Competitive biosorption of Pb(II) and Cd(II) by live *Dunaliella salina*

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Abstract— The main aim of this study is continuous bioremoval of Pb(II) and Cd(II) ions in the aqueous conditions using live *Dunaliella salina* microalgae. For the selective Pb(II) uptake in the presence of Cd(II), single and binary systems of ions were chosen. The mutual effect of each heavy metal ion in all systems on the total uptake percentage was also examined. Both Langmuir and Freundlich isotherm models were suitable for describing multicomponent binary systems depending on the presence of competitive ions in the mixture.

1. INTRODUCTION

The environmental pollution of heavy metal ions due to industrial development such as mining, tannery, petroleum refining, metallurgical and manufacturing activities have become a major global concern. These activities have led to the release of various amounts of toxic metal ions in the food chain of living creatures due to waste disposal in their ecosystem [1, 2]. Pb(II) and Cd(II) as heavy metal ions are used in a wide range of commercial procedures.

Dunaliella salina (D. salina) is one type of green microalgae with a very high capacity for binding metal ions due to the presence of functional groups such as amines, hydroxyls, carboxyl and sulfates, which can cross-link with heavy metal ions. Moreover, researchers confirmed that *D. salina* requires minimal nutrients and can survive even in harsh natural conditions [3]. Hence, this study recommends an effective and dynamic method to use live *D. salina* for the purification of waters from heavy metal ions at a low cost.

2. METHODOLOGY

Pb $(NO_3)_2$ (purity >99%, Merck), Cd $(NO_3)_2·4H_2O$ (purity >99%, Fluka), were used in stock solutions.

The concentration of Pb(II) and Cd(II) in the solution was determined using an atomic absorption spectrophotometer (AAS) (Analytik Jena AG, 07745 Jena, Germany). To study the influence of heavy metal ions on biosorption and total uptake, Pb(II) and Cd(II) with a concentration range of 0-300.0 mg L^{-1} were examined.

3. REZULTS AND DISCUTION

In order to investigate the effect of competitive ions on heavy metal ion uptake efficiency, two experimental sections were carried out. Table 1 shows the heavy metal ion uptake by *D. salina* in the single and binary systems.

The simultaneous Cd(II) and Pb(II) uptake from binary heavy metal ion solutions were examined. In the first section, initial Pb(II) concentration was fixed (50.0 mg L^{-1}) while, Cd(II) as competitive ion was varied (0 –300.0 mg L^{-1}). It was observed that the percentage of Pb(II) uptake decreased from 96.19 to 80.99. Also, Cd(II) uptake percentages was decreased as compared to single metal ion uptake. This phenomenon shows a competitive effect among Cd(II) and Pb(II) ions. However, Pb(II) uptake is higher than Cd(II) uptake. It was noticed that with increasing competitive ion concentration, the Pb(II) uptake% was reduced.

In next section, the concentration of Cd(II) ion was fixed (50.0 mg L^{-1}) and Pb(II) was increased from 0 to 300.0 mg L^{-1}. As shown in Table 1, Pb(II) uptake was higher than Cd(II) uptake percentages and Cd(II) uptake was decreased. It may be due to the possible interaction between various types of metal ions and *D. salina* cell wall as a dynamic sorbent in biosorption systems. Essential factors of biosorption may affect the binding site properties such as surface structure, functional groups, ionic size, ionic charge, ionic weight (the weight of an ion as determined by the sum of the atomic weights of its components), heavy metal ion concentration, standard redox potential of the metal ions, ionic strength and pH. Therefore, it is difficult to explain which common parameters have more influence on the interaction mechanism and selectivity of biosorption in a mixed heavy metal ion system.

Table1. Comparison of single and binary systems

Concentration (mg L^{-1})		Uptake%		
Pb(II)	Cd(II)	Pb(II)	Cd(II)	Total
50	0	96.19±2.1	0	96.19
50	50	95.91±5.4	76.22±5.7	86.06
50	100	94.99±4.5	73.50±0.8	84.24
50	150	94.35±7.2	68.34±3.2	81.34
50	200	93.79±0.9	60.96±1.1	77.37
50	250	91.22±3.7	43.84±4.8	67.53
50	300	80.99±7.8	22.00±0.9	51.49
0	50	0	80.00±1.5	80.00
50	50	95.91±5.4	76.22±5.7	86.06
100	50	91.32±6.1	69.26±3.5	80.29
150	50	88.92±4.4	60.45±1.8	74.68
200	50	84.34±7.2	55.67±1.1	70.00
250	50	81.44±6.2	49.92±4.1	65.68
300	50	78.51±3.1	35.64±1.1	57.07

For the investigation of multicomponent effects on Cd(II) and Pb(II), it is important to know the biosorption isotherm. Two major mathematical isotherm models namely Langmuir and Freundlich, described the distribution of the sorbent surface between *D. salina* (Table 2). When Pb(II) is the competitive ion, the isotherm best fit with Freundlich isotherm (0.9980) while, for Cd(II) as a competitive ion, the isotherm best fit with Langmuir under the R^2 values of 0.9644.

Table 2. Biosorption isotherm models

M (II)	Langmuir			Freundlich		
	b (Lmg^{-1})	qm (mg g^{-1})	R^2	1/n	Kf (mg g^{-1})	R^2
Pb	0.06	476.19	0.9712	0.46	57.46	0.998
Cd	0.05	217.39	0.9644	0.45	25.16	0.827

4. Conclusion

Biosorption of Cd(II) and Pb(II) have been investigated for single and binary systems. The biosorption capacity is highest for Pb(II) as compared to Cd(II) for all systems. Competitive isotherm models indicated that Pb(II) follows the Freundlich isotherm, while the Langmuir isotherm is governed by Cd(II). In the present study, *D. salina* was directly grown in saline water and used to treat heavy metal ions from contaminated waters. This is a feasible solution to environmental problems. Research findings, led to the recommendation of a novel model for using live microalgae as an eco-friendly and green approach that avoids the usage of any chemicals that may impose serious damage to the environment.

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