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Single and Binary Biosorption isotherms of Different Heavy Metal Ions Using Fungal Waste Biomass

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Abstract

The ability of fungal waste biomass type *White Agaricus Bisporus* to biosorb Pb(II) ,Cr(III), Cd(II) and Co(II) from wastewater was investigated in batch process. Single and binary mixtures were used at low metal concentration wastewater treatment. The size of the biosorbent ranged 0.3-1 mm. The biosorption capacity of the biosorbent was evaluated under equilibrium conditions at 25 °C. Results indicated that the biosorption capacity of waste of fungi for the binary mixture was always lower than that for a single component system. Eight isotherm models were used to fit the experimental data of single system and Langmuir model was found a suitable to describe the biosorption data. The maximum uptake capacity (q_e) of Pb(II), Cr(III), Cd(II) and Co(II) in single system was 158.73, 46.94, 40.16 and15.94 mg/g respectively with correlation coefficients 0.999,0.998,0.988 and 0.991 respectively. For binary system, four biosorption models were used to fit the experimental data. Extended Langmuir model gave the best fitting. The removal percentage of heavy metals onto fungal waste biomass was in order of Pb(II) > Cr(III) > Cd(II) > Co(II) in both single and binary system. The results show that the using waste of fungi as a biosorbent of heavy metals gave a higher uptake capacity of four heavy metals.

Key Words: Biosorption, Heavy metals, Waste of fungi, Wastewater treatment

1. Introduction

The wastewaters discharged from chemical industries which may contain heavy metal ions have toxic effect on all the living organisms, so heavy metal pollution of wastewater is a common environmental hazards, the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health and ecosystem.

Heavy metal ions have great effects on all forms of life. Heavy metal pollution is one of the most important environmental problems today because of their toxicity, bio-accumulation tendency, threat to human life and the environment [1].

According to WHO, the most toxic metal are chromium, cobalt, mercury, lead, copper, cadmium, zinc, nickel and among non-metals, arsenic [2].

The main source of heavy metal pollution are metal plating, mining , smelting, battery manufacturing, tanneries, petroleum refining, pigment manufacture, printing paint manufacture, pesticides, etc..

Heavy metals are commonly removed by many conventional methods including ion exchange, chemical precipitation, electrochemical processes and/or membrane processes, solvent extraction and adsorption. The application of such processes is often limited because of technical (inefficient) or economic constraints (expensive) especially for low strength wastewaters. Among them, adsorption was found to be the most effective method for removing dissolved metal ions from water [2].

Adsorption is well-known and widely used as industrial separation process. Traditional sorbent materials such as zeolites, granular activated carbon (GAC), silica and alumina have been used extensively in industrial scale liquid separation processes. Adsorption with activated carbon is known to be effective, but requires regeneration, besides the activated carbon is also expensive. So it is required to find inexpensive and renewable materials as alternative sorption materials produced from agricultural or biological sources which called biomass and biosorbent respectively. These drawbacks of traditional metal removal techniques have led researchers to investigate the use of microbial biomass as biosorbents for heavy metal removal.

It is well known that pure and mixed cultures of bacteria, algae, yeast, fungi and other microorganisms can remove heavy metal ions from solution in significant quantities [3]. This biosorption process offers the advantages of low operating costs, minimization of the volume of chemical and/or biological sludge to be disposed of and high efficiency in detoxifying very dilute effluents [4,5] . Biosorption is a process, whereby certain types of inactive, dead biomass may bind and concentrate heavy metals from aqueous solutions by “passive” driving forces. These driving forces are non-metabolic activity and different from “bioaccumulation”, which usually refers to the metal accumulation by living cells. In particular, it is the cell wall structure that is principally responsible for the metal-binding capacity [5].

In comparison with conventional treatment for waste water, there are several advantages in biosorption technology. First of all, the biosorption removal efficiency of toxic heavy metals is high. Metal levels can be decreased from 1-100 mg/L and for drinking water 0.01-0.1 mg/L in continuous flow biosorption columns [6, 7].

Second, biosorption may be implemented over a wide range of operating solution pH, pressures and temperatures. In addition, the regeneration can also be achieved relatively easily by acid elution. Thus, no sludge is produced in contrast to the precipitation process. The main advantage is the lower cost of the biosorbent, since it may be derived from various inexpensive raw materials. These include waste biomass from the fermentation industry and naturally abundant marine algae that are ubiquitous [8-12].

In the present investigation, the dead fungal biomass of *white Agaricus bisporus* was used to remove lead, chromium, cobalt and cadmium ions from wastewater in single and binary component systems. It aims to find the efficiency of fungal waste biomass for the simultaneous removal of heavy metal ions from simulated wastewater, to compare the adsorption capacity onto fungal waste biomass in single and binary systems and examine the applicability of various biosorption isotherm models to fit the experimental data.

2. Materials and Procedure

2.1 Adsorbate

Lead nitrate $Pb(NO_3)_2$, chromium nitrate $Cr(NO_3)_3.9H_2O$, cobalt nitrate $Co(NO_3)_2.6H_2O$,and cadmium nitrate $Cd(NO_3)_2.4H_2O$ were used. All chemicals used are of analytical grade supplied by Lobal Chemie Company India.

Thousand mg/L stock solutions of Pb (II),Cr(III), Co(II) and Cd (II) were prepared by weighted accurately amount of lead nitrate ($Pb(NO_3)_2$), chromium nitrate ($Cr(NO_3)_3.9H_2O$), cobalt nitrate ($Co(NO_3)_2.6H_2O$) and cadmium nitrate ($Cd(NO_3)_2.4H_2O$) then dissolved in distilled water and make up to 1 L. Experimental solutions of the desired concentration were prepared by diluting the stock solution with distilled water.

2.2 Biosorbent

A dead cell waste of fungi was sieved through a 1000, and 300 µm diameter mesh. The mean particle diameter of waste of fungi used is 0.57 mm using the relation $d_{pm} = (d_{p1}.d_{p2})^{0.5}$. Where d_{p1} and d_{p2} are the upper diameter and lower diameter practical size. Figure (1) shows dried biomass without any treatment. Figure (2) shows the waste of fungi after several treatments (such as grinding, screening, washing and drying) with mean particle diameter of 0.57mm. Figure (3) shows scanning electron micrographs for waste fungal biomass.

Figure 1: Untreated fungal waste biomass

Figure 2: Sample of treated waste of fungi, size (0.3-1.0 mm)

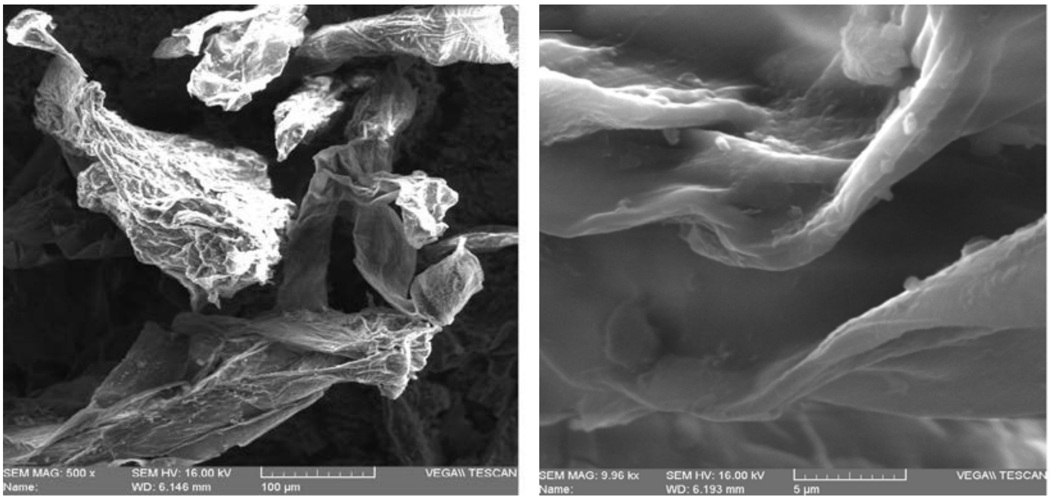


Figure 3: Scanning electron micrographs for waste of fungi

2.3 Batch Experiments

Batch experiments were carried out in 250 ml conical flasks containing different solutions with different concentrations ranged (10-200) mg/L as an experiment solution from standard solution after adjusting the pH of solution to required value by adding 0.1 M HCl or 0.1 M NaOH, then taking a desired amount from biosorbent. A sample of (100 mL) of each solution was placed in conical flasks of (250mL) in volume containing the desired amount of biosorbent ranging 0.1 mg - 2 gm. The flasks are placed on the shaker and agitated continuously for 3 hr at (298K).

The solution after shaking is centrifuged for 10 min and then filtrated using filter paper (0.45 um) Millipore, Spain) A sample of (10 mL) from each flask is taken for analysis by means of Atomic Absorption Spectrophotometer (A A S), type Shemazo 7000, Japan. The adsorbed amount and removal efficiency are then calculated using the following equations:

$$q_e = \frac{V}{W}(C_o - C_e) \qquad (1)$$

$$\%Removal = (C_o - C_e)/C_o \times 100 \qquad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations (mg/L) of metal ion in solution, V is the volume (L) and W is the weight (g) of the waste of fungi.

The adsorption isotherms are obtained by plotting the weight of solute adsorbed per unit weight of adsorbent (q_e) against the equilibrium concentration of the solute in the solution (C_e) and plotting the % removal of heavy metal against the equilibrium concentration of the solute in the solution.

3. Results and Discussion

3.1 Estimation of Biosorption Isotherms Constants

The adsorption of a single and binary component systems of Pb(II), Cr(III), Co(II) and Cd(II) ions onto waste of fungi was conducted with initial concentration of (50 mg/L) and particle size of (0.57 mm) at room temperature 25°C ∓ 1 in order to determine the isotherms constants for each system using different isotherm models.

3.1.1 Single System

The adsorption isotherms for single systems of Pb(II), Cr(III), Co(II) and Cd(II) onto fungal waste biomass were shown in Figure (4). Eight isotherm models were used to fit the experimental data. The parameters of eight models were obtained using non-linear statistical fit of the equation to the experimental data (Statistica-v6) and EXCEL-2010 software. Table (1) show all parameters isotherm for Pb(II), Cr(III), Co(II) and Cd(II) ions uptake onto waste of fungi with correlation coefficients R^2. It is clear from this table that the Langmuir fitted the experimental data with high values of R^2 Figure 5 (a, b) show the maximum uptake capacity and percentage removal efficiency of Pb(II), Cr(III), Co(II) and Cd(II) onto fungal waste biomass at 25 $^{\circ}$C.

From Figure (4): The experimental data of Pb(II), Cr(III), Co(II) and Cd(II) indicate that an increase in the metal ions concentration resulted in an increase in the amount of the ions adsorbed and the capacity of the fungal waste biomass followed the order Pb(II)> Cr(III) >Cd(II)> Co(II). One of the essential characteristics of the Langmuir model could be expressed by dimensionless constant called equilibrium parameters R_L.

$$R_L = \frac{1}{1+bC_o} \qquad (3)$$

Where C_o is the higest initial ion concentration (mg/L).

The value of R_L indicates the type of isotherm to be irreversible (R_L=0), favorable (0 <R_L <1), linear (R_L=1), or unfavorable (R_L>1). Also ,this figure indicates that the equilibrium isotherm curves for each metal ions is favorable because these curves have the same shape of favorable curves and show that relatively high loading can be obtained at low concentration of metal ion in water. It was found that all values of R_L were less than 1 and greater than 0 indicating that it is favorable.

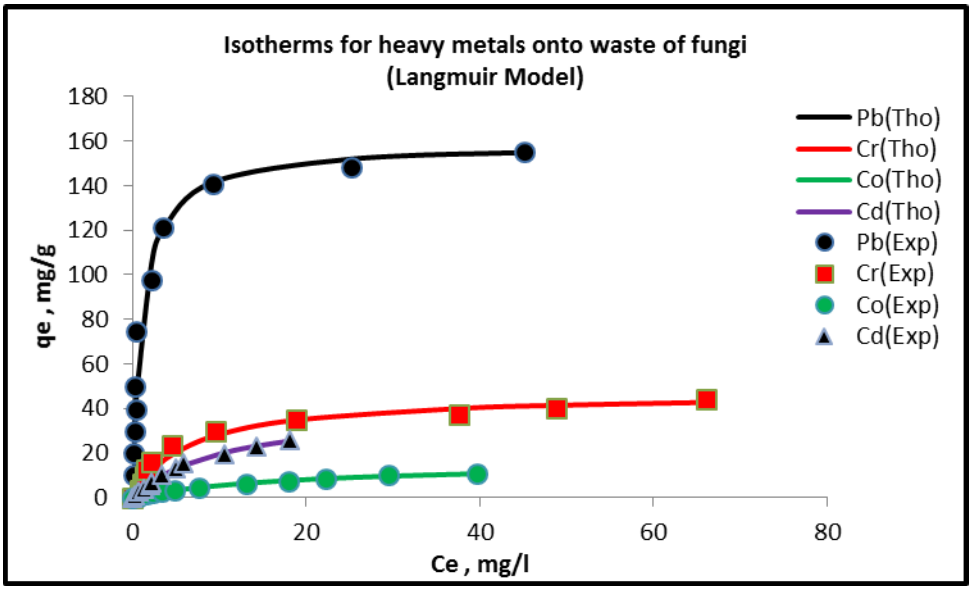
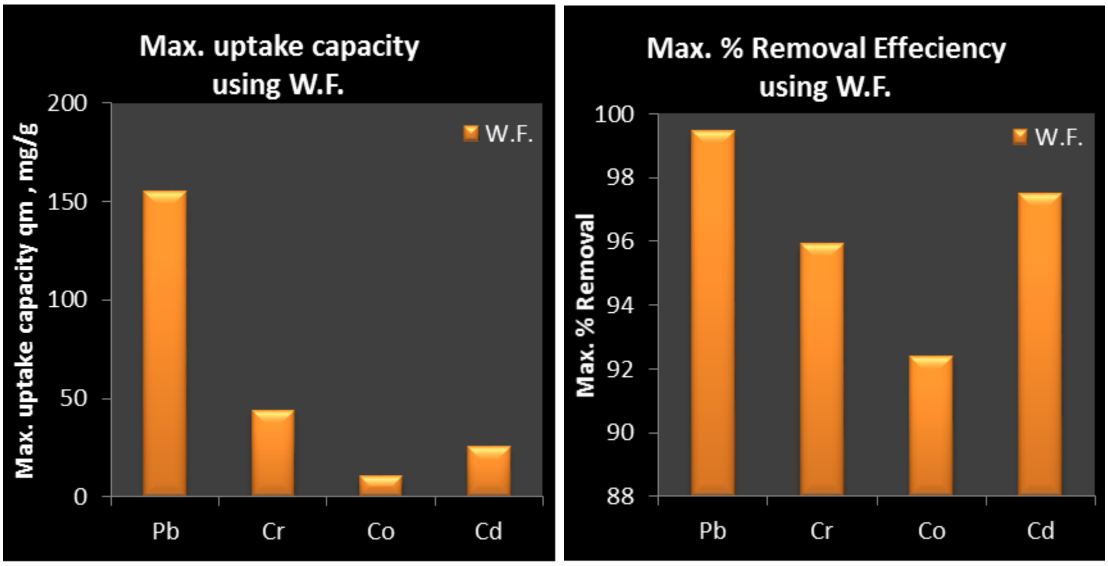


Figure 4: Single biosorption isotherm for Pb(II), Cr(III), Co(II) and Cd(II) onto W.F. (C_o=50 mg/L, Temp=25°C)



(a) **(b)**

Figure 5: (a) Maximum uptake capacity, (b) Maximum percentage removal efficiency of Pb(II), Cr(III), Co(II) and Cd(II) onto fungal waste biomass at 25 °C

Table 1: Isotherm parameters for single metal ions adsorbed onto W.F. with correlation coefficients

Model	**Parameters**	**Metal Ions**			
		Pb(II)	Cr(III)	Co(II)	Cd(II)
Langmuir $q_e = \frac{q_m b C_e}{1 + b C_e}$ [13]	q_m(mg/g)	158.73	46.948	15.9489	40.1606
	b(1/mg)	0.887	0.151	0.0507	0.0943
	R²	0.9992	0.998	0.9879	0.9905
Freundlich $q_e = K C_e^{1/n}$ [14]	K_f(mg/g)$(1/\text{mg})^{1/n}$	53.481	7.3333	0.912	3.475
	n	0.3843	0.4869	0.7149	0.7477
	R²	0.7762	0.8274	0.9873	0.9821
Temkin $q_e = \frac{RT}{b} \ln(K_T C_e)$ [14]	a	18.6566	2.2075	0.9254	2.07
	b	25.172	8.93	2.6989	6.1265
	R²	0.9448	0.9813	0.9393	0.9033
Dubinin-Radushkeich $\frac{q_e}{q_{DR}} = \exp(-\beta \in^2)$ [15]	k_{ad}	4.00E-08	8.00E-07	3.00E-07	7.00E-08
	q_s(mg/g)	8.2755	74.1284	2.098	2.9305
	R²	0.9395	0.6337	0.6988	0.6552
Sips $q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}}$ [16]	q_m(mg/q)	39.5442	9.3908	1.2501	6.6804
	$b(1/\text{mg})^{1/n}$	2.6324	0.9667	0.8865	1.0947
	n	0.3843	0.4869	0.7149	0.7443
	k_s	140.2909	7.3802	0.7919	4.0122
	R²	0.7762	0.8274	0.9873	0.9857
Khan $q_e = \frac{q_{\max} b_k C_e}{(1 + b_k C_e)^{a_k}}$ [17]	q_m(mg/g)	128.3700	40.7266	7.8508	52.0537
	$b_{k(1/mg)}$	1.5222	0.2317	0.1084	0.0713
	a_k	0.9515	0.9654	0.6735	1.1876
	R²	0.9814	0.9907	0.9985	0.9979
Toth $q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$ [14]	K_t(mg/g)	131.0851	37.9884	1.8297	17.6018
	a_t	0.6576	4.3274	2.9509	6.5187
	t	1.0507	1.0406	2.0062	1.2674
	R²	0.9814	0.9907	0.9971	0.9978
Koble-Corrigan $qe = \frac{K * Ce^{\alpha}}{1 + a * Ce^{\alpha}}$ [14]	A_{kc}(mg/g)$(\text{L/mg})^n$	158.3922	8.4283	8.7655	3.4871
	$B_{kc}(\text{L/mg})^n$	1.0005	0.1957	0.1	0.0997
	n	0.8885	1.1134	1.1608	1.1125
	R²	0.9808	0.9911	0.9991	0.9981

3.1.2 Binary System

The biosorption equilibrium isotherms for the binary systems were conducted by preparing a solution with initial concentrations of 10 to 200 mg/L for each pollutant and using waste of fungi as biosorbent with particle size 0.57 mm. The biosorption isotherms for binary component systems of Pb(II), Cr(III), Co(II) and Cd(II) ions onto fungal waste biomass were shown in Figure (6)(a,b,c,d,e,f) respectively. Table (2) represents the parameters of each model and their correlation coefficient R^2 by using extended Langmuir model, Combination of Langmuir-Freundlich model, modified Temkin model and Hasley-Henderson model.

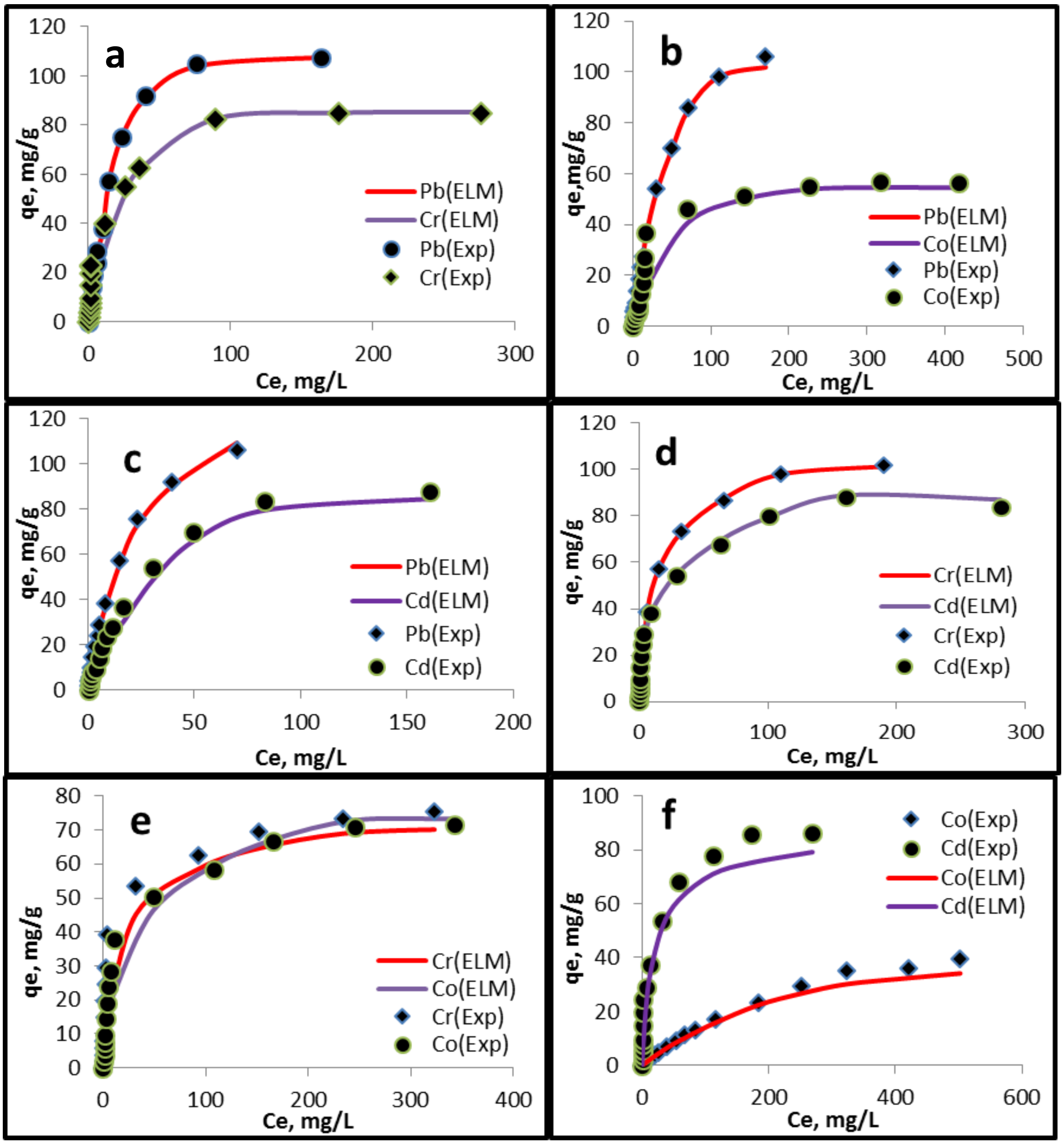


Figure 6: Biosorption isotherm of (a) Pb-Cr,(b)Pb-Co, (c) Pb-Cd, (d) Cr-Co, (e) Cr-Cd and (f) Co-Cd ions onto W.F.

For the binary system, the extended Langmuir model seems to give the best fitting for the experimental data at a large value of (R^2). In addition, combination of Langmuir-Freundlich model may participate with extended Langmuir model to give the best fit for some systems. The behaviour of the equilibrium isotherms for the binary system was of a favorable type. It can be seen from the figures and related table, Pb(II)always adsorbed more favorably onto fungal waste biomass than Cr(III), Co(II) and Cd(II) in the binary system.

In general, the application of the extended Langmuir model indicated that the presence of one metal ion in the biosorption system always lowers the biosorption capacity for the other metal.

The suppressing effect of one metal on biosorption capacity of fungal waste biomass for the other(s) indicated a competition for the same biosorption sites and functional groups. The above results indicate that Pb(II) was the metal that experienced a weak competitive biosorption process. Cr(III), Co(II) and Cd(II) had little influence on the Pb(II) biosorption in the presence of fungal waste biomass. Conversely Pb(II) significantly inhibited the retention of Cr(III), Co(II) and Cd(II).Co(II) was most affected in the competitive biosorption. The q_m values and the biosorption efficiency for the binary system were less than those in single systems due to competition between the solutes as mentioned in above figures and tables.

Table 2: Parameters of a binary solute isotherm for lead, chromium, cobalt and cadmium ions onto fungal waste biomass

Model	**Parameters**	**(Pb-Cr) Solution**		**(Pb-Co) Solution**		**(Pb-Cd) Solution**		**(Cr-Co) Solution**		**(Cr-Cd) Solution**		**(Co-Cd) Solution**	
		Pb	**Cr**	**Pb**	**Co**	**Pb**	**Cd**	**Cr**	**Co**	**Cr**	**Cd**	**Co**	**Cd**
Extended Langmuir Model $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1+\sum_{k=1}^{N} b_k C_{e,k}}$ [18]	q_m(mg/g)	120.48	90.91	136.98	63.29	133.33	105.26	76.33	75.18	108.69	86.95	65.35	90.91
	b(1/mg)	0.0588	0.0661	0.021	0.025	0.054	0.034	0.098	0.051	0.072	0.123	0.003	0.064
	R^2	0.991	0.991	0.991	0.986	0.995	0.991	0.997	0.992	0.996	0.996	0.990	0.993
Combination Of Langmuir -Freundlich Model $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1+\sum_{i=1}^{N} b_i C_{e,i}^{1/n_i}}$ [19]	q_m(mg/g)	116.88	130.08	131.91	149.5	140.02	132.21	67.36	74.69	110.95	141.09	66.18	48.35
	b(1/mg)	0.035	0.078	0.018	0.019	0.051	0.024	0.129	0.076	0.096	0.104	0.003	0.102
	n	0.813	1.329	0.936	1.271	1.024	0.986	0.584	0.999	1.123	1.718	1.019	1.491
	R^2	0.996	0.985	0.999	0.989	0.999	0.999	0.985	0.992	0.996	0.995	0.998	0.988
Modified Temkin Model $\frac{q_{e,i}}{C_{e,i}} = \frac{RT}{b}\ln(K_T\ bC_{e,i})$ [20,21]	B_1	18.94	15.11	20.33	11.47	19.85	16.63	11.61	12.44	17.96	12.53	9.02	14.33
	K_T	1.517	1.531	0.591	0.474	1.458	0.838	2.622	1.131	1.614	3.566	0.087	1.628
	R^2	0.947	0.985	0.949	0.955	0.952	0.951	0.983	0.991	0.989	0.986	0.947	0.982
Hasley-Henderson Model $\ln q_e = \frac{1}{n}\ln K - \frac{1}{n}\ln C_e$ [22]	K	22.42	50.84	5.81	5.79	14.41	8.80	139.67	30.79	33.92	155.84	3.75	48.58
	n	1.551	1.927	1.361	1.711	1.362	1.462	2.265	1.965	1.686	2.170	1.255	1.931
	R^2	0.972	0.871	0.987	0.911	0.986	0.983	0.871	0.901	0.938	0.944	0.994	0.913

Table 3: Competition results in single and binary Systems using fungal waste biomass

Heavy metal	Single system		Heavy metal	Metal competition in binary system		Total metal adsorbed (mg/g)
	$q_{e(mg/g)}$	%R		q_e(mg/g)	%R	
Pb(II)	94.74	99.46	Pb(II)	9.6	96.94	19.26
			Cr(III)	9.66	96.6	
			Pb(II)	9.28	92.86	17.7
			Co(II)	8.42	84.2	
			Pb(II)	9.72	97.2	19.03
			Cd(II)	9.31	93.1	
Cr(III)	53.12	95.72	Cr(III)	9.66	96.6	19.35
			Pb(II)	9.69	96.94	
			Cr(III)	9.75	97.5	19.41
			Co(II)	9.66	96.6	
			Cr(III)	9.74	97.4	19.6
			Cd(II)	9.86	98.6	
Co(II)	42.57	90.3	Co(II)	8.42	84.2	17.7
			Pb(II)	9.28	92.86	
			Co(II)	9.66	96.6	19.32
			Cr(III)	9.66	96.6	
			Co(II)	4.84	48.4	14.51
			Cd(II)	9.67	96.7	
Cd((II)	56	96.02	Cd(II)	9.31	93.1	19.03
			Pb(II)	9.72	97.2	
			Cd(II)	9.86	98.6	19.6
			Cr(III)	9.74	97.4	
			Cd(II)	9.67	96.7	14.51
			Co(II)	4.84	48.4	

Table 4: Percentage reduced of the metal uptake capacity in binary system compared with single system using fungal waste biomass

Metal ion	% Reduced	Metal ion	% Reduced
Pb	single	Co	single
Pb in (Pb-Cr)	89.86	Co in (Co-Pb)	80.22
Pb in (Pb-Co)	90.20	Co in (Co-Cr)	77.31
Pb in (Pb-Cd)	89.74	Co in (Co-Cd)	88.63
Metal ion	**% Reduced**	**Metal ion**	**% Reduced**
Cr	single	Cd	Single
Cr in (Cr-Pb)	81.81	Cd in (Cd-Pb)	83.37
Cr in (Cr-Co)	81.64	Cd in (Cd-Cr)	82.39
Cr in (Cr-Cd)	81.66	Cd in (Cd-Co)	82.73

Table 5: Maximum removal efficiency of each pollutant using fungal waste biomass

System	Pollutants System	C_o(mg/L)	C_e(mg/L)	q_e(mg/g)	%Max.R.
Single	Pb(II)	75	0.44	74.56	99.41
	Cr(III)	40	1.63	42.59	95.92
	Co(II)	30	2.46	13.8	92.0
	Cd(II)	75	2.24	24.25	97.01
Binary	Pb(II) in (Pb- Cr)	20	0.4	3.92	98
	Cr(III) in (Pb- Cr)	150	1.59	23.22	98.94
	Pb(II) in (Pb- Co)	30	1.47	5.71	95.1
	Co(II) in (Pb- Co)	50	7.9	8.72	89
	Pb(II) in (Pb- Cd)	20	0.5	3.83	97.5
	Cd(II) in (Pb- Cd)	30	1.34	5.73	95.55
	Cr(III) in (Cr- Co)	150	3.26	29.34	97.82
	Co(II) in (Cr- Co)	50	1.69	9.66	96.61
	Cr(III) in (Cr- Cd)	25	1.0	4.8	96
	Cd(II) in (Cr- Cd)	30	0.52	5.89	98.25
	Co(II) in (Co- Cd)	50	25.72	9.24	50.93
	Cd(II) in (Co- Cd)	50	1.63	9.67	97

From the above figures and tables, it can be seen the effect of metal concentration of Pb(II), Cr(III), Co(II) and Cd(II) onto fungal waste biomass. A linear relationship was not observed for any single or multi component systems, but the heavy metal uptake capacities of fungal waste biomass were directly proportional to the initial metal concentrations. Also there was a direct competition for the binding sites between Pb(II), Cr(III), Co(II) and Cd(II) ions in the binary system. Pb(II) uptake overtook the uptake of Cr(III), Co(II) and Cd(II) at all tested concentrations. Also, it can be shown that the metal biosorption uptake capacity of biosorbent in mixed systems was inhibited by the presence of the other heavy metals in the system. It is clear that maximum value of q_e occurs when the component being as single solute in a solution. There is a noticeable decrease in the q_e value as an additional one component presents with the single solute. This behaviour is true for all Pb(II)' Cr(III), Cd(II) and Co(II). In order to know the reduced percentage in the uptake capacity of all heavy metals used, Table (4) illustrates these phenomena. The decrease of adsorption capacity in multi systems reflects the existence of a competition between the metals studied for the binding sites present in biosorbent cell wall. These results agreed with the results obtained by Artola et al., [23,24].

Due to the fast occupation of the vacant sites as competition between the adsorbates to fill these sites, this in turn will reduce the q_e value. Lead ions always gave the highest q_e value for single and binary systems with respect to Cr(III), Cd(II) and Co(II). This is due to its highest hydrophobic nature and the physical, chemical properties associated with biosorption process. Cr(III) was ranked second for biosorption as a single and binary. Cd(II) was ranked third, while Co(II) considered as a weakest component that adsorbed by fungal waste biomass for all systems.

All the systems were favorable type in spite of the obvious variation in the degree of the favorability of these components. Pb(II) offers highest favorability behavior as a single and binary system, Cr(III) ranked the second, Cd(II) ranked the third. Finally Co(II) ranked as the less favorable system. Table (5) shows the relationship between the minimum equilibrium concentrations for Pb(II), Cr(III), Co(II) and Cd(II) with maximum removal efficiency using fugal waste biomass for the two types of systems(single and binary). It can be seen that, for a single system, the minimum equilibrium concentrations for Pb(II), Cr(III), Co(II) and Cd(II) ions were 0.44, 1.63, 2.46 and 2.24 mg/L corresponding to the removal efficiencies of 99.41, 95.92, 92.0 and 97.01% respectively when using fungal waste biomass. The removal efficiency of each single metal decreased with increasing the initial concentration. The removal efficiencies of each metal ion were in a similar range of about 90-99% as shown in Tables (5) .The same procedures were applied for competitive systems.

It is clear that at low concentrations, the single or multi heavy metals adsorbed increased due to the abundant adsorption sites on the biosorbent. As the concentration increased, the adsorption sites were also available to the more strongly adsorbed species, resulting in a decrease in the amount of the more weakly adsorbed species. Furthermore, when metals are competing for the same type of adsorbent, metals with greater affinity (strongly absorbed species) will displace others with a lower affinity (weakly adsorbed species) . Among the four metal ions, Co(II) was the weakest adsorbed ion, therefore the stronger species Pb(II) in solution competitive with the weakest adsorbed species Co(II), and undergoes the displacement .

For Pb(II) solution,. biosorbent uptake capacity reached an equilibrium 94.74 mg/g at the residual concentration of 2.23 mg/L . While in multi system, a reduction was 89.5%. (Figure 6 (a, b, c) and Tables (3,4)). The above results indicate that in multi system, the nature of the biomass plays an important role in competitive biosorption systems.

The biosorption capacity decreased more in the binary system compared with single systems Since in a binary system the vacant (unoccupied adsorption sites) will be reduce and that in turn affecting the biosorption capacity in these systems. For binary system, the decrease was 77-90%, 77-90% and 79-90% respectively. These decreasing percentages indicate that the Co(II) biosorption decreases more pronounced in binary system than Pb(II), Cr(III) and Cd(II).

The metal sorption capacities were lower in multi metal system. This confirms that metal competition was occurred and caused antagonistic effected on biosorption process.

Pb(II) was favorably adsorbed onto waste of fungi compared with Cr(III), Cd(II) and Co(II) in single and multi systems. This confirms that Pb(II) bind more selective to fungal waste biomass than other metal ions. However, it was difficult to find a common rule to determine how metal properties exactly affect the binding strength of metal ions to fungi waste biomass [25-28].

The metals sorption sequence were Pb(II)> Cr(III)> Cd(II)> Co(II) in single and multi- metal systems.

It can be observed from Table (3) that the adsorption capacity of the fungi waste biomass for the multi-component systems was always lower than that for the single component system. For instance, Cr(III) was set as a primary component and Pb(II), Co(II) and Cd(II) as secondary components, the adsorption capacity for Cr(III) onto W.F. was 81.81, 81.64 and 81.66% respectively. This indicated that there was a competitive adsorption of these four metals on the surface of the biosorbent.

The results indicated that there was a complex interaction between each metal species in the biosorbent. It was found that fungal waste biomass offered a wide range of chemical groups that can attract and sequester the metals in biomass. Cell walls are composed of structural polysaccharides, proteins and lipids that offer metal-binding functional groups [29, 30].

4. Conclusion

For single component system, it was found that the low cost fungal waste biomass can be successfully used to remove Pb(II), Cr(III), Co(II) and Cd(II) from simulated wastewater using single, and binary systems in batch process . biosorption capacity was found to vary with initial concentration led to a significant increase in heavy metal removal. biosorption mechanisms of Pb(II), Cr(III), Cd(II) and Co(II) ions onto the surface of fungal waste biomass are due to the electrostatic attractive interactions between the positive charge of metal ions and the negative surface charge. Pb(II) ions was the most favorable component rather than Cr(III), Cd(II) and Co(II) due to less solubility and highly molecular weight.

Knowing that the chemical characterizations of fungal waste biomass are composed mainly of cellulose, hemicellulose and lignin, which provides binding sites (anionic) for the basic (cationic) metal ions due to the presence of functional groups such as hydroxyl, carboxyl, methoxy, phenols, etc.

Lead was shown to be easily displaced than Cr, Cd and Co ions due in part to properties that are more favorable for binding, such as a higher electronegativity and smaller hydrated radius. A good matching was found between experimental and predicted data in the experiments for all components.

For binary component system, extended Langmuir Isotherm gives the best fit for the experimental data. The behaviour of the equilibrium isotherm is of the favourable type. Due to the competitive effect of four metal mixtures to occupy the available sites of the fungal waste biomass, Pb(II)ions offer the strongest component followed by Cr(III)and Cd(II)ions while Co(II)was the weakest adsorbed component. Compared with their adsorption in single component system the adsorption capacity and percentage removal of all four metals shows obvious decreases in the binary system. This is because of more than one component was found which enhance the competitive struggling race for occupying a certain site. The behavior of the equilibrium isotherms were of the favorable type. Lead is still most adsorbed component rather than chromium, cadmium, and cobalt. Competitive biosorption capacity of all four metals showed obvious decrease compared with single component system.

5. References

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مخططات الامتزازالحيوي المفرد والثنائي لمختلف المعادن الثقيلة باستخدام مخلفات عضوية فطرية

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الخلاصة

تمت دراسة قدرة عملية الامتزاز الحيوي لمخلفات الفطر نوع (*White Agaricus Bisporus*) لامتزاز ايونات الرصاص ,الكروم,الكادميوم,والكوبلت من المياه الملوثه عن طريق تجارب الدفعات (Batch experiments) وبقطر للمادة المازه 1-0.3 ملم وبدرجة حرارة 25 مئوية . لقد بينت النتائج ان الامتزازالحيوي الثنائي اقل من المفرد.

تم القيام بسلسلة من تجارب الدفعات للملوثات بصورة منفردة واستخدام ثمانية موديلات رياضية التي تصف عملية الامتزاز الحيوي , وجد ان موديل (Langmuir) افضل موديل رياضي يمثل النتائج العملية وان سعة الامتزاز الحيوي للكوبلت,الكادميوم , الكروم والرصاص هي 158.74,46.94,40.16,15.94 ملغم/غم بمعامل (correlation coefficients) 0.999,0.998,0.998,0.991 على التوالي اما بالنسبة للنظام الثنائي اربع موديلات اعتمدت ووجد ان (Extended Langmuir model)افضل موديل يمثل النتائج العملية.ان نسبة الازاله للعناصر الثقيله في النظام المفرد والثنائي كالاتي: Pb(II) > Cr(III) > Cd(II) > Co(II).لقد اظهرت النتائج ان سعة الامتزاز عالية لجميع ايونات العناصر الثقيلة على مخلفات الفطر.