

BIOSORPTION OF Pb(II), Cu(II) AND Cd(II) IN SINGLE- AND MULTI-METAL SYSTEMS BY PRETREATED AEROBIC GRANULE SLUDGE

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SUMMARY

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. Conventionally these heavy metals are removed from wastewater with physical and chemical methods such as chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment... However, these methods may result in the high capital investment and operating cost, incomplete removal, low selectivity, high-energy consumption. Recent research efforts have been made on the development of efficient and low cost metal organic adsorbents in treatment of industrial wastewater. The present work describes the study on the biosorption Lead (II), Copper (II) and Cadmium (II) ions onto pretreated aerobic granular sludge from single component and multi systems in equilibrium systems and in batch sorption experiment. Results showed that Ca-biomass was an efficient biosorbent for the removal of Pb²⁺, Cu²⁺ and Cd²⁺ ions from an aqueous solution. The single-metal sorption uptake capacity of the aerobic granules for Pb²⁺ was inhibited by the presence of Cd²⁺ and Cu²⁺ ion. The decreasing affinity of aerobic granular sludge for the three metal ions was established as: Pb²⁺ > Cu²⁺ > Cd²⁺. Factors such as hydration effects and electronegative charge may contribute to the competitive sorption results. The metal removal capacities of aerobic biomass were six times higher than those of activated Carbon; especially in the Cd²⁺ removal capacity was very high. The Langmuir model was better than the Freundlich model in regard of describing the Pb²⁺, Cu²⁺ and Cd²⁺ ion biosorption on raw biomass and Ca-biomass. The maximum capacity Q_{max} determined by the Langmuir model fit to experimental data.

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

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 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 (1) 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; (2) To identify the adsorption mechanism in the competitive condition; (3) To compare with previous experimental data obtained for other adsorbent at equivalent conditions.

MATERIALS AND METHODS

Materials

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 two months has the ratio protein/polysaccharide (PN/PS) 4.5.

The collected aerobic granular sludge was washed with water three times and centrifuged at 2000rpm for 10 minutes to remove supernatant and then were transferred into a 1L glass bottle. The bottle was sealed with a rubber stopper, and then stored at 4°C for 24 months, which was called viable biomass.

Raw biomass was prepared by viable biomass dried at 60°C until constant weight and then ground to a gritty consistency to yield granular biosorbent samples.

H-biomass was prepared by first combining viable biomass with 0.02M HCl in a 2 L beaker for 3 h at a biomass concentration of 20 g/L and pH value close to 2.5. Next, the acid solution was drained, and the biomass was washed with distilled water for 4 or 5 times. Finally, the wet protonated biomass was dried in the oven at 60°C until constant weight.

K-biomass and Ca-biomass were prepared by the same method as H-biomass but combining the dried and sieved biomass with 0.02 M KOH and 0.01 M Ca(OH)₂, respectively at a pH value close to 11.5. The base solution was drained, and the biomass was washed with distilled water 4 or 5 times. Finally, the wet biomass was dried overnight in the oven at 60°C until a constant weight was reached.

The stock solution of Lead (II), Copper (II) and Cadmium (II) (1000 mg/L) was prepared by dissolving Pb(NO₃)₂, Cu(NO₃)₂.3H₂O and Cd(NO₃)₂.5H₂O respectively into double distilled water, and was further diluted to the required concentrations using double distilled water. The pH value of metal solutions was adjusted using 0.1 N NaOH and 0.1 N HNO₃, solution.

Methods

Batch biosorption studies

Batch Isotherm experiments were conducted using 500 mL Erlenmeyer flasks at temperature 25°C for mono heavy metal Pb²⁺, Cu²⁺ and Cd²⁺ adsorption at pH 5.0.

Dry of biomass (0.2g) was added into the 200 mL solutions containing heavy-metal concentrations of 25 - 500 mg/L. After 24h of biosorption, samples were taken from the solutions subsequently centrifuged at 7500 rpm 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 Ca²⁺, Mg²⁺ and K⁺ ions from biomass as a result of biosorption of metal ions were studied, and the heavy metals in this biomass after equilibrium sorption were also determined.

Multi-heavy metals uptake

Batch isotherm experiments were also conducted for the interactive biosorption among Pb²⁺, Cu²⁺ and Cd²⁺. The experiments were carried out at pH 5.0 for the following metal ion combinations: Pb²⁺- Cu²⁺, Pb²⁺- Cd²⁺, Cu²⁺-Cd²⁺, Pb²⁺-Cu²⁺-Cd²⁺.

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

Analytical methods

Atomic Absorption Spectrometer (VarianModel-240FS, England) was used to analyze Pb²⁺, Cu²⁺ and Cd²⁺ 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 Ca²⁺, Mg²⁺ and K⁺ released into the solution during biosorption experiment.

Theoretical backgrounds

The Langmuir isotherm Equation

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

Q⁰= 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

RESULTS AND DISCUSSION

Effect of the ionic form of biosorbent on metal removal

Recent studies of biosorption phenomenon revealed that biosorbents, very much like synthetic ion-exchange resins, can be prepared in different ionic forms, *i.e.*, Na⁺, Ca²⁺, H⁺, *etc.*, by washing the biomass with mineral acids, salts, or basis. The pH value of the solution containing the heavy metals before adding it to the treated biomass was adjusted to 5.0 for all four cases.

Table 1. Effect of diferent ionic forms of biomass on metals uptake.

Metal ions	Raw biomass	Ca-biomass	K-biomass	H-biomass
Pb ²⁺	162.33	173.72	167.44	96.71
Cu ²⁺	55.77	58.24	57.05	32.44
Cd ²⁺	158.93	168.69	161.23	117.45

Sorption capacity mg/gDW

The obtained results were shown in Table 1 indicate that, the performance of H, K, and Ca-biomass was studied and compared to the untreated

biomass. The biosorption process was investigated in equilibrium batch tests. The Ca-biomass yielded a Q_{max} value is higher than the untreated biomass in

the case of the three metals tested (Fig.1). For the K-biomass the Q_{max} value was close to that of the untreated biomass; the Q_{max} value of the K-biomass for Lead, Copper and Cadmium was higher than that

for the untreated biomass. The performance of the H-biomass was not optimal since the Q_{max} value was less than that of the untreated biomass for all metals tested.

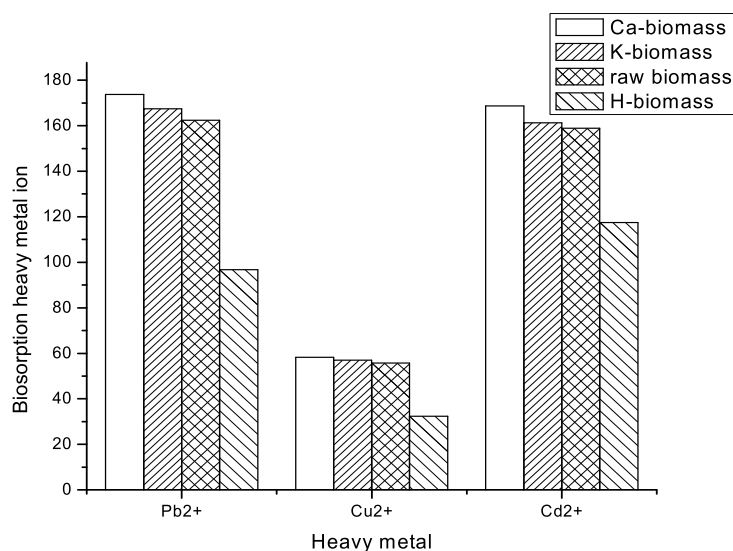


Figure 1. Effect of different ionic forms of biomass on metals uptake.

In the case of K and Ca-biomass the pH of the supernatant solution after the test remained almost constant. However, for the H-biomass the pH of the supernatant solution decreased to nearly 3.0. Whereas the pH value is lower, that would reduce the biosorption capacity. This problem would be discussed in the following section.

One disadvantage of using the H-biomass is that biosorption by protonated biomass would be accompanied by release of protons. This is reflected in the lowering of the solution pH. From these results, the raw biomass and Ca-biomass was used to carry out the subsequent studies.

Biosorption of single metal ions in batch system

Batch isotherm studies were carried out to investigate biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ on raw biomass and Ca-biomass 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.

Comparisons of model parameters obtained by

using both models are shown in Table 2. According to the statistical significance obtained for the Langmuir and Freundlich isotherm models for sorption of Pb²⁺, Cu²⁺ and Cd²⁺ on non-viable aerobic biomass (raw-biomass and Ca-biomass), it could be seen that both models can be used to describe the metal biosorption. The results in Table 2 show that the Langmuir model was better than the Freundlich model in regard of the Pb²⁺ and Cu²⁺ and Cd²⁺ ion biosorption on raw-biomass and Ca-biomass. It is implying that the biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ onto non-viable aerobic biomass was favorable and was monolayer sorption.

Comparison of model parameters obtained using both models for sorption of Pb²⁺, Cu²⁺ and Cd²⁺ on non-viable aerobic biomass (raw biomass and Ca-biomass) and viable biomass (granule). It can be seen that the Langmuir regression correlation coefficients were higher than of the Freundlich, while the heavy-metal biosorption by viable biomass is the opposite. The maximum capacity Q_{max} of Pb²⁺ and Cu²⁺ sorption by non-viable aerobic biomass determined from the Langmuir model were lower than experimental

data, but the maximum capacity Q_{max} of Cd^{2+} was higher than experimental data.

Comparison of metal adsorption capacities

(mmol/g) of pretreated aerobic biomass with activated carbon, commercial resins, brown algae, fungus, and selected solid waste were shown in Table 3.

Table 2. Comparison of adsorption parameters calculated using langmuir and freudlich isotherms for biosorption: Pb^{2+} , Cu^{2+} Cd^{2+}

Metal ions	Biomass type	Langmuir model			Freundlich model		R^2	Q_{maxexp}
		Q_{max}	b	R^2	K	1/n		
Pb^{2+}	Raw biomass	161.31	0.02	0.94	15.37	0.421	0.85	162.33
	Ca-biomass	173.70	0.02	0.96	11.39	0.489	0.92	173.72
	Granule	185.8	0.02	0.87	7.4	0.601	0.94	186.13
Cu^{2+}	Raw biomass	55.74	0.07	0.95	18.30	0.208	0.95	55.77
	Ca-biomass	58.10	0.05	0.96	18.19	0.209	0.96	58.24
	Granule	59.32	0.07	0.90	18.2	0.227	0.91	59.71
Cd^{2+}	Raw biomass	158.97	0.02	0.94	12.95	0.460	0.93	158.93
	Ca-biomass	168.71	0.02	0.96	13.14	0.456	0.92	168.69
	Granule	172.81	0.02	0.81	8.8	0.564	0.90	173.12

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.

Table 3. Comparison of metal adsorption capacities (mmol/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)
Brown algae	Lewatit TP207	0.96	1.34			Brown et al. (2000)
	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, Holan (1995)
	Rhizopus arrhizus	0.44	0.16	0.24		Volesky, 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	Hawari et al. (2006)
	Aerobic biomass		0.94	1.54	4.0	Liu et al. (2003)
	raw biomass	0.78	0.88	1.41	5.0	This study
	Ca-biomass	0.84	0.92	1.50	5.0	This study

Blank spaces denote data not available

To facilitate a comparison with the results presented here, the units for sorption capacity were converted from mg/g into mmol/g. The maximum capacity metal uptake values of the pretreated

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 pretreated biomass was six times 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, *Ascophyllum nodosum*, *Sargassum natans* and anaerobic biomass biosorbents.

As Compared with the research of Liu *et al.*, 2003 on live biomass, the removal capacities of Cu^{2+} and Cd^{2+} in these studied results were lower. However, the use of non-viable aerobic biomass offers the following advantages over viable cells (Hawari *et al.*, 2006).

More generally, Cadmium removal capacity of pretreated 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.

Biosorption of binary and ternary metals by pretreated biomass

Pb-system

The uptake capacity by the biomass of Lead alone and in the presence of Cu^{2+} and Cd^{2+} was evaluated. Figure 2 and figure 3 demonstrates that the single-metal sorption uptake capacity of the biomass for Pb^{2+} was inhibited by the presence of the Cu^{2+} in the system. The presence of Cu^{2+} ion in separate systems reduced the biomass uptake capacity of Pb^{2+} by 25.6 and 29.8% for raw biomass and Ca-biomass, respectively (Table 4).

The single-metal sorption uptake capacity of the biomass for Pb^{2+} was slightly inhibited by the presence of the Cd^{2+} in the system. The presence of Cd^{2+} ion in separate systems reduced the biomass uptake capacity of Pb^{2+} by only 17.9 and 21.4 % for raw biomass and Ca-biomass respectively.

Table 4. Binary and ternary metals sorption.

Heavy metals	Raw biomass mmol/gDW	Ca-biomass mmol/g DW	Total metal adsorbed in the systems	
			Raw biomass	Ca-biomass
Pb^{2+}	0.78	0.84		
Cu^{2+}	0.88	0.92		
Cd^{2+}	1.41	1.50		
$Pb^{2+}-Cu^{2+}$				
Pb^{2+}	0.58	0.59	0.94	0.95
Cu^{2+}	0.36	0.36		
$Pb^{2+}-Cd^{2+}$				
Pb^{2+}	0.64	0.66	0.99	1.02
Cd^{2+}	0.35	0.36		
$Cu^{2+}-Cd^{2+}$				
Cu^{2+}	0.62	0.65	0.98	1.02
Cd^{2+}	0.36	0.37		
$Cu^{2+}-Cd^{2+}-Pb^{2+}$				
Pb^{2+}	0.41	0.43	0.99	1.05
Cu^{2+}	0.36	0.38		
Cd^{2+}	0.22	0.24		

Di-metal competition sorption.

Cu-system

The uptake capacity of Copper alone and in combination with other single metals by the biomass was determined. Figure 2 and Figure 3 demonstrates that the single-metal sorption uptake capacity of the biomass for Cu^{2+} showed very sensitive to the presence of Pb^{2+} cations, 59.1 and 60.8 % reduction on the uptake capacity was observed for raw biomass and Ca-biomass respectively. This could indicate the higher selectivity of the biomass for Pb^{2+} over Cu^{2+} for both studied biomass.

The result shown 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 and 29.3 % than the single Cu^{2+} uptake capacity for raw biomass and Ca-biomass respectively.

Cd-system

Experiments to evaluate the uptake capacities of Cadmium were performed. Table 4 indicates that Cd^{2+} was the least favorable to be absorbed 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 and 76.0% for raw biomass and Ca-biomass respectively, which is higher than the case in the Pb-system where Pb^{2+} uptake capacity was reduced by only 17.9 - 21.4% in the presence of Cd^{2+} cations. The presence of Cu^{2+} cations inhibited the uptake capacity of Cd^{2+} by 74.4 and 59.8%, which is higher than the case in the Cu-system where Cd^{2+} inhibited the uptake capacity of Cu^{2+} by 20.51

and 29.3% for raw biomass and Ca-biomass respectively.

Tri-metal competition sorption

At equilibrium (Table 4), the main uptaking metals were Pb^{2+} , Cu^{2+} . In the system three metals compete each other, but affinity absorption of Pb^{2+} and Cu^{2+} was higher than Cd^{2+} , so the Cd^{2+} uptake decrease from 1.41 to 0.22 mmol/g DW and 1.50 to 0.24 mmol/g DW for raw biomass and Ca-biomass respectively.

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) 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 in 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 competitive sorption system, the presence of Pb^{2+} and Cu^{2+} cations inhibited the uptake capacity of Cd^{2+} it could be explained that the surface of the biomass plays an importance role in the uptake process and chemical property of Cd^{2+} complex.

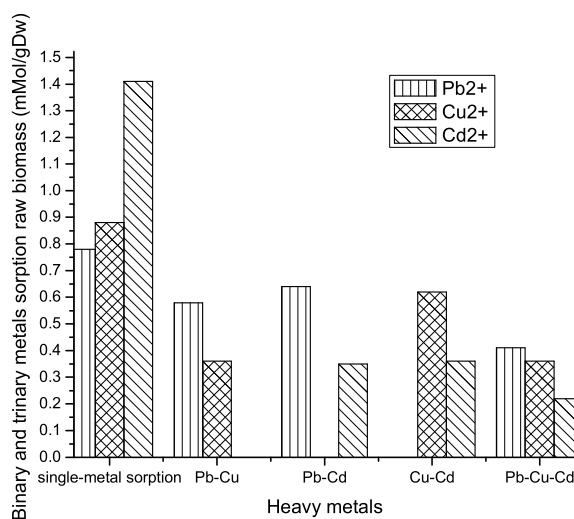


Figure 2. Binary and ternary metals sorption on raw biomass.

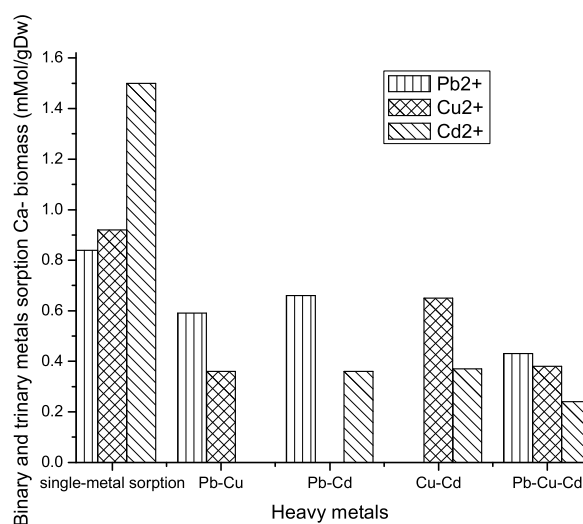


Figure 3. Binary and ternary metals sorption on raw biomass Ca-biomass.

Sorption mechanism

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

The amount of released Ca²⁺ is far larger than the other two light metal ions (Mg²⁺ and K⁺). The ratio of total released Ca²⁺, Mg²⁺ and K⁺ to the biosorbed heavy metal was 74.01, 71.03 and 62.97% for Pb²⁺, Cu²⁺ and Cd²⁺, 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 Pb²⁺, Cu²⁺ and Cd²⁺ biosorption by aerobic granules.

In study of metal biosorption by anaerobic granules, Hawari reported that 77, 82 and 50% of adsorbed Copper, Cadmium and Lead would be attributed to an ion-exchange mechanism (Hawari *et al.*, 2006); Xu, 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 (Xu, 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 (Tsezos, Volesky, 1981).

The result demonstrated that ion-exchange is a main mechanism of the biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ by aerobic granular sludge.

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

Pb²⁺ and Cu²⁺ ions are classified in the borderline category according to this classification, while Cd²⁺ ions fall into the soft category (Sen Gupta, 2000), the soft cations form more stable complexes with soft donors while hard cations prefer hard donors (Buffle, 1988). Examples of hard ligands are carbonate, phosphate, sulfate, carboxylate and hydroxyl groups, while soft ligands include sulfhydryl and amino groups (Bell, 1977).

Because of the aerobic component has the ratio protein/polysaccharide (PN/PS) 4.5; it means that amino groups more than other function groups; therefore, Cd²⁺ 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.

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.

Table 5. Parameters characterizing the binding strength of metals

Ion	Charge, z ^a	Ionic radius r _{cryst} (Å)	Hydrated ion Radius r _{hyd} (Å)	Pauling electronegativity	Parameter for covalent binding x ² (r _{cryst} + 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 B.J. 1990)	(Nieboer E. 1973)	(Jain MK. 1970)

The hydrated radii of Pb²⁺, Cu²⁺ and Cd²⁺ is 4.01, 4.19 and 4.26 Å respectively; therefore, Pb²⁺ has more accessibility to the surface and pores than Cu²⁺ and Cd²⁺ cations, which occurs to the adsorption follow of Pb²⁺ > Cu²⁺ > Cd²⁺.

In general, the larger the effective hydrated radius, the higher the hydration energy of an ion (Russell JB, 1980), the 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. Pb²⁺ has the highest adsorption capacity and highest electronegativity (McKay, 1997). Competition of Pb²⁺, Cu²⁺ and Cd²⁺ ions for surface sites occur and depend on the ion's characteristics. First Pb²⁺ ions dominate sorption surface area of aerobic granules so the sorption capacity for Pb²⁺ in the ternary systems is always significantly greater than Cu²⁺ and Cd²⁺ ions follow by sorption capacity for Cu²⁺ greater than Cd²⁺. 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 stronger strengths of covalent binding than the lower affinity metal ions Cadmium.

CONCLUSIONS

The sorption capacity of Ca-biomass was higher

than K-biomass and H-biomass. The maximal adsorption capacity (mmol/g DW) of the Ca-biomass was 0.84 Pb²⁺, 0.92 Cu²⁺ and 1.50 Cd²⁺.

The metal removal capacities of pretreated aerobic biomass were six times higher than those of activated Carbon, especially the Cadmium removal capacity of Ca-biomass was very high.

The biosorption of Pb²⁺, Cu²⁺ and Cd²⁺ ions from multi metals systems were studied in the equilibrium systems and batch sorption experiment. The single-metal sorption uptake capacity of the aerobic granules for Pb²⁺ was slightly inhibited by the presence of Cd²⁺ and Cu²⁺ ion. The affinity order of aerobic granular sludge for the three metal ions was established as: Pb²⁺ > Cu²⁺ > Cd²⁺. Factors such as hydration effects and electronegative ions may contribute to the competitive sorption results. The Langmuir model was better than the Freundlich model corrected as mentioned above, the Pb²⁺, Cd²⁺ and Cu²⁺ ion biosorption on raw biomass and Ca-biomass. The maximum capacity Q_{max} determined from the Langmuir model fit to experimental data.

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SINH HẤP PHỤ CÁC ION $Pb(II)$, $Cu(II)$ VÀ $Cd(II)$ TRONG HỆ ĐƠN VÀ ĐA KIM LOẠI BỞI HẠT BÙN HIẾU KHÍ ĐÃ ĐƯỢC XỬ LÝ

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TÓM TẮT

Hạt bùn hiếu khí (aerobic granule sludge) được nghiên cứu làm chất hấp phụ kim loại nặng, hạt bùn này sau khi được xử lý với ion Canxi tạo ra dạng Ca-biomass, nó được dùng như tác nhân hấp phụ các ion Cr^{3+} , Cd^{2+} và Cu^{2+} . Thông qua quá trình nghiên cứu, đánh giá khả năng hấp phụ của Ca-biomass trong cả hai hệ là đơn và đa kim loại, kết quả nghiên cứu chỉ ra rằng Ca-biomass 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. Khả năng hấp phụ ion kim loại nặng của Ca-biomass nhiều gấp 06 lần so với Carbon hoạt tính, đặc biệt là Ca-biomass có khả năng hấp phụ rất cao đối với ion Cd^{2+} . Trong hệ hỗn hợp nhiều kim loại thì có sự cạnh tranh hấp phụ giữa các kim loại. Khả năng hydrat hóa và độ âm điện của các ion có vai trò quan trọng ảnh hưởng đến khả năng cạnh tranh hấp phụ của các ion kim loại lên trên tác nhân hấp phụ. 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 Ca-biomass tuân theo quy luật $Pb^{2+} > Cu^{2+} > Cd^{2+}$. Nhưng trong hệ khi có dư sinh khối là chất hấp phụ, thì sự hấp phụ chỉ phụ thuộc vào bản chất của chất hấp phụ. Kết quả nghiên cứu cho thấy mô hình Langmuir mô tả quá trình hấp phụ các ion kim loại nặng bởi Ca-biomass tốt hơn mô hình Freundlich. Vật sản phẩm phụ trong quá trình xử lý nước thải bằng phương pháp hiếu khí là hạt bùn hiếu khí (aerobic granule sludge), sau khi được xử lý thành dạng Ca-biomass 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 công nghiệp.

Từ khóa: Hạt bùn hiếu khí, sinh hấp phụ, cạnh tranh hấp phụ, $Cd(II)$, $Pb(II)$, $Cu(II)$

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