

Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature

Gülşad Uslu*, Mehtap Tanyol

Department of Environmental Engineering, Firat University, 23100 Elazig, Turkey

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Abstract

The biosorption of lead (II) and copper (II) ions, single component and binary systems, by dried *P. putida* was investigated in a batch system. The effects of initial pH, temperature, initial single and binary mixture concentrations on the biosorption kinetics and equilibrium uptake of each component, both single and binary mixtures were investigated. The bacterial biomass exhibited the highest single and binary lead (II) and copper (II) ions uptake capacity at 25 and 30 °C, respectively, the initial pH value of 5.5 and at the initial metal ions concentration of 100 mg dm⁻³. The Freundlich and Langmuir adsorption models were used for the mathematical description of the biosorption equilibrium and isotherm constants were evaluated at different temperatures. Adsorption data were well described by the Langmuir model, although they could be modeled by the Freundlich equation. The thermodynamics constants of the adsorption process: ΔH° , ΔS° and ΔG° were evaluated. The results showed that biosorption of single and binary lead (II) ions on *P. putida* were exothermic and spontaneous. While biosorption of single and binary copper (II) ions on *P. putida* was endothermic and spontaneous.

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1. Introduction

The pollution of the environment with toxic heavy metals is spreading through the world along with industrial progress [1,2]. Heavy metals are major pollutants in marine, ground industrial and even treated wastewaters [3,4]. The specific problem associated with heavy metals in the environment is their accumulation in the food chain and their persistence in nature. Aqueous effluents emanating from the mining industry and metal plating factories contain dissolved heavy metals. If these discharges are emitted without treatment, they may have an adverse impact on the environment [5].

Besides classical physicochemical techniques (precipitation, electro dialysis or ion exchange), processes based on metal uptake capacities of microorganisms have been developed [6]. Biotechnological approaches to the abatement of toxic metal

pollution consist of selectively using and enhancing these natural processes to treat particular wastes.

Many studies showed that soluble metal ions in the environment could be captured by cell wall because of negative charged groups attach within its fabric. In last ten decades, bacteria, algae and fungi or their separated components have been used successfully as biosorbent for heavy metal removal. The metal uptake process, however, is complex and dependent on the chemistry of the metal ions, specific surface properties of the organisms, cell physiology and the physicochemical influence of the environment like pH, temperature and metal concentration [7–10].

The microorganisms respond to heavy metals by several processes, including transport across the cell membrane, biosorption to cell walls and entrapment in extra cellular capsules, precipitation, complexation and oxidation–reduction reactions [11–13]. The bioremediation of heavy metals using microorganisms has received a great deal of attention in recent years, not only as a scientific novelty but also for its potential application in industry [11,13]. Investigations on the biosorption mechanism of heavy metals show that the metal ions are deposited

* Corresponding author. Tel.: +90 424 2370000/5602; fax: +90 424 2415526.
E-mail address: guslu@firat.edu.tr (G. Uslu).

by adsorption to the functional groups present on the cell wall [14,15]. While knowledge of the toxicity and general uptake of single species of heavy metal ions by microorganisms is increasing, relatively little is known about the combined effects of two or more metals and simultaneous removal of metal ions from a mixture of metal ions [16–18].

The combined effects of two or more components on microorganisms also depend on the number of pollutants competing for binding sites, pollutant combination, levels of pollutant concentration, order of pollutant addition and residence time [19–22].

Lead (II) and copper (II) are known to be one of the heavy metals most toxic to living organisms and its one of the more widespread heavy metal contaminants on the environment [1,2]. Fungi belonging the genera *Rhizopus* and *Penicillium* have already been studied as potential biomass for removal of heavy metals from aqueous solution. However, much less is known about pH and temperature dependence of biosorption equilibrium and thermodynamics using *Pseudomonas putida*. Chang and Chen [18] studied on biosorption of copper (II), lead (II) and cadmium (II) ions on *P. aeruginosa* and the multimetal adsorption results showed that lead and copper significantly inhibited the adsorption of cadmium, while the effects of cadmium on the adsorption of copper and lead were limited. They also reported the combined effects of two or more metal ions on inactivated *P. aeruginosa* depend on the number of the metals competing for binding sites, metal combination, levels of metal ion concentration, order of metal addition, and residence time. Chang et al. [23] investigated the biosorption characteristic of two types of biosorbents. The inactivated cells are chemically stable and easy to handle, but some of the metal binding sites may be destroyed during the autoclave. However, since no heat treatment is employed, resting cells are expected to have higher metal binding capacity than inactivated cells do. The kinetics of biosorption and effects of environmental factors on biosorption were systematically examined. Leung et al. [24] selected *Pseudomonas* as biosorbent for lead, copper and nickel, among 12 bacteria isolated from activated sludge. They reported the maximum sorption capacity 271.7 and 46.8 mg g⁻¹ for lead (II) and copper (II) ions, respectively. The increasing order of affinity of the three metals toward *P. pseudoalcaligenes* was Ni < Cu < Pb. Abu Al-Rub et al. [25] investigated with *C. vulgaris* for heavy metal removal from aqueous solution. They reported that, *C. vulgaris* algal cells were effective in removing copper ions from aqueous solutions. The copper biosorption was dependent on equilibrium pH and biosorbent dose. Kiran et al. [26] investigated biosorption of heavy metal ions on *Neurospora crassa*. They reported the maximum sorption capacity 49.04 and 12.28 mg g⁻¹ for lead (II) and copper (II) ions, respectively. Akar and Tunali [27] reported the maximum copper (II) sorption capacity values as 9.23 mg g⁻¹ for *Botrytis cinerea* fungal biomass.

Pardo et al. [28] studied with *P. putida* for biosorption of heavy metals and demonstrated that cadmium and lead are toxic at very low concentrations, whereas, copper and zinc are essential but recognized as potentially toxic and higher concentrations. They evaluated optimum pH for each metal ion. In this study, a process of fully competitive biosorption of lead (II) and

copper (II) ions to *P. putida* from single and binary metal mixtures is described. The metal binding capacity of *P. putida* is shown to be a function of pH, temperature and metal concentration. Heavy metal adsorption equilibrium over a temperature range of 20–35 °C was modeled by using the Langmuir and Freundlich models. In the literature, only a limited number of studies have so far been focused on the thermodynamic analysis of biosorption of single and binary metal ions so the thermodynamics of the biosorption process was also investigated.

1.1. Equilibrium modeling in a batch system

Adsorption is a well-known equilibrium separation process for wastewater treatment. Adsorption isotherms are the equilibrium relationships between the concentrations of adsorbed metal and metal in solution at a given temperature. Single lead (II)–copper (II) and binary lead (II)–copper (II) biosorption isotherms have been successfully described by the well accepted adsorption isotherm models of Freundlich and Langmuir.

The well-known expression of the Langmuir model is given by Eq. (1)

$$q_{\text{eq}} = \frac{q_{\text{max}} K C_{\text{eq}}}{1 + K C_{\text{eq}}} \quad (1)$$

where K is the adsorption equilibrium constant including the affinity of binding sites (dm³ mg⁻¹), C_{eq} and q_{eq} are unadsorbed metal ions in solution and adsorbed metal ions on the sorbent at equilibrium, respectively. q_{max} is the maximum amount of metal ion per unit weight of adsorbent to form a complex monolayer on the surface (mg g⁻¹) [29,30].

The empirical Freundlich equation based on sorption on a heterogeneous surface is given by Eq. (2)

$$q_{\text{eq}} = K_{\text{F}} C_{\text{eq}}^{1/n} \quad (2)$$

where K_{F} and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively [31–33].

1.2. Thermodynamics of biosorption

In engineering practice, entropy and Gibbs free energy factors should be considered in order to determine what processes will occur spontaneously. Thermodynamic parameters such as enthalpy change (ΔH°), Gibbs free energy change (ΔG°) and entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature. The Gibbs free energy change of the sorption reaction is given by the following Eq. (3)

$$\Delta G^{\circ} = -RT \ln K \quad (3)$$

where R is universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is absolute temperature [33–37].

The equilibrium constant may be expressed in terms of enthalpy change of adsorption as a function of temperature as follows

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2} \quad (4)$$

According to Eq. (4), the effect of temperature on the equilibrium constant K is determined by the sign of ΔH° . Thus, when ΔH° is positive, i.e. when the adsorption is endothermic an increase in T results in an increase in K . Conversely, when ΔH° is negative, i.e. when the adsorption is exothermic, an increase in T causes a decrease in K .

The change with temperature of the free energy change and the equilibrium constant can be represented as follows

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \quad (5)$$

Eq. (5) can be written as

$$-RT \ln K = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

or

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (7)$$

where values of ΔH° and ΔS° can be determined from the slope and the intercept of the plot between $\ln K$ versus $1/T$ [33,38].

2. Materials and methods

2.1. Microorganisms and growth conditions

Pseudomonas putida (NRRL B-255) obtained from the American Type Culture Collection was used in the study. The bacterium was grown at 30 °C in agitated liquid media containing in g dm⁻³, yeast extract, 2; peptone, 2; K₂HPO₄, 1; KH₂PO₄, 1; (NH₄)₂SO₄, 1; MgSO₄·7H₂O, 0.05; glucose, 5. The medium was sterilized by autoclaving at a pressure 1.1 atm and temperature of 121 °C. The pH was adjusted to 6.0 with diluted HNO₃ and NaOH solutions.

2.2. Chemicals

The test solutions single lead (II) or copper (II) ions were prepared by diluting 1 g dm⁻³ of stock solutions of lead (II) and copper (II) to the desired concentrations. Stock solution of lead (II) and copper (II) were obtained by dissolving exact quantities of Pb₂NO₃ and Cu(NO₃)₂·3H₂O, in 1 dm³ of double-distilled water, respectively.

For binary lead (II) and copper (II) ions mixture studies, desired combinations of lead (II) and copper (II) ions were obtained by diluting 1.0 g dm⁻³ of stock solutions of component and mixing them in the test medium before mixing with the bacterial suspension.

2.3. Batch biosorption studies

The factors that affect the adsorption rate and uptake capacity of the biosorbent were examined in a batch system. A microorganism suspension of 10 cm³ was mixed with 90 cm³ of solution containing a known concentration of single lead (II)–copper (II) ions and binary lead (II)–copper (II) ions of these components in on Erlenmeyer flask at the desired temperature and pH. All the final solutions contained 1 g dm⁻³ mass of biosorbent. The

flasks were agitated on a shaker at a 150 rpm constant shaking rate for 24 h to ensure equilibrium was reached. Samples of 5 cm³ were taken before mixing the biosorbent solution and single lead (II)–copper (II) ions and binary lead (II)–copper (II) ions bearing solution, at 5 min intervals at the beginning of adsorption and 15–30 min intervals after reaching equilibrium, centrifuged at 6000 rpm for 3 min and then the supernatant liquid was used to analyses for each metal ions. During the biosorption studies the pH values were measured at the different interval and it was observed that the pH of the medium changed a bit, the difference was always less than 0.5 pH degree for single and binary metal ions, so pH change did not cause metal ion precipitation. The biosorption experiments were done in duplicates. The data presented are the mean values from three independent experiments. Experimental errors were estimated and are depicted with error bar and standard deviations are indicated wherever necessary. All statistical analysis was done using SPSS 10.0 for Windows, where it is possible to evaluate whether the effect and the interaction among the investigated factors are significant with respect to the experimental error.

2.4. Analysis of lead (II) and copper (II) ions

The concentration of residual lead (II) and copper (II) ions in the biosorption mediums were determined in UNICAM 929 atomic absorption spectrophotometer.

3. Results and discussion

Simultaneous biosorption of lead (II) and copper (II) to dried *P. putida* from binary mixture was investigated and compared with single lead (II) or copper (II) ions situation in a batch stirred reactor in this study. The kinetics and equilibrium results were given as the initial adsorption rate (r_{ad} : mg g⁻¹ min⁻¹), unit of each adsorbed metal ion quantity per gram dried *P. putida* at equilibrium (q_{eq} : mg g⁻¹), each unadsorbed metal ion concentration in the mixture at any time and at equilibrium (C_0 : mg dm⁻³, C_{eq} : mg dm⁻³), respectively, and adsorption yield ($Ad\% = 100 \times (C_0 - C_{eq})/C_0$).

The initial adsorption rate was obtained by calculating the slope of a plot of the adsorbed metal ion quantity per gram of dried microorganism (q) versus time at $t = 0$.

The lead (II) and copper (II) ions binding capacity of microorganism was shown as a function of initial pH, temperature and single–binary–pollutant concentrations. The single and binary component sorption phenomena were expressed by the single component (noncompetitive) and multicomponent (competitive) Langmuir and Freundlich adsorption models and adsorption isotherms were developed for both single and binary component systems at different temperature. The effect of temperature on sorption process was studied in terms of the thermodynamics parameters like Gibbs free energy, enthalpy and entropy change.

3.1. Effect of initial pH

One of the most critical parameters in the treatment of this single and binary lead (II) and copper (II) ions by the dried *P.*

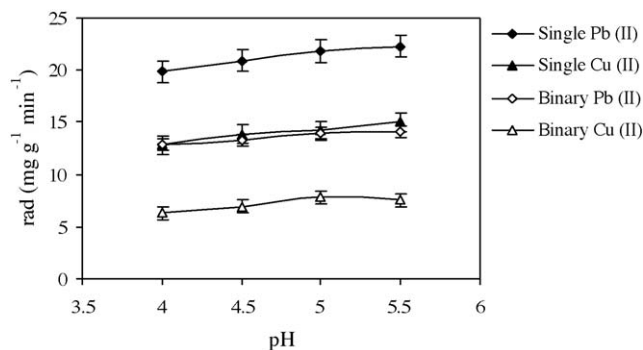


Fig. 1. The effect of initial pH on initial adsorption rates (initial metal concentration: 60 mg dm^{-3} , biomass concentration: 1.0 g dm^{-3} , $T=25^\circ\text{C}$ for single and binary Pb (II), $T=35^\circ\text{C}$ for single and binary Cu (II), stirring rate: 150 rpm).

putida is the initial pH of biosorption medium. Previous investigations concerning the single component situation have shown that the optimum adsorption pH dependent on both cell surface binding sites and chemistry of components in aqueous solution. The effect of initial pH on single and binary lead (II) and copper (II) ions uptake capacity of *P. putida* was investigated between pH 4.0–5.5 at 60 mg dm^{-3} initial concentration and the variation of initial adsorption rate with initial pH was given in Fig. 1.

As seen from Fig. 1, the removal of both the single and binary mixtures of lead (II) and copper (II) ions from aqueous solution was more efficient at increasing pH values. The optimum pH for lead (II) and copper (II) in single and binary systems was determined as 5.5 ± 0.5 and used in further experiments. The initial biosorption rate of single lead (II) and copper (II) ions on *P. putida* decreased from 22.29 to $19.85 \pm 1.07 \text{ mg g}^{-1} \text{ min}^{-1}$ and 15.02 to $12.83 \pm 0.91 \text{ mg g}^{-1} \text{ min}^{-1}$, when the pH was lowered from 5.5 ± 0.5 to 4.0 ± 0.5 , respectively. At higher pH values, lead (II) and copper (II) ions precipitated because of the high concentration of OH^- ions in the adsorption medium and so adsorption studies at these values ($\text{pH} > 6.0$) could not be performed.

Biosorption process with nonliving biomass is analogous to an ion exchange process, and therefore, pH has a significant effect on metal uptake [33]. The different pH binding values for these components could be due to the nature of the chemical interactions of each component with the microbial cells. At highly acidic pH values, metal cations and protons compete for binding sites on cell wall, which results in lower uptake of metal [33,34]. The low level of metal ions uptake at lower

pH values could be attributed to the increased concentration of hydrogen (H^+) and hydronium (H_3O^+) ions for metal ions binding sites on the biomass [33]. It is to be expected that as pH values are increased, more ligand with negative charge would be exposed with subsequent increase in attraction for positively charged metal ions. At pH values above the isoelectric point, there is a net negative charge on the cell surface and the ionic state of ligands such as carboxyl, phosphate, and amino group, will be such as to promote reaction with the metal cations.

It is also obvious that the proposed biosorption mechanisms due to in the initial pH are not sufficient to explain the biosorption of both components observed at all the pH values studied. It is thought that additional types biosorption mechanisms such as ion exchange, complex formation or membrane transport and physicochemical forces such as van der Waals, H-binding are also important for the bioremoval of lead (II) and copper (II) ions by biomass, irrespective of initial pH. However, the initial pH of wastewater could provide selectivity for the removal of the desired component in the mixture of lead (II) and copper (II) and this situation was observed in the simultaneous removal of these components studying at these pH values.

The equilibrium uptakes and adsorption yields obtained at single and binary lead (II) and copper (II) ions situation at pH 5.5 are presented Table 1. As seen from Table 1, the adsorption capacity of dried *P. putida* for copper (II) was generally less than of the lead (II) and increasing the initial concentration increased the equilibrium uptake and decreased the adsorption yield of both the components. The competitive biosorption at lead (II) and copper (II) from the binary mixture was investigated at pH 5.5. Equilibrium copper (II) uptake increased with, increasing the initial copper (II) ion concentration up to 60 mg dm^{-3} . The equilibrium uptake of copper (II) decreased regularly with increasing lead (II) ion concentration. Decrease in the uptake of copper (II) in presence of the lead (II) ions seems simple to explain. The presence of the other component develops a competition for the adsorption sites on the surface and some sites are occupied by the second component. As a consequence, the first component has a smaller parking space and its uptake is decreased. The greater the total metal concentration, the most effective was the competitive lead uptake because of a strong driving force or a large difference in concentration between adsorbent surface and metal solution. In both single and binary lead (II) and copper (II) ion systems, neither significant increases in the adsorbed amounts nor release of metal ions after the equilibrium stage was observed.

Table 1
Comparison of the equilibrium uptakes and adsorption yields obtained at different initial lead (II) and copper (II) ions concentrations for the single and binary mixtures (pH = 5.5, single and binary Pb (II) $T=25^\circ\text{C}$, single and binary Cu (II) $T=30^\circ\text{C}$)

$C_{0,\text{Pb}}$ (mg dm^{-3})	$q_{\text{eq,Pb}}$ (mg g^{-1})	Ad_{Pb} (%)	$C_{0,\text{Cu}}$ (mg dm^{-3})	$q_{\text{eq,Cu}}$ (mg g^{-1})	Ad_{Cu} (%)	$C_{0,\text{Pb+Cu}}$ (mg dm^{-3})	$q_{\text{eq,Pb+Cu}}$ (mg g^{-1})	$\text{Ad}_{\text{Pb+Cu}}$ Pb (%)	$C_{0,\text{Pb+Cu}}$ Cu (mg dm^{-3})	$q_{\text{eq,Pb+Cu}}$ Cu (mg g^{-1})	$\text{Ad}_{\text{Pb+Cu}}$ Cu (%)
12.42	10.75	86.7	12.49	6.24	50.0	11.75	6.85	58.7	10.56	4.40	41.7
29.38	24.20	82.3	27.35	13.65	50.0	25.54	14.05	55.0	27.63	11.47	41.5
66.25	54.17	81.8	62.50	27.91	44.6	56.03	30.08	53.6	61.69	18.91	30.6
132.15	101.77	77.0	128.08	45.56	35.6						
166.86	124.64	74.7	170.68	48.93	28.6						
270.62	180.41	66.7	243.68	49.50	20.3						

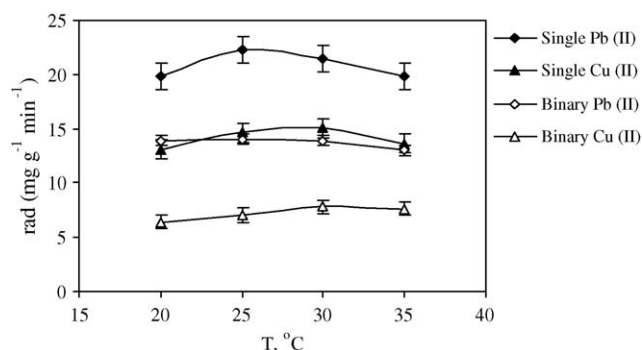


Fig. 2. The effect of initial temperature on initial adsorption rates (initial metal concentration: 60 mg dm^{-3} , biomass concentration: 1.0 g dm^{-3} , pH: 5.5, stirring rate: 150 rpm).

3.2. Effect of single and binary lead (II)–copper (II) concentration on temperature dependent adsorption

The variation of adsorption rates with temperature is given Fig. 2. The optimum biosorption temperature for lead (II) and copper (II) ions were determined to be 25 and 30 °C, respectively, owing to the influence of physical adsorption (Fig. 2). The results indicated that an increase of the temperature in the interval 20–25 °C and 20–30 °C deals with an increase in the equilibrium uptake capacity of *P. putida* for single and binary lead (II) ions and single and binary copper (II) ions, respectively. At low temperature, the binding of heavy metal ions to the *P. putida* occurs by a physical adsorption process. Adsorption decreased with further increasing temperature due to the decreased surface activity. Therefore, the initial adsorption rate decreased with increasing temperatures over 25 and 30 °C, for lead (II) and copper (II), respectively. Table 1 shows that, the equilibrium sorption capacity of the biosorbent increased with increasing initial metal ion concentration. At 25 °C, when the initial single and binary lead (II) ion concentrations increased from 12.49 to $270.62 \text{ mg dm}^{-3}$ and 11.75 to 56.03 mg dm^{-3} the uptake capacity increased from 10.77 to 185.57 mg g^{-1} and 6.9

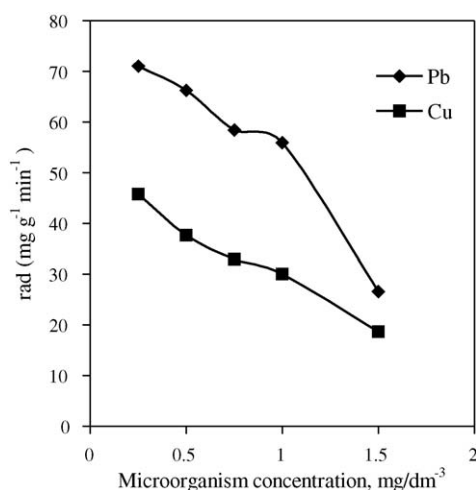


Fig. 3. The effect of microorganism concentration on initial adsorption rates (initial metal concentration: 60 mg dm^{-3} , pH: 5.5, stirring rate: 150 rpm).

to 30.50 mg g^{-1} , respectively. At 30 °C, when the initial single and binary copper (II) ion concentrations increased from 12.42 to $243.68 \text{ mg dm}^{-3}$ and 10.56 to 61.69 mg dm^{-3} the uptake capacity increased from 6.40 to 51.27 mg g^{-1} and 4.4 to 20.93 mg g^{-1} , respectively, of *P. putida*.

3.3. Effect of biosorbent concentration

The effect of biosorbent concentration on the initial adsorption rate of single and binary lead (II)–copper (II) ions is shown in Fig. 3. The bacterial concentration was varied from 0.25 to 2.00 g dm^{-3} to determine the effects of the microorganism concentration on the initial adsorption rate. It was observed that, the initial adsorption rates decreased with increasing the biosorbent concentrations.

3.4. Equilibrium modeling in batch system

The Freundlich and Langmuir adsorption constants evaluated from the isotherms at different temperatures with the correlation coefficients are presented in Table 2. Adsorption model constants, which express the surface properties and affinity of the biosorbent, can be used to compare the biosorptive capacity of biomass for different components.

From Table 2, the magnitude of K_F and n ; the Freundlich constants, shows easy uptake of heavy metal ions from wastewater with high adsorptive capacity of dried *P. putida*, especially at single and binary lead (II) and copper (II) ions at 25 and 30 °C, respectively. The highest K_F value was found as 6.66 (for single lead (II)), 1.8 (for single copper (II)), 1.54 (for binary lead (II)), and 1.21 (for binary copper (II)), at these temperatures in

Table 2
Isotherms constants for lead (II) and copper (II) ions concentrations for the single and binary mixtures on *P. putida*

Temperature (°C)	Langmuir model			Freundlich model		
	Q^0	b	r^2	K_F	n	r^2
Single lead (II)						
20	168.37	0.0249	0.981	4.44	1.173	0.99
25	270.37	0.0251	0.998	6.66	1.113	0.99
30	159.96	0.0208	0.997	3.47	1.145	0.98
35	131.41	0.0177	0.994	2.44	1.114	0.97
Binary lead (II)						
20	99.27	0.0138	0.99	1.248	1.095	0.99
25	107.72	0.0188	0.99	1.800	1.142	0.99
30	100.78	0.0141	0.99	1.543	1.112	0.99
35	63.31	0.0117	0.99	1.399	1.183	0.99
Single copper (II)						
20	79.08	0.0069	0.990	0.706	1.165	0.99
25	87.98	0.0094	0.99	1.114	1.221	0.99
30	96.85	0.0110	0.99	1.538	1.274	0.99
35	92.45	0.0106	0.99	1.286	1.245	0.99
Binary copper (II)						
20	44.37	0.0115	0.99	0.887	1.369	0.97
25	49.89	0.0124	0.98	1.082	1.406	0.95
30	59.33	0.0131	0.98	1.213	1.331	0.98
35	52.12	0.0130	0.98	1.170	1.399	0.96

Table 3
The thermodynamic constants of adsorption obtained Pb (II) and Cu (II) for mixed binary metal ions

	$-\Delta G^\circ$	ΔH°	ΔS°	Standard deviations	r^2
Single Pb (II)	21.20	-18.69	8.4	± 0.17	0.861
Binary Pb (II)	19.71	-13.13	21.12	± 0.13	0.888
Single Cu (II)	16.50	23.12	128.0	± 0.21	0.809
Binary Cu (II)	16.94	6.75	78.2	± 0.06	0.861

Table 2, also indicates that n is greater than unity, indicating that the heavy metal ions are favorably adsorbed by dried biomass at all the temperature studied.

The q_{\max} for single and binary lead (II) and copper (II) ions on *P. putida* were increased from 270.44, 96.85, 107.72 and 59.33, respectively. A large value of K also implied strong bonding of metal ions to the dried *P. putida* at these temperatures.

The data obtained in the single and binary systems indicated that the adsorption capacity of *P. putida* for copper (II) was generally less than that of lead (II) ions. There are possible interaction effects between different species in solution and in particular potential interactions on the surface depending on the biosorption mechanism.

3.5. Thermodynamic parameters of adsorption in batch system

The standard Gibbs free energy of each single lead (II)–copper (II) and binary lead (II)–copper (II) ions system were evaluated using K value obtained from the Langmuir model optimum temperatures and presented in Table 3. The negative value of ΔG° confirms the feasibility of the process and spontaneous nature of metal ion adsorption with high preference of single and binary metal ions for sorbent. Using Eq. (7), standard enthalpy and the entropy changes of sorption process were determined from the $\ln K$ versus $1/T$ plots (Fig. 4) and are also presented in Table 3.

The enthalpy changes of the biosorption of single lead (II) or copper (II) and binary mixture on *P. putida* were found as values were -18.69 , 23.12 , -13.13 and 6.75 kJ mol^{-1} , respectively.

As seen from the table, the positive values of ΔH° suggested the endothermic nature of adsorption and possible strong bonding between single and binary copper ions and sorbent, while

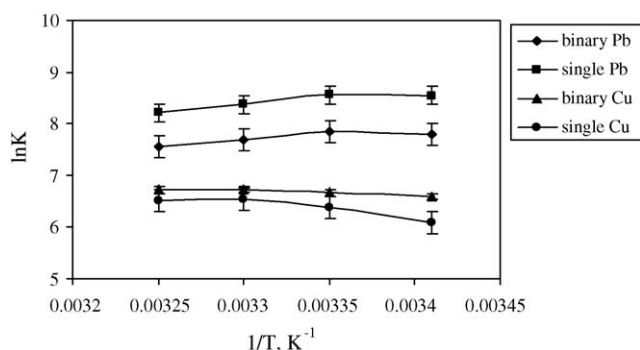


Fig. 4. $\ln K$ vs. $1/T$ plot.

ΔH° is negative values, indicating that the single and binary lead (II) adsorption by dried *P. putida* is exothermic, an increase in T causes a decrease in K , while positive ΔS° values reflect the affinity of all sorbents to single and binary metal ions in solution and some structural changes in sorbate and sorbents. The biosorption heats of these heavy metal ions decreased in the following sequence: single Cu (II) > binary Cu (II) and single Pb (II) > binary Pb (II). The adsorption with high enthalpy changes are very temperature-sensitive such as the biosorption of single copper (II) ions, the adsorption with low enthalpy changes are relatively temperature insensitive such as the biosorption as binary lead (II) ions.

4. Conclusions

In this study, the biosorption of lead (II) and copper (II) ions, in single and binary systems was studied using *P. putida* in the batch system. The results indicated that, adsorption capacity of the sorbent was affected by pH, temperature and initial metal ions concentration. The dried *P. putida* biomass selectively adsorbed lead (II) ions at pH 5.5, while copper (II) ions were preferentially adsorbed by the biomass at pH 5.5 and 25 and 30 °C, respectively.

The Langmuir and Freundlich adsorption models were used for the mathematical description of the biosorption equilibrium of lead (II)–copper (II) and lead (II)–copper (II) binary mixtures to dried *P. putida* depending on temperature and the isotherm constants evaluated from the isotherms were used to compare the biosorption capacity of the dried *P. putida* for single and binary systems. It was seen that the isotherms constants increased with increasing temperature up to 25 and 30 °C for lead (II) and copper (II) ions, respectively. The results obtained showed that the adsorption equilibrium data fitted the Langmuir model in the studied concentration range at all the temperatures studied.

The negative value of ΔG° confirmed the spontaneous nature adsorption process. The positive value of ΔS° showed the increased randomness at the solid–solution interface during adsorption and the positive value of ΔH° indicated the adsorption process was endothermic. The results also indicated that single and binary lead (II) biosorption processes by *P. putida* are exothermic, single and binary copper (II) biosorption processes by *P. putida* are endothermic.

It may be concluded that dried *P. putida* may be used as a low-cost, natural and abundant source for the removal of heavy metal ions and it may be an alternative to more costly methods such as active carbon adsorption, solvent extraction and chemical oxidation for removal of single and binary mixture heavy metal ions from wastewaters. This work could enable to extrapolate the prediction of adsorption equilibrium of the single and binary system if experimental dates are not available for a certain level of biosolute concentrations.

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