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Competitive biosorption of Pb(II), Cr(III), and Cd(II) from synthetic wastewater onto heterogeneous anaerobic biomass in single, binary, and ternary batch systems

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ABSTRACT

Biosorption of lead, chromium, and cadmium ions from aqueous solution by dead anaerobic biomass (DAB) was studied in single, binary, and ternary systems with initial concentration of 50 mg/l. The metal-DAB affinity was the same for all systems. The main biosorption mechanisms were complexation and physical adsorption of metallic cations onto natural active functional groups on the cell wall matrix of the DAB. It was found that biosorption of the metallic cations onto DAB cell wall component was a surface process. The main functional groups involved in the metallic cation biosorption were apparently carboxyl, amino, hydroxyle, sulfhydryl, and sulfonate. These groups were part of the DAB cell wall structural polymers. Hydroxyle groups (–OH) were responsible for 37, 52, and 31% of the removal of Pb(II), Cr(III), and Cd(II) by DAB through complexation mechanisms; whereas carboxylic groups (C=O) were responsible for 21, 14, and for 34%of the removal of Pb(II), Cr(III), and Cd(II), respectively. Biosorption data were fitted to four isotherm models. Langmuir model was best fitted to the experimental data than Freundlich, Sips, and Redlich–Peterson models for single system. While for binary and ternary metal systems, extended Langmuir model were fitted experimental data better than interaction factor, a combination of Langmuir–Freundlich and Redlich–Peterson models. The maximum uptake capacities were 54.92, 34.78, and 29.99 mg/g for Pb(II), Cr(III), and Cd(II), respectively. Optimum pH was found to be 4.

Keywords: Biosorption mechanisms; Dead anaerobic biomass; Isotherms; Heavy metals; FT-IR; Uptake capacity

1. Introduction

Heavy metals are toxic pollutants released into the environment as a result of different activities such as industrial, mining, landfill leaches, municipal wastewater, urban runoff, and agricultural activities. Lead is extremely toxic and can damage the nervous system, kidneys, and reproductive system. Chromium causes respiratory problems and weakened immune systems; and cadmium is known to cause renal dysfunction, bone degeneration, liver damage, and blood damage. Most heavy metal salts are soluble in water and, as a consequence cannot be separated by ordinary physical separation methods [1]. Different methods are used such as precipitation, evaporation, electrodialysis, ion

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exchange filtration, and membrane processes [2]. 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 its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials [3]. Despite the fact that single toxic metallic species components exist in wastewaters and the presence of a multiplicity of metals often gives rise to interactive effects, insufficient attention seems to have been paid to this problem. The examination of the effects of metal ions in various combinations is more representative of the actual environmental problems faced by treatment technologies than single metal studies [4]. The conventional methods used are ineffective and extremely expensive when the initial heavy metal concentrations are in the range of 10–100 mg/l [5]. Live and dead anaerobic biomass (DAB) can be used for the effective removal and recovery of heavy metal ions from wastewater streams [5–8]. The cell wall of micro-organisms essentially consisting of various organic compounds such as chitin, acidic polysaccharides, lipids, amino acids, and other cellular components could provide a passive uptake of metal ions in a manner of surface adsorption [3], where the solutes can be deposited in the surface or within the cell wall structure. Several functional groups are presented on the micro-organism's cell wall including carboxyl, hydroxyl, and others as they are negatively charged and abundantly available; carboxyl groups actively participate in the binding of metal cations [9]. Biosorption of metal ions onto micro-organisms involves a combination of mechanisms for metal-binding: physical biosorption caused by van der Waal's forces and complex formation on the cell surface after the interaction between metal ions and active groups [10]. Precipitation mechanism consequence of the chemical interaction between the metal and the cell surface [7], and the various biosorption mechanisms mentioned above can take place simultaneously. The aim of this study is to focus on competitive biosorption of heavy metals onto anaerobic biomass taking into account the characteristic of biomass and physicochemical properties of heavy metals. The effect of contact time, dosage of adsorbent, and agitation speed was studied, and the relation between pH and removal efficiency was analyzed.

2. Adsorption isotherm models

Different isotherm models are 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.

3. Experimental work

3.1. Materials

3.1.1. Adsorbate

A stock solution of lead, chromium, and cadmium ions with a concentration of 1,000 mg/l was prepared by using $Pb(NO_3)_2$, $Cr(NO_3)_3$, and $Cd(NO_3)_2$ (BDH, England with minimum purity 99.5%). The salts were obtained from local market. About 0.1599, 4.577, and 2.103 g of lead nitrate, chromium nitrate, and cadmium nitrate were dissolved in 1,000 ml distilled water, respectively. Metal concentrations were determined by a flame atomic absorption spectrophotometer (Type, Buck, Accusys 211, USA).

3.1.2. Adsorbent

Heterogeneous cultures including mostly anaerobic bacteria, yeast fungi, and protozoa of sorbents were taken from the third extension drying bed in Al-Rostomia'a Treatment Plant/Baghdad-Iraq. The physical, chemical, and biological properties were measured and listed in Table 1. Anaerobic and facultative anaerobic micro-organisms (*Aeromonas species, E-coli, Pseudomonas aerginrsa, Clostridium, Staphylococcus sp. and Salmonella sp., and Rhizopusarrhizus, Saccharomyces erevisiae)* were found in biomass from the drying bed using API Instrument (Biomerieux, France). DAB was prepared using heterogeneous culture of live anaerobic biomass (LAB), dried at temperature between 37 and 45°C for five days, crushed, sieved, washed with distilled water, and then dried at 70°C for 6 h.

3.2. Methods

3.2.1. The determination of an optimum pH

The effect of pH on Pb (II), Cr(III), and Cd(II) ions biosorption onto DAB was studied; about 0.05 g biomass of DAB was mixed with 100 ml of single metal ion solutions with 50 mg/l concentration of Pb(II), Cr(III), and Cd(II) ions. The solutions were maintained at different pH values ranging from 3 to 8 by using 0.1 M NaOH or HNO_3 solution in six flasks placed on a shaker (Type, HV-2 ORBTAL, Germany) at agitation speed of 200 rpm for a period of 4 h were at room temperature (35°C). Samples of 10 ml were

Table 1
Physical chemical and biological characteristic of DAB

Biomass			
Physical characteristic (dead biomass)		Biological characteristic (live biomass)	
Particle diameter, mm	0.775	Bacteria	
Surface area, m^2/g	94.53[(a)]	Aeromonas species, CFU/ml	222,000
Actual density, kg/m^3	1741.6	*E. coli*, CFU/mL	430,000
Bulk density, kg/m^3	609.9[(b)]	*Pseudomonas aerginrsa*, CFU/ml	703,500
Particle porosity	0.584	Klebsiella species, CFU/ml	210,000
Total suspended solid, mg/l	153,950	Clostridium, CFU/ml	370,000
Volatile suspended solid, mg/l	78,126	Staphylococcus sp., CFU/ml	210,000
Chemical characteristic (dead biomass)		Streptococcus sp., CFU/ml	490,000
pH	5.5–6.3	Salmonella sp., CFU/ml	190,000
CEC, meq/100 g	51.2	Shiglladysente, CFU/ml	410,000
Lead, mg/l	0. 02	Fungi	
Chromium, mg/l	0.01	Penicillium sp., CFU/ml	180,000
Cadmium, mg/l	0.02	Yeast	
		Candida albicans, CFU/ml	460,000
		Protozoa	
		Entamoeba species, CFU/ml	16,000
		Giardia lambihia, CFU/ml	90,000

Notes: (a) Surface area analyzer, BET method, Quantachrome.com (USA), (b) apparent density instrument, Autotap, Quantachrome (USA), CEC - cat ion exchange capacity, CFU - colony-forming unit.

taken from each flask and analyzed by the atomic absorption (AA) device.

3.2.2. Fourier-transforms infrared analysis (FT-IR)

DAB samples, before and after adsorption of lead, chromium, and cadmium were examined with the spectrophotometer (Type, Shimadzu FT-IR 8000). This technique was used to elucidate the chemical characteristics relevant to metallic ion sorption by DAB, in order to identify functional groups (carbonyl, carboxylic, hydroxyl, and others) involved in the biosorption process. About 0.6 g of DAB was mixed with 100 ml of 50 mg/l of each metal solute. The contents of flasks were adjusted to pH 4. The samples were mixed for 4 h at agitation speed of 200 rpm; the supernatant was discarded and the biomass was left to dry. Dried samples were collected and analyzed by FT-IR.

3.2.3. Equilibrium isotherm experiments

Different weights (0.05, 0.1, 0.15 … to 0.6 g) of dry DAB were used; biosorbents were placed in 12 flasks of 250 ml. About 100 ml of solution with concentration of 50 mg/l was added to each flask of single, binary, and ternary 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 solutions was adjusted to the desired value of 4 using 0.1 M NaOH or 0.1 M HNO_3. The flasks were then placed on the shaker 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 0.1 M HNO_3 were added to samples to decrease the pH below 2 in order to fix the concentration of the heavy metals during storage before analysis [14]. The final equilibrium concentrations were measured by AA device. The adsorbed amount is then calculated by the following equation [11].

$$q_e = \frac{V_L(C_0 - C_e)}{W_A} \quad (1)$$

wherever (mg/g) is the amount of heavy metal ions uptake by (DAB), C_0 (mg/l) and C_e (mg/l) are initial and final metal ions concentration, respectively, V_L(l), is the volume of solution and W_A(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) [14].

3.2.4. Reaction kinetics experiments

Reaction kinetics experiments were found using 2 L Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 L of 50 mg/l concentration solution and the agitation was started before adding the DAB. At time zero, the accurate weight of DAB was added and the samples were taken at specified time intervals. The necessary dosage of DAB to reach equilibrium-related concentration of C_e/C_o that equals to 0.05 was calculated from isotherm model and mass balance (Eq. (1)). The external mass transfer coefficient (k_f) was calculated using the concentration decay curve obtained from experimental data at optimum agitation speed 400 rpm by using the analytical method [14].

$$k_{\mathrm{f}} = -\frac{R_p \rho_p V_{\mathrm{L}}}{3 W_A t} \ln\left(\frac{C_t}{C_o}\right) \quad (2)$$

where R_p and ρ_p are the particle radius and density; C_o and C_t are concentrations at time zero and time t, respectively.

4. Results and discussion

4.1. Effect of pH

The pH of the metal solution usually plays an important role in the biosorption of metals. Fig. 1 shows that over pH 4 the biosorption uptake effect was significant for Pb(II), Cr(III), and Cd(II) ions. The biosorption capacities were enhanced significantly from 34.2 to 51.56 mg/g for lead ions and 25.78 to 28 mg/g for chromium ions, while the cadmium ions uptake capacity increased from 19.2 to 29.2 mg/g, when pH value was raised from 3 to 4. Beyond the value of pH 6.0, precipitations of heavy metals will occur. This is due to insoluble metal hydroxides that start precipitating from the solutions at higher pH values. This should be avoided during sorption experiments to distinguish between sorption and precipitation [16].

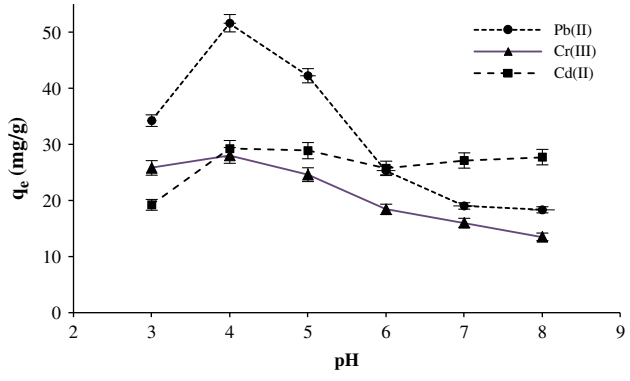

Fig. 1. Effect of different pH on lead, chromium and cadmium uptake onto DAB, $C_{\mathrm{biomass}} = 0.5$ g/l, $C_{0(\mathrm{Pb,\ Cr\ and\ Cd})} = 50$ mg/l.

4.2. FT-IR analysis

In order to understand the surface binding mechanism, it is essential to identify the functional groups presented on the biomass involved in the process. The main effective binding sites can be identified by FT-IR spectral. The main functional groups proposed for the metal uptake are amino, carbonyl, carboxylic, hydroxyl, phosphate, and others, mainly those from polysaccharide material which constitutes most of the cell wall. The spectra were measured within the range of 400–4,000 cm^{-1}. However, FT-IR spectroscopic analysis showed strong bands at 3,760–2,900 cm^{-1}, which is an indication of (–OH) as the hydroxyl groups and (N–H) for amide groups. A peak at 1,802 cm^{-1} can be attributed to the C=O stretching band of the carboxylic groups or ester groups. The peaks around 1,650 cm^{-1} show the carbonyl (–C=O) stretching vibration of the carboxyl groups of amino acids; peaks ranging from 1,300 to 1,000 cm^{-1} are described generally to the(C–O) stretching vibration in carbonayl and alcohols [13]. The results show that Pb(II), Cr(III), and Cd(II) may be adsorbed or complexed by H and O atoms of hydroxyle and carboxylic bonds, which shifted the bands to lower frequencies. These shifts may be attributed to the changes in counter ions associated with hydroxyle, amide, carboxylic of amino acids and amide, carboxylate, phosphate, sulfonate, and amino. These results agreed with the result obtained by Hawari and Mulligan [17]. Table 2 shows the main functional groups before and after dried anaerobic biomass loaded with Pb(II), Cr(III), and Cd (II) ions. The bands of functional groups shifted to lower frequency with total amount of 151, 90, and 70 for biomass loaded with Pb(II), Cr(III), and Cd(II), respectively. Therefore, the order of biosorption of heavy metals removed by complexation mechanisms on the surface of biomass is the following: Pb(II) > Cr(III) > Cd(II). Furthermore as the biosorption by DAB is related to the molecular weight of the adsorbate and as the molecular weight increases the biosorption rate increase, hence the sequence of the molecular weights for the salts used are: $Pb(NO_3)_2 > C(NO_3)_3 > Cd(NO_3)_2$. The electronegativities for lead are higher than chromium and cadmium ions; 2.33, 1.66, and 1.69, respectively, therefore, lead ions has higher strength of covalent binding than the lower affinity metals ions (chromium and cadmium). As the

Table 2
Functional groups before and after DAB loaded with Pb(II), Cr(III), and Cd(II) ions in single systems

Assignment groups	Unloaded (cm^{-1})	Loaded with Pb(II) (cm^{-1})	Δ	Loaded with Cr(III) (cm^{-1})	Δ	Loaded with Cd(II) (cm^{-1})	Δ
Hydroxyle (–OH)	3,760	3,745	15	3,749	11	3,752	8
	3,621	3,613	8	3,611	10	3,617	4
	3,540	3,527	13	3,523	17	3,537	3
	3,102	3,091	11	3,098	4	3,097	5
	2,921	2,912	9	2,916	5	2,919	2
Sum			56		47		22
Amide (N–H)	2,862	2,853	9	2,857	5	2,859	3
Carboxylic of amino acids	1,802	1,789	13	1,794	8	1,788	14
and amide (C=O)	1,663	1,643	20	1,658	5	1,653	10
Sum			33		13		24
Carboxylate (COO–)	1,443	1,437	6	1,440	3	1,441	2
Phosphate P–OH	1,036	1,021	15	1,026	10	1,029	7
Sulfonate R–S(=O)2–R	878	861	16	874	4	871	7
Amino (–NH)	790	782	8	788	2	787	3
	710	702	8	704	6	708	2
Sum			16		8		5
Total sum			151		90		70

electronegativity of the atom increases, its ionic forms seem to be more easily sorbed by the biosorbent. Finally, the biosorption of heavy metal ions increases with decrease in the solubility of solute [18] (Fig. 2).

4.3. Adsorption isotherm

4.3.1. Single component system

The adsorption isotherm for single component systems of Pb(II), Cr(III), and Cd(II) ions onto DAB is shown in Fig. 3. The parameters for each model obtained from nonlinear statistical fit of the equation to the experimental data using Statistica-v6 are summarized in Table 3. The equilibrium isothermfor each single component is of the favorable type $0 < R_L < 1$. The biosorption capacity (q_e) and heavy metals removal rate were related to the amount of biosorbent added; the greater biosorption capacity was obtained at lower biosorbent dose. The higher removal rate was achieved at higher biosorbent dose. The Langmuir model gives the best fit for the experimental data for single component adsorption system for lead, chromium, and cadmium ions recognized by the highest values of (R^2); this model has been used successfully to describe equilibrium biosorption isotherm.

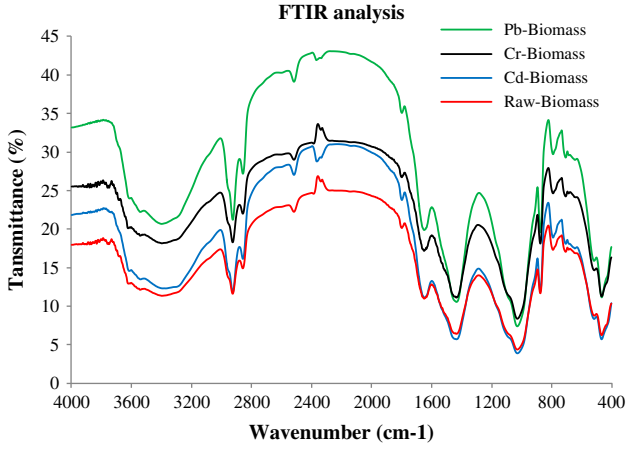

Fig. 2. FTIR spectra for raw DAB biomass before and after loaded with 50 mg/l of Pb(II), Cr(III) and Cd(II), single system.

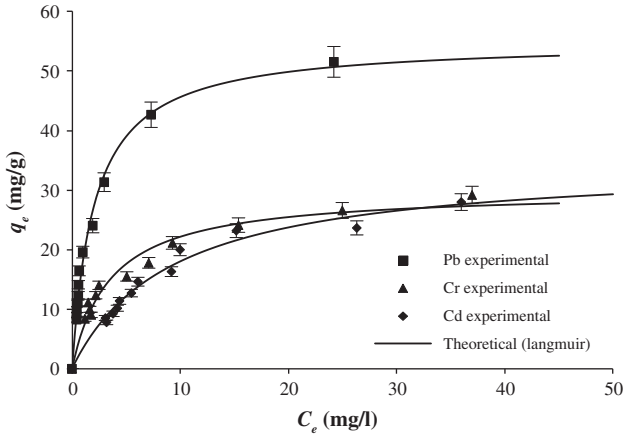

Fig. 3. Biosorption isotherms of lead, chromium and cadmium ions as single solutes onto DAB.

Table 3
Parameters of single solute isotherm for Pb(II), Cr(III), and Cd(II) ions onto DAB

Model		Parameters	Pb(II)	Cr(III)	Cd(II)
Freundlich [10]	$q_e = K_F C_e^{\frac{1}{n}}$	K,	17.450	9.238	5.986
		n, −	2.731	3.023	2.262
		R^2	0.9697	0.9895	0.9725
Langmuir [9]	$q_e = \frac{q_m b C_e}{(1+bC_e)}$	q_m (mg g^{-1})	54.92	34.78	29.99
		b (L mg^{-1})	0.493	0.107	0.285
		R_L	0.036	0.211	0.105
		R^2	**0.9952**	**0.9902**	**0.9851**
Temkin [10]	$q_e = \frac{RT}{b_{Te}} \ln(a_{Te} C_e)$	a_{Te} (mg g^{-1})	5.610	0.825	3.335
		$B = RT/b$ (L mg^{-1})	10.85	7.58	6.01
		R^2	0.9902	0.95	0.9802
Redlich–Peterson [15]	$q_e = \frac{K_{RP} C_e}{1+a_{RP} C_e^{\beta} RP}$	k_{RP} (mg g^{-1})	30.02	16.63	3.171
		a_{RB} (L mg^{-1})	0.66	1.11	0.047
		β, −	0.94	0.80	1.181
		R^2	0.9861	0.9842	0.9824
Toth [12]	$q_e = \frac{q_m b_T C_e}{[1+(b_T C_e)^{n_T}]^{\frac{1}{n_T}}}$	q_m (mg g^{-1})	59.741	49.17	54.462
		b_T	0.544	0.176	0.803
		n_T	1.236	1.14	2.594
		R^2	0.9894	0.976	0.9867
Sips [10]	$q_e = \frac{K_s C_e^{\beta_s}}{1+a_s C_e^{\beta_s}}$	k_s	25.885	10.023	2.450
		βs	0.8952	0.5943	1.3166
		a_s	0.4440	0.2260	0.0823
		R^2	0.9864	0.9838	0.9819
Khan [10]	$q_e = \frac{q_m b_k C_e}{(1+b_k C_e)^{a_k}}$	q_m (mg g^{-1})	43.404	13.181	62.141
		b_k (L mg^{-1})	0.6695	1.0186	0.0541
		a_k	0.917	0.770	1.391
		R^2	0.9862	0.9836	0.9801

Results of the three adsorbates can be compared in term of adsorption capacity parameters: Pb(II) > Cr(III) > Cd(II). 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 Åm for Pb(II), Cr (III), and Cd(II) ions, respectively) while cadmium ions are the least favorable and have the highest hydration radius. This coincides with the fact that less hydrated ions radius are preferably accumulated at interface [17]. Furthermore, the biosorption by DAB is related to the molecular weight of the adsorbate. As the molecular weight increases the biosorption rate also increases. The sequence of the molecular weights for the salts used is: $Pb(NO_3)_2 > Cr(NO_3)_3 > Cd(NO_3)_2$. The electronegativities for lead ions are higher than chromium and cadmium ions (2.33, 1.66, and 1.69, respectively). Therefore, lead ions have higher strength of covalent binding than the lower affinity metals ions (chromium and cadmium). As the electronegativity of the atom increases, its ionic forms seem to be more easily sorbed by the biosorbent. Finally, the biosorption of heavy metal ions increases with decreasing the solubility of solute [19]. As lead is less soluble in water (52, 81, and 136 g/100 ml for Pb(II), Cr(III), and Cd(II) ions, respectively), it is expected to be higher adsorbed onto biosorbent.

4.3.2. Binary and ternary component systems

The parameters for each model obtained from non-linear statistical fit to the experimental data are shown in Table 4. The adsorption isotherms for binary and ternary systems of Pb(II), Cr(III), and Cd(II) ions onto DAB are shown in Fig. 4. The decrease of adsorption capacity in binary and ternary systems compared with the single metal systems observed for all metals with exception of lead reflects the existence of a competition between the metals studied for the binding sites presented in biomass cell wall. These results agreed with the results obtained by Naddafi et al. [16]. It seems that the total metal adsorption capacity onto the biomass decreases when increasing the number of metals presented. This fact supports the competition between metals for the biomass binding sites and

Table 4
Parameters of binary and ternary systems solutes isotherms for lead, chromium, and cadmium ions onto DAB

Model	Parameters	Binary system						Ternary system		
		Pb(II), Cr(III) system		Pb(II), Cd(II) system		Cr(III), Cd(II) system				
		Pb(II)	Cr(III)	Pb(II)	Cd(II)	Cr(III)	Cd(II)	Pb(II)	Cr(III)	Cd(II)
Extended Langmuir $q_i = \frac{b_i q_{m,i} C_{e,i}}{(1+\sum_{j=1}^{n} b_j C_{e,j})}$ [10]	q_m (mg/g)	35.12	23.84	38.6	11.8	24.51	23.86	15.68	13.86	4.18
	b (l/mg)	0.311	0.165	0.142	0.185	0.382	0.039	0.048	0.03	0.09
	R_L	0.084	0.203	0.154	0.314	0.096	0.518	0.571	0.706	0.727
	R^2	0.958	0.999	0.996	0.992	0.993	0.999	0.995	0.986	0.992
Interaction factor $q_i = \frac{b_i q_{m,i} (C_{e,i}/\eta_i)}{1+\sum_{j=1}^{n} b_j (C_{e,j}/\eta_j)}$ [11]	q_m (mg/g)	46.32	26.63	57.17	8.96	24.33	76.33	15.59	9.5	2.5
	η	86.24	7.13	90.88	1.53	7.22	4.50	5.68	6.03	2.79
	R^2	0.961	0.989	0.960	0.993	0.992	0.991	0.992	0.981	0.985
Redlich–Peterson $q_i = \frac{K_{R,i} q_{m,i} C_{e,i}}{(1+\sum_{j=1}^{n} a_{R,j} C_{e,j}^{B_j})}$ [12]	q_m, −	5.56	0.29	3.47	9.87	8.94	5.65	11.6	7.9	2.8
	β, −	9.23	1.12	0.39	0.49	0.79	0.16	7.4	0.3	0.21
	R^2	0.882	0.952	0.956	0.989	0.935	0.984	0.832	0.854	0.841
Combination of Langmuir–Freundlich $q_i = \frac{q_{m,i} b_i C_{e,i}^{(\frac{1}{n_i})}}{(1+\sum_{j=1}^{n} b_j C_{ej}^{(\frac{1}{n_j})})}$ [14]	q_m (mg/g)	24.08	13.15	31.3	6.5	27.17	9.77	18.2	9.3	7.7
	b (l/mg)	0.08	0.09	0.02	0.50	0.16	0.09	0.03	0.01	0.03
	n	3.73	7.4	2.3	1.1	1.2	4.4	2.1	1.3	1.02
	R^2	0.997	0.731	0.992	0.956	0.994	0.991	0.82	0.84	0.79

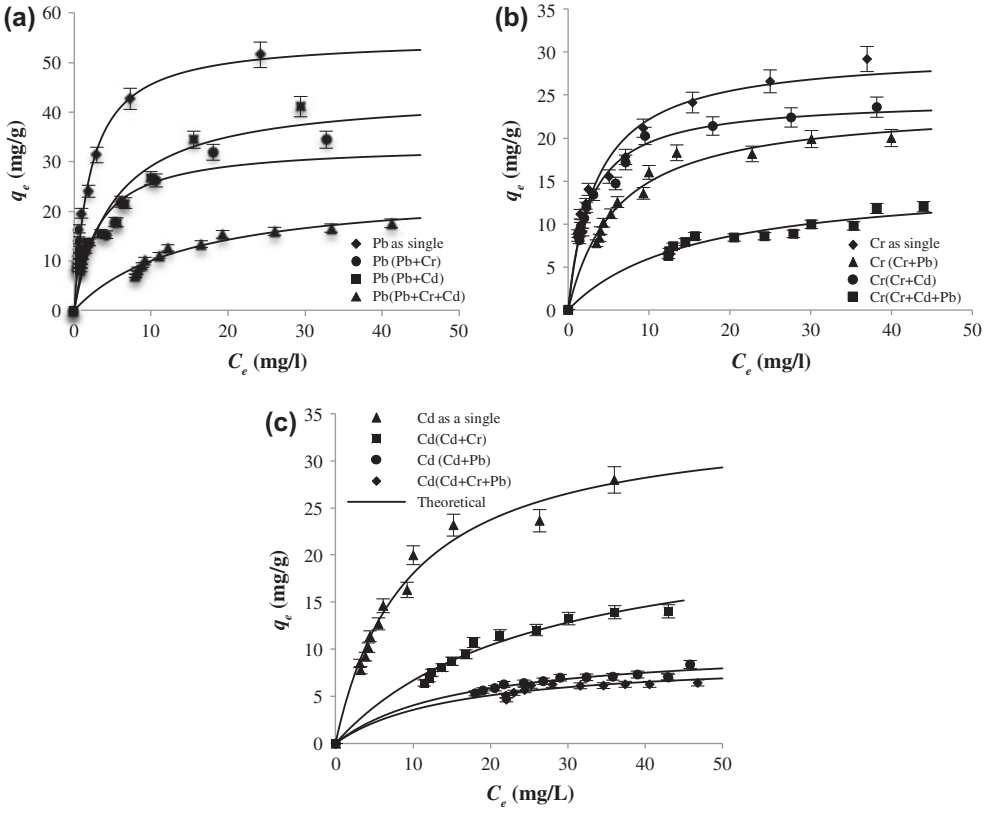

Fig. 4. (a)–(c) Biosorption isotherms for lead ions onto DAB, in single, binary and ternary systems $C_0 = 50$ mg/l, respectively.

tends to decrease the relative amount of each adsorbed element. The removal efficiency achieved with DAB when using initial concentration of 50 mg/l for each metal ions for single system were 99.14, 97.67, and 93.2% for Pb(II), Cr(III), and Cd(II), respectively. Whereas, the removal efficiency of DAB were 98.24, 64%, for Pb(II)–Cd(II) system, 99.1, 93%, for Pb (II)–Cr(III) system, and 97.2, 77.2%, for Cr(III)–Cd(II) system. For Pb(II)–Cr(III)–Cd(II) system, the removal efficiency were 84, 75.2, and 55.9%, respectively.

For both the binary and ternary systems, the extended Langmuir model seems to give the best fitting for the experimental data at highest value of R^2. It can be seen from the figures and related table, Pb(II) always adsorbed more favorably onto the biomass than Cr(III) and Cd(II) in both binary and ternary systems. The decrease of adsorption capacity in binary and ternary systems compared to the single metal systems observed for all metals with exception of lead, reflects the existence of a competition between the metals studied for the binding sites present in biomass cell wall. It seems that the total metal adsorption capacity onto the biomass decreases when increasing the number of metals present. This fact supports the assumed competition between metals for the biomass binding sites and tends to decrease the relative amount of each adsorbed element.

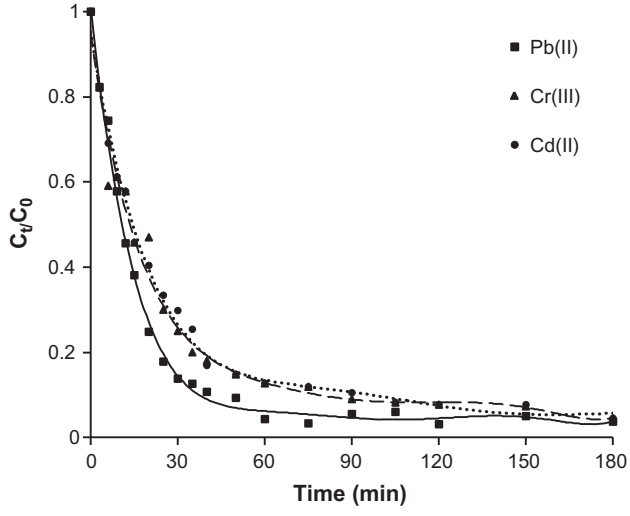

Fig. 5. Concentration—time decay data with that predicated by pore diffusion model for Pb(II), Cr(III), and Cd(II) ions.

Table 5
Kinetic model parameters for Pb(II), Cr(III), and Cd(II) ions biosorption onto DAB

Model	Parameters	Pb(II)	Cr(III)	Cd(II)
Intraparticle diffusion [19] $q_t = K_{id}t^{0.5} + C$	C (mg/g)	10.96	14.61	22.66
	K_{id} (mg/g.min$^{0.5}$)	2.64	3.34	0.42
	Correlation coefficient	0.827	0.692	0.538
Fractional power [19] $\ln(q_t) = \ln(k) + x\ln(t)$	K (mg/g)	5.16	2.41	2.5
	V (min^{-1})	1.45	1.44	1.29
	Correlation coefficient	0.856	0.772	0.556
Pseudo-first-order [12] $q_t = q_e(1 - \exp(-k_1 t))$	q_e (mg/g)	18.28	5.86	1.9
	K_1 (min^{-1})	2.7×10^{-2}	4.3×10^{-2}	2.8×10^{-2}
	Correlation coefficient	0.956	0.924	0.781
Pseudo-second-order [12] $\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right)$	q_e cal. (mg/g)	33.33	12.98	7.51
	K_2 (mg/g.min)	2.2×10^{-3}	8.77×10^{-3}	3.42×10^{-2}
	h_0	2.533	1.478	1.920
	Correlation coefficient	0.998	0.995	0.997
Elovich [19] $\frac{dq}{dt} = a\exp(-bq_t)$	a_E (mg/g.min)	5.88	3.39	11.94
	β_E (g/mg)	0.155	0.39	0.93
	Correlation coefficient	0.953	0.853	0.69

4.4. Biosorption kinetics

The amount of DAB used for the adsorption of Pb(II), Cr(III), and Cd(II) ions was calculated for final equilibrium-related concentration of $C_e/C_o = 0.05$; the Langmuir model constants were used with the mass balance in one liter of solution. The initial concentration was 50 mg/l with doses of DAB to be 1.573×10^{-3}, 3.894×10^{-3}, and 6.473×10^{-3} kg for Pb (II), Cr (III), and Cd (II) ions, respectively, as shown in Fig. 5. The average calculated values of k_f for each solute was found to be 4.53×10^{-6}, 2.28×10^{-6}, and 1.933×10^{-6} m/s for Pb(II), Cr(III), and Cd(II) ions, respectively. This indicates that the rate of mass transfer of Pb(II) is higher than the other components. In other words, Pb(II) is adsorbed by dried biomass at higher rate than others.

In order to evaluate the kinetic mechanism that controls the adsorption process, the intraparticle diffusion, fractional power, pseudo-first-order, pseudo-second-order, and Elovich kinetic models were employed to interpret the experimental data. The kinetic parameters based on the correlation coefficient (R) of each kinetic model, therefore, adsorption of Pb(II), Cr(III), and Cd(II) ions are perfectly fit the pseudo-second-order model rather than others as shown in Table 4.

5. Conclusions

The equilibrium isotherm for each single component is of a favorable type and Langmuir isotherm model gives the best fit of the experimental data for this system (Table 5). In this system, Pb(II) was the most favorable component than Cr(III), and Cd(II), due to its physiochemical characteristics that make it the most favorable adsorbed component, due to less solubility andhighly molecular weight. An adsorption capacity parameters were: Pb(II) > Cr(III) > Cd(II). Optimum pH was 4 for Pb(II), Cr(III), and Cd(II). Amino, carbonyl, carboxylic, and hydroxyl play the major rule for removal of Pb(II), Cr (III), and Cd(II) ions by complexation mechanism. For both binary and ternary component systems, extended Langmuir Isotherm gives the best fit for the experimental data. The behavior of the equilibrium isotherm is of the favorable type. Pb(II) ions are still most adsorbed component than Cr(III) and Cd(II) ions. Due to the competitive effects of Pb(II), Cr(III), and Cd(II) with each other to occupy the available site(s) of the DAB, Pb(II) ions offer the strongest component that is able to displace Cr(III) and Cd(II), while Cd(II) was the weakest adsorbed component. Compared with their adsorption in single component system, the adsorption capacity of all three metals shows obvious decrease in the binary and ternary system. The percentage of the removal of each single component decreased as each component is presented with the other(s) in the binary and/or ternary system. This is due to the presence of more than one component that will enhance the competitive struggling race for occupying a certain site. The external mass transfer coefficient (k_f) was obtained using the concentration decay curve of the experimental data at

optimum agitation speed. The adsorption followed pseudo-second-order kinetics.

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Nomenclature

B_R	—	Redlich–Peterson model parameter $(l/mg)^{m}{}_{R}$
B	—	Langmuir adsorption constant related to the affinity to binding sites, l/mg
bi	—	individual Langmuir adsorption constant of each component, l/mg
C_o	—	initial heavy metal concentration, mg/l
C_e	—	equilibrium concentration, mg/l
DDW	—	deionized distilled water
DAB	—	dead anaerobic biomass
CFU	—	colony forming unit
K_F	—	Freundlich adsorption constant, related to adsorption intensity (mg/g) $(l/mg)^{1/nF}$
K_{Fi}	—	individual Freundlich adsorption constant of each component (mg/g) $(l/mg)^{1/nF}$
K_{Ri}	—	individual Redlich–Peterson adsorption constant of each component (L/mg)
m_{Ri}	—	Redlich–Peterson model parameter
n_F	—	Freundlich adsorption constant, related to the affinity to binding sites
n_{Fi}	—	individual Freundlich adsorption constant of each component
q_{eq}	—	adsorbed phenol/lead quantity per gram of DAB at equilibrium, mg/g
q_m	—	Langmuir adsorption constant of the pollutants shows the maximum amount of pollutants bound to the DAB, mg/g
q_{ei}	—	amount of adsorbate adsorbed per mass of adsorbent of component i, mg/g
q_{mi}	—	individual Langmuir adsorption constant of each component, mg/g
V_L	—	volume of solution, l
W_A	—	mass of DAB, g

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