Comparative Biosorption Of Pb(II), Cr(III) AND Cd(II) Ions In Single Component System By Live And Dead Anaerobic Biomass, Bath Study

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ABSTRACT

In this study, dead and live anaerobic biomass was used in biosorption of Pb(II), Cr(III) and Cd(II) ions from a synthetic wastewater. The biosorption was investigated by batch adsorption experiments. It was found that, the biosorption capacities were significantly affected by biosorbent dosage. The process follows Langmuir isotherm (regression coefficient 0.995, 0.99 and 0.987 for Pb(II), Cr(III) and Cd(II) ions, respectively, onto dead anaerobic biomass) model with uniform distribution over the biomass surface. The experimental uptake capacity was 51.56, 29.2 and 28 mg/g for Pb(II), Cr(III) and Cd(II), respectively, onto dead anaerobic biomass, compared with 35, 13.6 and 11.8 mg/g for Pb(II), Cr(III) and Cd(II), respectively, onto live anaerobic biomass. The percentage reductions of live compared with dead anaerobic biomass in uptake capacity were 32.3, 53.4 and 57.8 for Pb(II), Cr(III) and Cd(II), respectively. The results indicated that, the dead anaerobic biomass is suitable as an efficient biosorbent for the removal of Pb(II), Cr(III) and Cd(II) ions from wastewater.

Keywords: **Wastewater, Heavy metal, Live / dead anaerobic biomass, Biosorption, Isotherm**

الخلاصة

تم استخدام الكتلة الحيوية اللاهوائية الميتة والحية في عملية الامتزاز الحيوي لايونات عناصر الرصاص، الكروم الثلاثي والكادميوم من مياه الصرف. تم التحري عن الامتزاز الحيوي بواسطة تجارب نظام الدفعة. وجد ان قابلية الامتزاز الحيوي تتاثر بشكل واضح بواسطة كمية المادة الحيوية المستعملة. عمليات الامتزاز الحيوي اتبعت موديل Langmuir مع معامل انحدار 0.995، 0.99 و0.987 لكل من ايونات الرصاص، الكروم الثلاثي والكادميوم على الكتلة الحيوية اللاهوائية الميته مع توزيع منتظم على سطح الكتلة الحيوية. كانت قدرة الامتزاز التجريبية 51.56، 29.2 و 28 mg/g لايونات الرصاص، الكروم الثلاثي والكادميوم على الكتلة اللاهوائية الميتة مقارنة مع 35، 13.6 و 11.8 mg/g لايونات الرصاص، الكروم الثلاثي والكادميوم على الكتلة اللاهوائية الحية. كانت النسبة المئوية لانخفاض قدرة الامتزاز الكتلة اللاهوائية الحية مقارنة مع الكتلة اللاهوائية الميتة 32.3، 53.4 و 57.8 لايونات الرصاص، الكروم الثلاثي والكادميوم على التوالي. النتائج بينت انه الكتلة الحيوية اللاهوائية الميتة مناسبة بشكل فعال لازالة ايونات الرصاص، الكروم الثلاثي والكادميوم من مياه الفضلات.

الكلمات الرئيسية: مياه الصرف، معادن ثقيلة، كتلة حيوية اللاهوائية حية/ ميتة، الامتزاز الحيوي، التمثيل الرياضي

1. INTRODUCTION

Presence of heavy metals in wastewaters causes significant environmental problems. High concentrations of heavy metals are known to be toxic and carcinogenic to living organisms. When heavy metals are present even in a very low concentration, their concentration may be elevated through bio-magnification to a level that they start to exhibit toxic characteristics. The metals which are of greatest environmental concern are cadmium, mercury, lead, chromium, cobalt, copper, nickel and zinc, (Sahmoune et al., 2009). Metals are non-renewable from the point of resource and recovery, and important from the point of contaminants in water and wastewater; Different methods are used for the removal and recovery of heavy metals, (Spearot and Peck, 1984). Chemical methods, to effectively decrease heavy metals to acceptable levels require a large excess of chemicals, which increase the costs because of generating the voluminous sludge, (Yun and Volesky, 2003). In the meantime, biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. The major advantages of biosorption technology are their effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials (Naja, and Volesky, 2006). It is important for a biosorption process to select the most available and reliable biosorbent, (Liu et al., 2003). Both live and dead biosorbent, is derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams*;* These include bacteria, fungi, yeast and marine algae (Huifen et al., 2010). Because of the many problems inherent in maintaining active microbial populations under highly variable conditions of wastewaters, living systems are often unreliable, while non-living form, can serve as a basis for development of biosorbent materials for the efficient removal of heavy metals (Puranik et al., 2005). The use of living organisms may not be an option for the continuous treatment of highly toxic organic/inorganic contaminants, once the toxicant concentration becomes too high or when the process is operated for a long time. The amount of toxicant accumulated inside the organisms will reach saturation, beyond this point; an organism's metabolism may be interrupted, resulting in death of the organism (Vijayaraghavan and Yun, 2008). Another advantage of using dead biomass is, the sorbed metal ions can be easily desorbed and the biomass can be reused (Liu et al., 2003). The capacities of many biosorbent were found to be much higher than those of other types of adsorbents, activated carbon, natural zeolites and synthetic ion exchange resins, (Sheng, 2004), because the cell walls of these types of biosorbents contain polysaccharides and proteins having various functional groups such as amine, carboxyl, hydroxyl, sulphates, and phosphates responsible for interacting with the metals ions and dyes (Sahmoune et al., 2009). Das et al., 2007 investigated the removal of heavy metals by dead biomass in batch experiments at different pH values ranging from 3-8. The results indicated that, maximum adsorption of different metal species occurred at pH values of 4. Different models are to be developed from simple mathematical relationships, characterized by a limited number of adjustable parameters, which give a good description of the experimental behavior over a large range of operating conditions. The model used to describe the results should be capable of predicting heavy metal binding at both low and high concentrations (Vijayaraghavan and Yun, 2008). One of these models is the Langmuir isotherm model which can be represented as:

$$q_e = \frac{q_{max} b C_e}{(1+bC_e)} \qquad (1)$$

Where: q_e(mg/g), the amount of adsorbate adsorbed per mass of adsorbent of component; q_{max} (mg/g), corresponds to the maximum achievable uptake by a system; b (l/mg), is related to the affinity between the sorbate and sorbent, and C_e(mg/l) is the final metal ions concentrations in the solution. The Langmuir model assumes that the adsorption is limited to a monolayer. The important characteristic of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter R_L. This is defined by: (Sahmoune et al., 2009)

$$R_L = \frac{1}{b+C_e} \qquad (2)$$

The parameter R_L indicates the shape of the isotherm as shown in **Table 1**.

Table 1 Constant parameter R_L

Another model is the Freundlich isotherm model, represented as: (Vijayaraghavan and Yun, 2008)

$$q_e = KC_e^{1/n} \qquad n > 1 \qquad (3)$$

It incorporates two constants: K $(mg/g)/(mg/l)^{1/n}$, which corresponds to the maximum binding capacity; and n, characterize the affinity between the sorbent and sorbate (adsorption intensity). The Freundlich isotherm model assumed that the adsorption is a multilayer, was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites with various affinities.

The Sips isotherm model can also represents the adsorption process:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \qquad (4)$$

K_S, is the Sips model isotherm constant; a_S, the Sips model constant; and β_S, the Sips model exponent Langmuir–Freundlich isotherm which derive from the limiting behavior of the equation (4), at low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. While at high sorbate concentrations, it predicts the monolayer sorption capacity characteristics of the Langmuir isotherm (Huifen et al., 2010). The role of different physiochemical parameters associated with the sorption of lead, chromium and cadmium ions from aqueous solution by live/dead anaerobic biomass through batch method is described to compare between the biosorption capacity of dead and live anaerobic biomass for removal of these metals.

2. MATERIAL AND METHODS

2.1 Materials (Stock Solutions)

A stock solution of lead, chromium and cadmium ions with a concentration of (1000 mg/l) were prepared by using $Pb(NO_3)_2$, $Cr(NO_3)_3$ and $Cd(NO_3)_2$ (BDH, England with minimum purity 99.5%). A 0.1599, 4.577 and 2.103 g of lead nitrate, chromium nitrate and cadmium nitrate, respectively were dissolved in 1000 ml distilled water. Dissolved metal concentrations in solution were determined by a flame atomic absorption spectrophotometer (AA) (Buck, USA).

2.2 Preparation of Biosorbent

Heterogeneous cultures including mostly anaerobic bacteria, yeast fungi and protozoa of sorbents were taken from Al-Rostomia'a third extension drying bed. Anaerobic and facultative anaerobic microorganisms (*Aeromonas species, E-coli, Pseudomonas aerginrsa, Clostridium, Staphylococcus sp and Salmonella sp)* were found in the sludge taken from the drying beds.

2.2.1 Live anaerobic biomass (LAB)

A mixed culture of anaerobic bacteria, yeast and fungi were grown in laboratory for 30 days. Nutrients were added as a soluble organic mixture. Growth media contains: 13.34, 4, 0.4, 12.5 and 37 g of Glucose, Peptone, K_2HPO_4, $NaHCO_3$, and Na_2SO_4, respectively, trace metals 0.12, 0.78, 0.04, 0.04 and 0.045 g of $CoCl_2.6H_2O$, $FeCl_2.4H_2O$, $MnCl_2.4H_2O$, $NaMoO_4.2H_2O$ and $NiCl_2.6H_2O$ were dissolved in 5 liters of distilled water, pH was controlled to be neutral by adding 0.1M NaOH or 0.1M HNO_3, temperature was fixed to be 37°C using a heater and thermostat.

2.2.2 Dead Anaerobic Biomass (DAB)

Heterogeneous culture of live anaerobic biomass (LAB) was dried at atmospheric temperature (37-45°C) for 5 days crushed, sieved, washed with distilled water and dried at 70°C for 6 h. The geometric mean diameter was obtained to be 0.775 mm.

2.3 Batch Biosorption Experiments

Different weights of live/dead anaerobic biomass were used, (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, and 0.6) g wet/dry basis by electronic balance (Sartorius BL 210S); biosorbents were placed in 12 volumetric flasks of 250 ml. A sample of 100 ml of measured concentration solution of 50 mg/l was added to each flask for single systems of Pb(II), Cr(III) and Cd(II) ions respectively. The experiment was performed at sufficiently high metal concentrations so that maximal uptake would be achieved. The pH of the metal solutions was adjusted to the desired value (pH=4) using 0.1M NaOH or 0.1M HNO_3. The flasks were then placed on a shaker (HV-2 ORBTAL, Germany) and agitated continuously for 4 h at 200 rpm and (33±3°C). The samples were filtered by 42 Whatman filter paper, few drops of 0.1M HNO_3 were added to the samples to decrease the pH value below 2 in order to fix the concentration of the heavy metals during storage before analysis (APHA, 1995). The final equilibrium concentrations were measured by means of an atomic absorption device (AA). The adsorbed amount was then calculated by the following equation:

$$q_e = \frac{V\ (C_0 - C_e)}{W_{(wet/dry\ base)}} \qquad (5)$$

q_e (mg/g), is the amount of heavy metals ions uptake by (LAB/DAB), C_0(mg/l) and C_e(mg/l), are the respective initial and final metal ion concentrations in the solution, respectively, V (l), is the volume of solution and W(g), is the weight of the biomass. The adsorption isotherms were obtained by plotting the weight of solute adsorbed per unit weight of biomass (q_e) against the equilibrium concentration of the solute in the solution (C_e) (Vijayaraghavan and Yun, 2008).

3. RESULTS AND DISCUSSION

The obtained data for single component systems were correlated with the Langmuir, Freundlich and Sips isotherm models. The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data (Statistica-v6). **Table 2** shows parameters of single solute isotherm for Pb(II), Cr(III) and Cd(II) ions uptake onto live and dead anaerobic biomass. Biosorption capability of dead and live anaerobic biomass (DAB/LAB) for the metal ions Pb(II), Cr(III) and Cd(II) were compared individually. **Fig.1** to **Fig. 3** show that the Langmuir isotherm model was found to be favorable, R_L was found between 0 and 1for Pb(II), Cr(III) and Cd(II) ions for both dead and live anaerobic biomass.

Fig.1. Biosorption isotherm of lead ions onto dead and live anaerobic biomass

Fig.2. Biosorption isotherm of chromium ions onto dead and live anaerobic biomass

Fig.3. Biosorption isotherm of cadmium ions onto dead and live anaerobic biomass

Table 2 Parameters of single solute isotherm for Pb(II), Cr(III) and Cd(II) ions for live and dead anaerobic biomass.

Fig.4, shows the experimental uptake capacity was 51.56, 29.2 and 28 mg/g for Pb(II), Cr(III) and Cd(II), respectively, onto dead anaerobic biomass (DAB), compared with 35, 13.6 and 11.8 mg/g for Pb(II), Cr(III) and Cd(II), respectively, onto live anaerobic biomass (LAB). The percentage reductions of live compared with dead in uptake capacity were 32.3, 53.4 and 57.8 for Pb(II), Cr(III) and Cd(II), respectively.

Fig.4. Maximum experimental uptake capacity for Pb(II), Cr(III) and Cd(II) onto live and dead anaerobic biomass.

Results can be compared for the three adsorbates in terms of adsorption capacity parameters: Pb(II) > Cr(III) > Cd(II). Since lead nitrate salt is less soluble in water in comparison with chromium nitrate and cadmium nitrate salts (solubility of salts in water are 52, 81 and 136 g/100 ml for Pb(II), Cr(III) and Cd(II) ions). It will be expected to have a highest biosorption rate. The lead which has the highest affinity order for being adsorbed by the biomass, has the lowest hydration radius (4.01, 4.13 and 4.26 A°m for for Pb(II), Cr(III) and Cd(II)) while cadmium ion the least favorable by the biomass, has the highest hydration radius. This coincides with the fact that less hydrated ions radius are preferably accumulated at interface (Hawari and

Mulligan, 2006). **Fig.5**, shows that the removal efficiency was 99.14, 97.67 and 93.63 percent for Pb(II), Cr(III) and Cd(II) ions, respectively, onto dead anaerobic biomass, while it was 88.56, 79.8 and 78.56 percent for Pb(II), Cr(III) and Cd(II) ions, respectively, onto live anaerobic biomass. It was demonstrated that a concentration of 6 g/l of biomass for both dead and live anaerobic biomass could achieve very good removal efficiency when the solution concentration was 50 mg/l for Pb(II), Cr(III) and Cd(II) ions. These results encourage using the dead biomass in all the following experimental work as biosorbent.

Fig.5. Maximum removal efficiency for Pb(II), Cr(III) and Cd(II) onto live and dead anaerobic biomass

Similar results were found when dead biomass of different types to be a more efficient biosorbent of heavy metals (Huifen et al., 2010). The difference between live and dead anaerobic biomass can be explained on the basis of active metabolizing cells plasma membrane generating competing H^+ ions (Yun and Volesky, 2003). Alternatively, in dead state, the cells become more porous and allow the metal to enter and bind to the internal surfaces and functional groups as well, thus increasing metal biosorption (Liu et al., 2003). The uptake by live anaerobic biomass occurs by precipitation and transport across cell membrane and accumulation inside the cells, while by dead anaerobic biomass, it depends on precipitation, physical adsorption, ion exchange and complexation (Hawari and Mulligan, 2006). Another reason demonstrates the cause of uptake is higher by dead than live anaerobic biomass is due to the difference in surface area per unit mass of dead and live biomass. Dead biomass has higher surface area per unit mass compared with live biomass due to 70% total weight of the cell is water, thus by drying the biomass into pellets the surface area of a unit weight will increase. Therefore, to overcome the disadvantages of using live anaerobic biomass, dead biomass was recommended for heavy metals removal.

4. CONCLUSIONS

Uptake capacity by dead anaerobic biomass (DAB) is greater than the uptake capacity of live anaerobic biomass (LAB) for Pb(II), Cr(III) and Cd(II) ions. In single system Pb(II) ions was the most favourable component rather than Cr(III) and Cd(II) ions. This is due to its physiochemical characteristics that makes it the most favourable adsorbed component, due to less solubility and highly molecular weight. Results for the three adsorbates in term of adsorption capacity parameters was: Pb(II) > Cr(III) > Cd(II).

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Table 1 Constant parameter R_L

R_L	Type of isotherm
$R_L > 1$	unfavorable
$R_L = 1$	linear
$R_L = 0$	irreversible
$0 < R_L < 1$	favorable

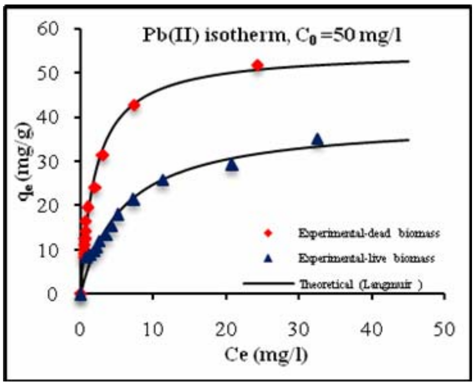

Fig.1. Biosorption isotherm of lead ions onto dead and live anaerobic biomass

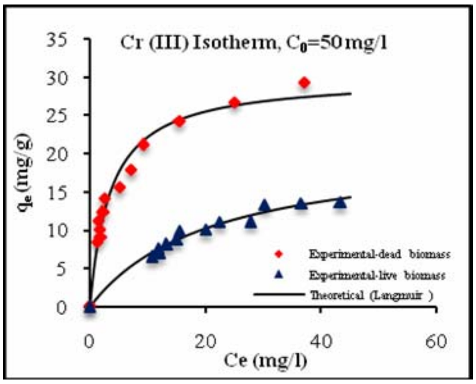

Fig.2. Biosorption isotherm of chromium ions onto dead and live anaerobic biomass

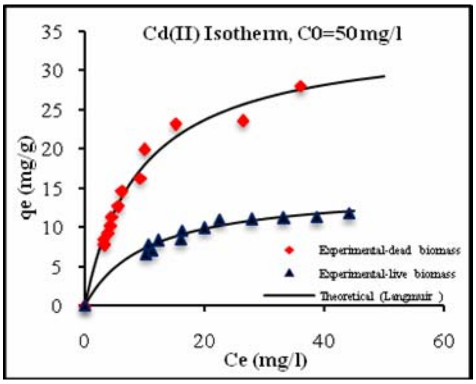

Fig.3. Biosorption isotherm of cadmium ions onto dead and live anaerobic biomass

Table 2 Parameters of single solute isotherm for Pb(II), Cr(III) and Cd(II) ions for live and dead anaerobic biomass

Model	Parameters	Pb(II)		Cr(III)		Cd(II)	
		Dead	Live	Dead	Live	Dead	Live
Langmuir	$q_{max,}$	54.92	39.3	34.78	20.32	29.99	14.9
	b	0.493	0.17	0.107	0.048	0.285	0.097
	R_L	0.036	0.13	0.212	0.506	0.104	0.409
	R^2	0.995	0.987	0.99	0.983	0. 987	0.985
Freundlich	K	17.45	8.6	9.24	2.33	5.986	3.6
	n	2.73	2.43	3.02	2.06	2.26	3.07
	R^2	0.969	0.95	0.989	0.983	0.973	0.971
Sips	k_s	25.89	8.54	10.02	0.663	2.45	0.773
	$ß_s$	0.895	0.63	0.594	1.199	1.317	1.13
	a_s	0.44	0.13	0.226	0.037	0.082	0.058
	R^2	0.986	0.98	0.984	0.981	0.982	0.891

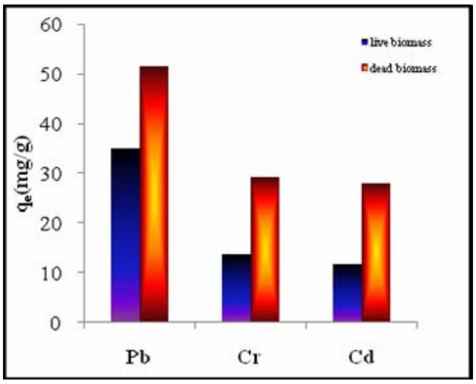

Fig.4. Maximum experimental uptake capacity for Pb(II), Cr(III) and Cd(II) onto live and dead anaerobic biomass

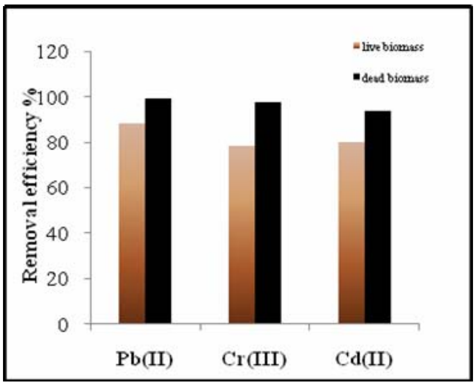

Fig.5. Maximum removal efficiency for Pb(II), Cr(III) and Cd(II) onto live and dead anaerobic biomass