored for a long period of time, and the biosorption tend to be rapid (Hawari et al., 2006).

According to Yan and Viraraghavan, pre-treatment of the biomass would expose more available binding sites to metal biosorption and would remove surface impurities from the biomass (Yan et al., 2000). Modification of a biomass by using chemical pretreatments such as using acids, alkalis and organic chemicals showed enhancement or improvement in metal biosorption (Zubair et al., 2008).

A limited number of the study reported about the binary, ternary-metal system competitive adsorption by pretreated aerobic granular sludge.

Therefore, the main objectives of our research are: to investigate the Lead (II), Copper (II) and Cadmium (II) - binding capacity of pretreated aerobic granular sludge at optimal pH sorption under single - and multi-metal system; To identify the adsorption mechanism in the competitive

condition; To compare with previous experimental data obtained for other adsorbent at equivalent conditions.

2. Methods

2.1. Preparation of biomass

Aerobic granular sludge used for biosorption test was collected from an environmental laboratory of Kunming University of Science and Technology. Aerobic granules after cultivating in SBR fed with glucose as sole carbon for 2 months have the ratio protein/polysaccharide (PN/PS) 4.5.

The collected aerobic granules were washed with water three times and centrifuged at 2000 rpm for 10 min to remove supernatant, dried at 60 °C until constant weight and then ground to a gritty consistency to yield granular biosorbent samples, that was used for batch biosorption tests.

The dried aerobic granules biomass was ground and sieved into different size fractions. The fraction collected between mesh sizes 16 and 20, corresponding to a particle size ranging from 0.84 to 1.18 mm, was used in the continuous column experiments. This particle size would ensure a low pressure drop or that no clogging of the column would occur.

2.2. Batch biosorption studies

Batch Isotherm experiments were conducted using 500 mL Erlenmeyer flasks at temperature 25°C for mono-heavy metal Pb^{2+} , Cu^{2+} and Cd^{2+} adsorption at pH 5.0.

0.2 g dry of biomass was added into the 200 mL solutions containing heavy metal concentrations of 25-500 mg/L. After 24 h of biosorption, samples were taken from the

solutions subsequently centrifuged at 7500rpm for 10 minutes, the solution suspensions were filtered through 0.45 μm cellulose-acetate membrane. The heavy metal concentration in supernatants was measured. Release of Ca^{2+} , Mg^{2+} and K^{+} ions from biomass as a result of biosorption of metal ions were also studied.

Batch isotherm experiments were also conducted for the interactive biosorption among Pb^{2+} , Cu^{2+} and Cd^{2+} . The experiments were carried out at pH 5.0 for the following metal ions combinations: Pb^{2+} - Cu^{2+} , Pb^{2+} - Cd^{2+} , Cu^{2+} - Cd^{2+} , Pb^{2+} - Cu^{2+} - Cd^{2+} .

Transfer 0.2 g dry biomass into a conic flask containing 200 ml of binary, ternary metal-bearing solution, with concentration was 1mmol /L. After 24 h sorption at 25°C, the metal-loaded biomass was harvested, the heavy metals in this biomass were determined.

2.3. Multi-heavy metals uptake in a fixed-bed column

Equimolar metal solution was used for the multi-heavy metals system biosorption tests. The experiments were carried out following metal ions combinations: Pb^{2+} - Cu^{2+} - Cd^{2+} . Eleven grams of dry aerobic biomass were packed into a 15 cm long column of 2.0 cm inner diameter. A bed of 2 mm diameter glass spheres was placed at the bottom of the column prior the active biomass bed to ensure homogeneous distribution of the feeding solution.

The metal solution was pumped from a 2.5 L storage tank into the column. The initial concentration of each metal was 1 mmol/L. The pH value in the storage tank was adjusted to 5.0 using a 0.1 N HCl solution. The mixed metal solution was fed into the column from the top, at a flow rate equal to 1.5 mL/min which allowed 30 min of detention time in the column.

Samples of column effluent were collected from the bottom by means of a fraction collector at 30 min time intervals and were analyzed for heavy metals content using the atomic absorption spectrophotometer. When the biomass in the column was saturated with the metals, that is, the final column effluent concentration approached the influent concentration the column feed was switched to distilled water for several hours and then followed by a 0.1 N HCl solution in order to elute the heavy metals.

2.4. Analytical methods

Atomic Absorption Spectrometer (Varian Model-240FS, England) was used to analyze Pb^{2+} , Cu^{2+} and Cd^{2+} ion concentrations in sample solutions and in the biomass after digested by aqua regia solution.

Inductively Coupled Plasma (ICP) (IRIS Intrepid II XSP, American) was used to analyze Ca^{2+} , Mg^{2+} and K^{+} released into the solution during biosorption experiment.

2.5. Theoretical backgrounds

With non-linearized form Lagergren pseudo first order equation

$$q_t = q_e(1 - e^{-K_1 t})$$

K_1 = Lagergren rate constant for adsorption (h⁻¹);

q_e = amount of metal ion adsorbed at equilibrium (mg/g)

q_t = amount of metal ion adsorbed (mg/g) at any given time t (h).

Non-linearized form HO's pseudo second order

$$\frac{t}{q_t} = \frac{1}{2K'q_e^2} + \frac{t}{q_e}$$

K' = second order reaction rate constant for adsorption (g/mg.h);

The Langmuir isotherm Equation

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}$$

Q^0 = the monolayer adsorption capacity (mg/g)

b = the constant related to the free energy of adsorption

C_e = concentration of solute in solution at equilibrium (mg/L),

Freundlich isotherm Equation

$$q_e = K C_e^{1/n}$$

K = equilibrium constant indicative of adsorption capacity

n = adsorption equilibrium constant

3. Results and discussion

3.1. Kinetic studies

The non-linearized form of the Lagergren pseudo first order and HO's pseudo second order reaction rate model was used to analyze the adsorption kinetics. Batch kinetic data was fitted to the model by non-linear regression analysis with software package Originlab 8.0.

Adsorption kinetic constants and correlation coefficients at initial Pb^{2+} , Cu^{2+} and Cd^{2+} concentrations C_e values 200mg/L are given in Table 1. Compared correlation coefficients between the pseudo-first-order and pseudo second-order, it can be noticed that the correlation coefficients of the pseudo-first-order model higher than of second-order (0.98- 0.99). Therefore, the pseudo-first-order model was more suitable to describe the kinetic biosorption

Pb²⁺, Cu²⁺ and Cd²⁺ process accurately. Similar result has been observed in the adsorption of Pb²⁺ on aerobic granular biomass (L.Yao et al., 2008). Gai et al., reported that the

biosorption of Cu²⁺ follow the pseudo second-order (L.H.Gai et al., 2008), that difference may be due Cu²⁺ adsorption by live aerobic granular biomass.

Table 1. Comparison of pseudo-first-order and pseudo-second-order adsorption rate constants at pH 5.0 and C_e values 200mg/L

Metal ion uptake by biomass	First-order kinetic model			Second-order kinetic model		
	K1 (1/min)	Q1 (mg/g)	R21	K' (1/mg.min)	Q2 (mg/g)	R22
Pb ²⁺	0.169	163.41	0.99	0.001	164.14	0.97
Cu ²⁺	0.11	58.14	0.98	0.001	71.9.03	0.97
Cd ²⁺	0.145	161.71	0.98	0.001	188.61	0.97

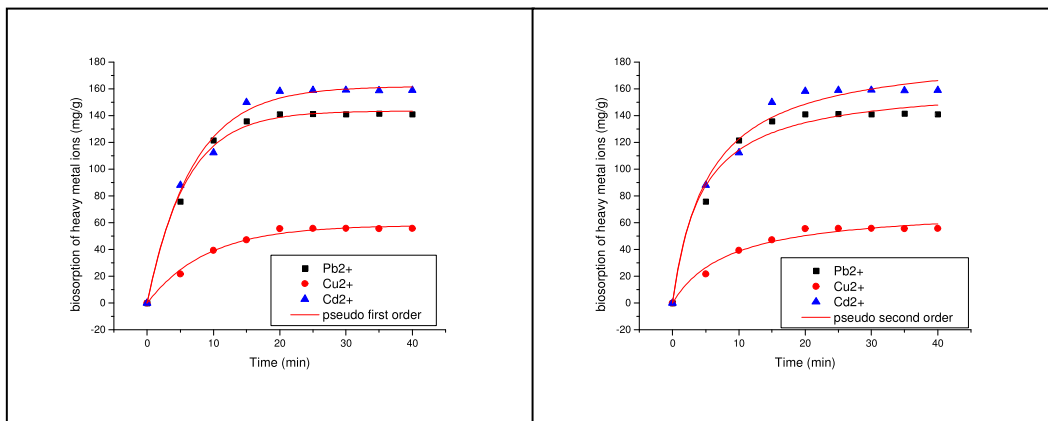


Fig 1. Experimental data points and prediction curves for the Lagergren and Ho's model applied to biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ on aerobic granule.

Table 2. Comparison of adsorption parameters calculated using Langmuir and Freundlich isotherms for biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ by aerobic granules

Metal ions	Langmuir model			Freundlich model			Q _{maxexp}
	Q _{max}	b	R ²	K	1/n	R ²	
Pb ²⁺	161.31	0.02	0.94	15.37	0.421	0.95	162.33
Cu ²⁺	55.74	0.07	0.95	18.30	0.208	0.96	55.77
Cd ²⁺	158.97	0.02	0.94	12.95	0.460	0.93	158.93

Q_{max} sorption capacity mg/gDW; Q_{maxexp}: maximum adsorption capacity experiment

Q_{maxexp}: the maximum metal ions uptakes by biomass after the sorption process reach equilibrium.

Figures 1 show the Pb^{2+} , Cu^{2+} and Cd^{2+} concentration profiles versus agitation time of aerobic granules, adsorption at initial 200mg/L concentration and pH values 5.0. It can be seen that biosorption consisted of two phases: a primary rapid phase and a second slow phase.

The rapid phase was fast and accounted for the major part in the total metal biosorption, while the second phase was slow and contributed to a relatively small part. The time of first phase very rapid, within the first 15 min of contact, nearly 78% of the total metals uptake was completed. The first phase of metal biosorption may be attributed to the surface adsorption due to the action of ion exchange with the participation of some functional groups; while the second slower phase may represent metal ions competition sorption with another light metal in the biomass structure.

In this study, biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} on aerobic biomass reached equilibrium in 20 minute. The reasons attributed to many factors such as function group on biomass, surface area of the biomass, and may be due to mechanisms like adsorption of metal ions on activated carbon.

3.2. Biosorption of single metal ions in batch system

Batch isotherm studies were carried out to study biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} on aerobic granule sludge at optimal sorption pH 5.0 values. The Langmuir and Freundlich models were used to describe adsorption. The batch isotherm data was fitted to the models using non-linear regression analysis with the software package Originlab 8.0.

A comparison of model parameters obtained using both models are shown in Table 2. According to the statistical significance obtained for the Langmuir and Freundlich isotherm models for sorption of Pb^{2+} , Cu^{2+} and

Cd^{2+} on aerobic biomass, it could be seen that both models can be used to describe the metal biosorption. The results show that the Freundlich model was better than the Langmuir model to describe the Pb^{2+} and Cu^{2+} ions biosorption on this studied biomass. The maximum capacity Q_{max} determined from the Langmuir model fit in experiment data.

On the contrary, the Langmuir model was better than the Freundlich model to describe the Cd^{2+} ions biosorption on aerobic biomass. It may be the biomass component and chemical property of Cd^{2+} are complex.

To facilitate a comparison with the results presented here, the units for sorption capacity were converted from mg/g to mmol/g. The maximum capacity metal uptake values of the non-viable aerobic biomass were compared with the metal adsorption capacities reported for other adsorbents, namely, activated carbon, waste adsorbents, fungus, brown alga and some commercial cation exchange resins (Table 3) with the same adsorbed condition. The metal removal capacity of aerobic biomass was higher than that of activated carbon in the granular or powder form. Comparing to solid waste and fungus, aerobic biomass appeared to be more efficient in metal uptake than sugar beet pulp, activated sludge, *Penicillium chrysogenum*, and *Rhizopus arrhizus* fungus.

Lead removal capacity of aerobic biomass was lower than Amberlite IRC-718, *Ascomyllum nodosum*, *Sargassum natans* and anaerobic biomass biosorbents

Comparing to result of Y. Liu et al., show that Cu^{2+} and Cd^{2+} removal capacity in our studied results were lower, because of the result of their research on live biomass. However, the use of non-viable aerobic biomass offers the following advantages over viable cells: a metal removal system that is not subject to toxicity

limitations, no requirements for growth media and nutrients, biosorbed metal ions that can be easily desorbed and biomass that can be reused, much simpler process control, biomass can be stored for a long period of time, and biosorption that tends to be rapid (A.H. Hawari et al 2006).

More generally, cadmium removal capacity of aerobic biomass was higher than most of the biosorbents. The considerably lower cost of the aerobic biomass, its physical characteristics and the high uptake capacity of the heavy metals makes it a very attractive biosorbent.

Table 3. Comparison of metal adsorption capacities (mmole/g) of activated carbon, commercial resins, brown algae, fungus, and selected solid waste

Adsorbent		Pb ²⁺	Cu ²⁺	Cd ²⁺	pH	Reference
Activated carbon (AC)	Granular AC	0.08	0.08	0.03	5.0	An et al. (2001)
	Powder AC	0.13	0.07	0.03	5.0	An et al. (2001)
Commercial resins	Duolite GT-73	0.59	0.97	0.94	4.8	Vaughan et al. (2001)
	Amberlite IRC-718	1.40	2.00	2.30	4.8	Vaughan et al. (2001)
	Lewatit TP207	0.96	1.34			Brown et al. (2000)
Brown algae	Ascophyllum nodosum	1.31		1.18	3.5	Thomas et al. (2003)
	Sargassum natans	1.22		1.17	3.5	Thomas et al. (2003)
Fungus	Penicillium chrysogenum	0.59	0.14	0.50		Volesky and Holan (1995)
	Rhizopus arrhizus	0.44	0.16	0.24		Volesky and Holan (1995)
	Sugar beet pulp	0.36	0.33	0.22	5.5	Reddad et al. (2002)
Waste sorbents	Anaerobic biomass	1.25	0.87	0.53	5.0	A. H. Hawari et al. (2006)
	Aerobic biomass		0.94	1.54	4.0	Y. Liu et al. (2003)
	Aerobic biomass	0.78	0.88	1.41	5.0	This study

Blank spaces denote data not available

3.3. Biosorption of binary and ternary metals Pb²⁺, Cu²⁺ and Cd²⁺ by aerobic granular sludge

3.3.1 Biosorption of multi metal ions in batch system

The uptake capacity by the biomass of Pb²⁺, Cu²⁺ and Cd²⁺ by aerobic granular sludge in the batch system was shown in Table 4.

Di-metal competition sorption Pb-system

The uptake capacity by the biomass of lead alone and in the presence of Cu²⁺ and Cd²⁺ was evaluated. The result in Table 4 demonstrates that the single-metal sorption uptake capacity of the biomass for Pb²⁺ was inhibited by the presence of

the Cu²⁺ in the system. The presence of Cu²⁺ ion in separate systems reduced the biomass uptake capacity of Pb²⁺ by 25.6 %.

The single-metal sorption uptake capacity of the biomass for Pb²⁺ was slightly inhibited by the presence of the Cd²⁺ in the system. The presence of Cd²⁺ ion in separate systems reduced the biomass uptake capacity of Pb²⁺ by only 17.9 %

Cu-system

The uptake capacity of copper alone and in combination with other single metals by the biomass was determined. The result in Table 4 demonstrates that the single-metal sorption

uptake capacity of the biomass for Cu^{2+} showed very sensitivity to the presence of Pb^{2+} cations, 59.1 % reduction on the uptake capacity was observed for aerobic biomass. This could indicate the higher selectivity of the biomass for Pb^{2+} over Cu^{2+} for studied biomass.

The result in Table 4 demonstrates that, the presence of Cd^{2+} cations inhibited the uptake of the Cu^{2+} cations, the biomass uptake capacity for Cu^{2+} was reduced almost 20.5 % than the single Cu^{2+} uptake capacity for this studied biomass.

Table 4 Binary and ternary metals sorption

Heavy metals	Biosorption capacity	Total metal adsorbed in the systems
Pb ²⁺	0.78	
Cu ²⁺	0.88	
Cd ²⁺	1.41	
Pb ²⁺ - Cu ²⁺		
Pb ²⁺	0.58	0.94
Cu ²⁺	0.36	
Pb ²⁺ - Cd ²⁺		
Pb ²⁺	0.64	0.99
Cd ²⁺	0.35	
Cu ²⁺ - Cd ²⁺		
Cu ²⁺	0.62	0.98
Cd ²⁺	0.36	
Cu ²⁺ - Cd ²⁺ - Pb ²⁺		
Pb ²⁺	0.41	0.99
Cu ²⁺	0.36	
Cd ²⁺	0.22	
Biosorption capacity mmol/gDW		

Cd-system

Experiments to evaluate the uptake capacity of cadmium were performed. Table 4 indicates that Cd^{2+} was the least favorable to be adsorbed by the biomass among the two other metals

studied. The presence of Pb^{2+} cations inhibited the uptake capacity of Cd^{2+} by 75.1 %, which is higher than the case in the Pb-system where Pb^{2+} uptake capacity was reduced by only 17.9 % in the presence of Cd^{2+} cations. The presence of Cu^{2+} cations inhibited the uptake capacity of Cd^{2+} by 74.4 %, which is higher than the case in the Cu-system where Cd^{2+} inhibited the uptake capacity of Cu^{2+} by 20.51% by this studied biomass.

Tri-metal competition sorption

At equilibrium, the main metal uptake were Pb^{2+} , Cu^{2+} , in the system have the competition between three metals with each other, but affinity absorption of Pb^{2+} and Cu^{2+} were higher than Cd^{2+} , so the Cd^{2+} uptake decrease from 1.41 to 0.22 mmol/g DW.

The results from the competition experiments of equimolar binary solutions of Pb^{2+} , Cu^{2+} and Cd^{2+} , are summarized in Table 4. The total metal adsorbed (last column of Table 4.17) increased in all cases compared to the values obtained for each metal in single-metal tests except in Cd^{2+} case. In spite of that, the total capacity of adsorption was always lower than the sum of the individual adsorption capacities of each metal taking part in the test. The decrease of adsorption capacity compared to the single-metal systems observed for Pb^{2+} , Cu^{2+} ion, it reflects the existence of competition between the three metals studied for the binding sites present in the cell wall. For Cd^{2+} in single-metal tests the capacity uptake highest, but in the competition sorption system, the presence of Pb^{2+} and Cu^{2+} cations inhibited the uptake capacity of Cd^{2+} it can be explained in the mechanism section.

For comprehensive multi metals competitive adsorption process, the multi-heavy metal uptake in a fixed-bed column was explained in next section.

3.3.2 Biosorption of multi metal ions in a fixed-bed column

As can be seen from the previous section the feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on the composition of the wastewater. To confirm the competition between metals for the binding sites of the aerobic granule sludge established in multi-metal systems, an adsorption test in a flow-through column was undertaken. The column was fed with an equimolar mixture of Pb^{2+} , Cu^{2+} , and Cd^{2+} .

The selectivity of the biomass for Pb^{2+} over the other two metals is exhibited by the results obtained using the flow-through column. Fig. 2 displays the concentrations of Pb^{2+} , Cu^{2+} , and Cd^{2+} in the column effluent as a function of

bed volumes for the sorption experiment during which the column packed with the biomass was fed with an equimolar mixture of the each metals 1 mmol/L. As can be seen in Fig. 2, Cd^{2+} due to its low affinity, broke through the column faster than Pb^{2+} and Cu^{2+} at the 16 bed volume mark. Also Cu^{2+} broke through the column faster than Pb^{2+} at the 24 bed volume mark. Lead ion was the last metal to break through the column at the 28 bed volume mark.

At approximately the 20, 31, and 35 bed volume marks, the concentrations of Cd^{2+} , Cu^{2+} , and Pb^{2+} in the column effluent plotted in Fig. 2 reached the levels of Cd^{2+} , Cu^{2+} , and Pb^{2+} in the feed, i.e. $(C/C_0)=1$, respectively. At this point, the column feed was completely in equilibrium with all metal ions adsorbed on the biomass.

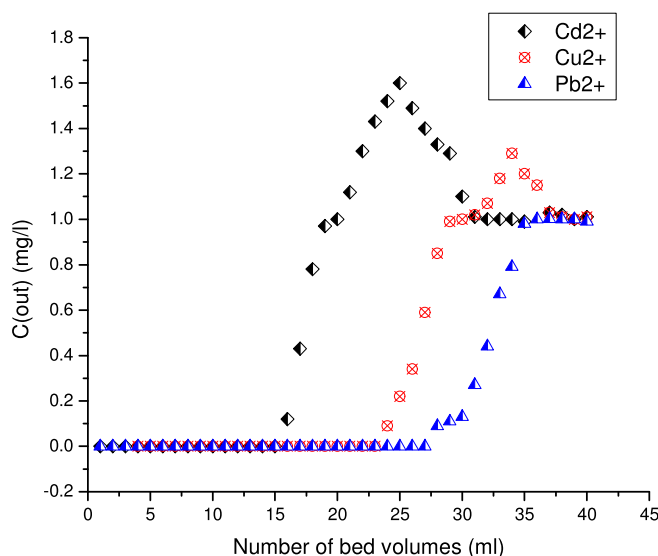


Fig 2. Breakthrough curves of equimolar mixture of Pb^{2+} , Cu^{2+} , and Cd^{2+} from a flow-through column.

Subsequently, thereafter Cd^{2+} , and Cu^{2+} were no longer taken up by the biosorbent and hence trickled through the packed-column as an inert. The fact that the C/C_0 for Cd^{2+} , and Cu^{2+} continued rising above 1 value in Fig. 2 even

after 20, and 31 bed volumes, respectively, may be explained by the ion exchange between Cd^{2+} and Cu^{2+} and Pb^{2+} , whereby Pb^{2+} and Cu^{2+} from the solution were displacing Cd^{2+} bound to the biosorbent, Pb^{2+} also displaced Cu^{2+} bound to

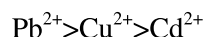
the biosorbent. Since no more Cd^{2+} and Cu^{2+} were being adsorbed from the liquid beyond 20 and 31 bed volumes, respectively, the released Cd^{2+} and Cu^{2+} increased the overall concentrations of Cd^{2+} , and Cu^{2+} in the liquid above the levels present in the column influent.

This phenomenon is commonly referred to as ‘‘over-shooting’’ (M.M Figueira et al., 2000; Senthilkumaar S et al 2000). The overshooting of Cd^{2+} is caused due to an ion exchange effect, whereby the high affinity Cu^{2+} and Pb^{2+} desorbed the low affinity Cd^{2+} which had previously adsorbed on to the biomass in the bed.

The high affinity Pb^{2+} also desorbed the lower affinity Cu^{2+} which had previously adsorbed on to the biomass and this caused the overshoot of Cu^{2+} . The fact that no overshoot of Pb^{2+} occurred shows the high affinity of Pb^{2+} to the biomass compared with the other two metals. The two other metals could not desorb Pb^{2+} bound to the biosorbent. Therefore, the overshoot provides yet another piece of evidence that the principal mechanism of biosorption in the aerobic biomass is ion exchange. The overshoot phenomenon was reported by A.H. Hawari et al when they studied effect of the presence of lead on the biosorption of copper, cadmium and nickel by anaerobic biomass (A.H. Hawari et al 2007).

The condition under which overshoots occur can be formulated as follows: low affinity species present in the feed solution would overshoot in the column effluent only if a species with higher affinity is present in the feed solution.

The overshoot peak depends on the relative affinity of the individual metals for the biosorbent. Comparing the peaks obtained from Fig. 2, the affinity order of aerobic biomass for the three metals under study would be established as:



Consequently, a metal species may or may not overshoot in the column effluent depending on the metal species in the influent solution. Effluents containing one toxic species at a relatively high level in combination with one or more heavy metals at low levels may not be considered toxic represent a special class of heavy metal pollution.

The results in the section 3.2 and 3.3 indicated that in the multi metal sorption system, when redundant adsorbent the biosorption follow single metal sorption order, in the system is shorted of adsorbent that occur competitive sorption follow of order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$.

3.4. Sorption mechanism

In order to investigate the mechanisms of mono heavy metal biosorption by aerobic granules, concentration analyses of light metal ions in the solution before and after biosorption experiments were conducted.

The amount of released Ca^{2+} is far larger than the other two light metal ions (Mg^{2+} and K^+). The ratio of total released Ca^{2+} , Mg^{2+} and K^+ to the biosorbed heavy metal was 74.01, 71.03 and 62.97 % for Pb^{2+} , Cu^{2+} and Cd^{2+} , respectively. The simultaneous release of light metals with the uptake of heavy metals by aerobic granules may indicate that an ion exchange mechanism would be involved, but the observed non-stoichiometric exchange of ion also shows that the ion exchange mechanism was not the sole mechanism involved in Pb^{2+} , Cu^{2+} and Cd^{2+} biosorption by aerobic granules.

In study of metal biosorption by anaerobic granules, A.H. Hawari et al reported that 77, 82 and 50% of adsorbed copper, cadmium and lead

would be attributed to an ion exchange mechanism (A.H. Hawari et al., 2006). H. Xu and Y.liu reported that 75.5, 71.3 and 82.4 % of adsorbed cadmium, copper and nickel on aerobic granule sludge would be attributed to an ion exchange mechanism (H.Xu and Y.liu., 2008). Furthermore, Schneider et al., 2001) demonstrated that the surface group responsible for metal exchange was primarily the carboxylate group, while Tsezos and Volesky reported the bivalent metal ions exchange with counter ions of polysaccharides.

The result demonstrated that ion exchange is a main mechanism of the biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} by aerobic granular sludge.

The comparison classification categorized metals into three broad categories: those that are polarizable or ‘‘soft’’, those that are non-polarizable or ‘‘hard’’ and those that are borderline (Williams CJ et al 1998).

Pb^{2+} and Cu^{2+} ions are classified in the borderline category according to this classification, while Cd^{2+} ions fall into the soft category (Sen Gupta AK. 2000). Soft cations form more stable complexes with soft donors while hard cations prefer hard donors (Buffle J. 1988). Examples of hard ligands are carbonate, phosphate, sulfate, carboxylate and hydroxyl groups, while soft ligands include sulfhydryl and amino groups (Bell CF. 1977).

Because of the aerobic component have the ratio protein/polysaccharide (PN/PS) 4.5, it mean that amino groups more than other function groups therefore Cd^{2+} ions were the most favorable by the biomass in the single metal system.

The mechanism of multi metal ions biosorption in the competitive system depends upon other different factors, such as hydration effects, electronegative ions and covalent binding of a metal ion.

Table 5. Parameters characterizing the binding strength of metals

Ion	Charge, za	Ionic radius rcryst (Å)	Hydrated ion Radius rhyd (Å)	Pauling electronegativity	Parameter for covalent binding $x2(rcryst + 0.85)$ (Å)
Pb ²⁺	2	1.19	4.01	2.33	7.18
Cu ²⁺	2	0.74	4.19	1.90	6.41
Cd ²⁺	2	0.95	4.26	1.69	5.53
			(Alloway BJ. 1990)	(Nieboer E. 1973)	(Jain MK. 1970)

Multi-component systems have additional features versus those of single components. Interaction effects are possible between different species in solution and potential interactions on the surface. Surface interactions depend on both the sorption mechanism and reversibility.

In order to assess the mechanism of the adsorption for three metal ions on the aerobic granule sludge a number of ionic properties are collected and presented in Table 5.

The hydrated radii of Pb^{2+} , Cu^{2+} and Cd^{2+} are 4.01, 4.19 and 4.26 Å respectively; therefore, Pb^{2+} have more accessibility to the surface and pores than Cu^{2+} and Cd^{2+} cations which occurs to the adsorption follow of $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The theory that fit to studied results of biosorption of multi metal ions in a fixed-bed column.

In general, the larger the effective hydrated radius, the larger the hydration energy of an ion (Russell JB 1980). Hydration effects can

dominate when the binding is weak (Jain MK 1980). In this case, larger ions (comparing crystal radii of ions of the same charge) that are less strongly hydrated are preferably accumulated at the interface. However, the larger ions may fit into a binding site and bind to several groups simultaneously (Haug, A 1970).

More electronegative ions will be more strongly attracted to the surface. Pb^{2+} has the highest adsorption capacity and highest electronegativity (G. McKay 1997). Competition of Pb^{2+} , Cu^{2+} and Cd^{2+} ions for surface sites occurs and depends on the ion's characteristics. First Pb^{2+} ions dominate sorption surface area of aerobic granules so the sorption capacity for Pb^{2+} in the ternary systems is always significantly greater than Cu^{2+} and Cd^{2+} ions follow by sorption capacity for Cu^{2+} greater than Cd^{2+} . Thus, the relative electronegative orders are good quantitative indicators of the relative sorption capacities of multi component metal ion systems.

Table 5 also shows that the more adsorbed lead and copper ions have higher strengths of covalent binding than the lower affinity metal ions cadmium

4. Conclusions

This study investigated the feasibility of aerobic granules as a novel effective biosorbent for Pb^{2+} , Cu^{2+} and Cd^{2+} ions removal. The main conclusions can be drawn as follows:

1. The pseudo-first-order model was more suitable to describe the kinetic biosorption Pb^{2+} , Cu^{2+} and Cd^{2+} process accurately, biosorption of metal ions on aerobic biomass reached equilibrium in 20 minute.

2. The Freundlich model was better than the Langmuir model to describe the Pb^{2+} and Cu^{2+} ions biosorption on this studied biomass. The

maximum capacity Q_{max} determined from the Langmuir model was fitted to experiment data. The metal removal capacity of aerobic biomass were six times higher than that of activated carbon, especially the cadmium removal capacity was very high.

3. The biosorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from multi metals system were studied in equilibrium systems and in both batch sorption experiment and continuous flow column. The single-metal sorption uptake capacity of the aerobic granules for Pb^{2+} was slightly inhibited by the presence of Cd^{2+} only 17.9 % and by the presence of Cu^{2+} ion by 25.6 %.

In the multi metal sorption system, when redundant adsorbent the biosorption follow single metal sorption order, if shorted adsorbent in the system that occur competitive sorption follow of order $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

Ion exchange was identified to be the dominant mechanism for the biosorption for Pb^{2+} , Cu^{2+} and Cd^{2+} by the aerobic biomass. Factors such as hydration effects and electronegative ions may contribute to the competitive sorption results.

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Sinh hấp phụ của các ion Pb(II), Cu(II) và Cd(II) trong hệ đơn và đa kim loại bởi hạt bùn hiếu khí trong hai hệ hấp phụ tĩnh và động

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Tóm tắt: Hạt bùn hiếu khí (aerobic granule sludge) được nghiên cứu làm chất hấp phụ kim loại nặng, nó được dùng như tác nhân hấp phụ các ion Chì, Đồng và Cadimi. Thông qua quá trình nghiên cứu, đánh giá khả năng hấp phụ của hạt bùn hiếu khí trong cả hai hệ là đơn và đa kim loại thông qua 2 quá trình hấp phụ tĩnh và động (batch sorption experiment and continuous flow column), kết quả nghiên cứu chỉ ra rằng hạt bùn hiếu khí có khả năng loại bỏ các ion Pb^{2+} , Cu^{2+} and Cd^{2+} ra khỏi dung dịch nghiên cứu một cách rất hiệu quả. Hấp dung của hạt bùn hiếu khí đối với các ion kim loại nặng gấp 06 lần so với Carbon hoạt tính, đặc biệt là nó có khả năng hấp phụ rất tốt đối với ion Cadimi.

So với khả năng hấp phụ đơn lẻ, thì hấp dung của hạt bùn hiếu khí đối với Pb^{2+} giảm 17.9 % khi có mặt của ion Cd^{2+} và giảm 25.6 % khi có mặt của ion Cu^{2+}

Trong hệ hỗn hợp nhiều kim loại thì có sự cạnh tranh hấp phụ giữa các kim loại. trong hệ gồm 3 ion Pb^{2+} , Cu^{2+} and Cd^{2+} , thì trật tự cạnh tranh hấp phụ giữa các ion kim loại bởi hạt bùn hiếu khí tuân theo quy luật $Pb^{2+} > Cu^{2+} > Cd^{2+}$. Kết quả nghiên cứu cho thấy mô hình Langmuir mô tả quá trình hấp phụ các ion kim loại nặng bởi hạt bùn hiếu khí tốt hơn mô hình Freundlich. Vậy sản phẩm phụ trong quá trình xử lý nước thải bằng phương pháp hiếu khí là hạt bùn hiếu khí, có thể sử dụng như một chất hấp phụ rẻ tiền và là tác nhân xử lý kim loại nặng hiệu quả trong xử lý nước thải dân dụng và công nghiệp.

Keywords: Hạt bùn hiếu khí, Sinh hấp phụ, cạnh tranh hấp phụ, Cd (II), Pb(II), Cu(II).