

Biosorption of copper and lead ions by waste beer yeast

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Abstract

Locally available waste beer yeast, a byproduct of brewing industry, was found to be a low cost and promising adsorbent for adsorbing copper and lead ions from wastewater. In this work, biosorption of copper and lead ions on waste beer yeast was investigated in batch mode. The equilibrium adsorptive quantity was determined to be a function of the solution pH, contact time, beer yeast concentration, salt concentration and initial concentration of copper and lead ions. The experimental results were fitted well to the Langmuir and Freundlich model isotherms. According to the parameters of Langmuir isotherm, the maximum biosorption capacities of copper and lead ions onto beer yeast were 0.0228 and 0.0277 mmol g⁻¹ at 293 K, respectively. The negative values of the standard free energy change (ΔG°) indicate spontaneous nature of the process. Competitive biosorption of two metal ions was investigated in terms of sorption quantity. The amount of one metal ion adsorbed onto unit weight of biosorbent (q_e) decreased with increasing the competing metal ion concentration. The binding capacity for lead is more than for copper. Ion exchange is probably one of the main mechanism during adsorptive process.

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1. Introduction

Heavy metals are discharged from various industries such as electroplating, metal finishing, textile, storage batteries, mining, ceramic and glass. As they pose serious environmental problems and are dangerous to human health, considerable attention has been given to the methods for their removal from industrial wastewaters. So in recent years the removal of heavy metals ions from waster water has received a great attention for global awareness of the underlying detriment of heavy metals in the environment [1–3]. There are several methods for treating metal contaminant effluent such as ion exchange, adsorption, chemical precipitation, oxidation, reduction, and reverse osmosis. However, many of these approaches can be less cost effective or difficult for practical use. Especially the main disadvantages of the sorption methods are the high price of the adsorbents, which increases the cost of wastewater treatment. Since, searching for a low cost and easily available adsorbent has led to the investiga-

tion of materials from agricultural and biological origin, along with industrial by-products, as adsorbents. Biological materials are known for their potential to adsorb heavy metals. Biosorption technology can remove metals from solution through adsorption. Plant-derived materials, such as rice husk, wheat shell, cereal chaff, rawdust, pine bark, etc., be used to adsorb heavy metals [4–8], but there are many reviews and reports on algae, bacteria, fungi that remove or adsorb heavy metals from solution [9–12]. The work reported by Selatnia et al. [11] showed that a *Streptomyces rimosus* biomass treated with NaOH had potential as adsorbents to remove lead from solution. Kapoor and Viraraghavan [12] reported that *Aspergillus niger*, one of fungi, was capable of removing heavy metals such as lead, cadmium and copper from aqueous solutions. The experimental results suggested that carboxylate and amine groups be important in metal ion biosorption on *A. niger* biomass.

Waste beer yeast, a by-product from brewing industry, can be used as feeding stuff. Some research have focused on utilization of the waste beer yeast to remove heavy metals form solution. Padmavathy et al. [13] used deactivated protonated yeast as biosorbents to adsorb Ni(II). The adsorption capacity was pH dependent. They also studied effect of thermal treat-

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ment on Ni(II) adsorption on baker's yeast and adopted FT-IR to studied the mechanism of adsorbing [14]. Carboxylate and amine in yeast play great role in Ni(II) adsorption. Goksungur et al. [15] studied the biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. The yeast had larger biosorption capacity than native yeast. Han et al. [16] studied Zn(II) biosorption by waste beer yeast and found that the adsorbed quantity was also pH dependent. Ambient temperature is efficient for zinc cation biosorption.

Copper and lead ions were chosen for biosorption studies with regard to their wide use in industry and potential pollution impact. Copper, which is very widely used metal in our daily life, but like any other heavy metal it is potentially toxic for all the living organisms. Lead can contaminate the environment from anthropogenic sources as well as natural geochemical processes. It can accumulate along the food chain and is not amenable to biological degradation [17,18].

The physical and chemical characteristic of the beer waste yeast in an experiment has been expressed and can adsorb heavy metal ions [16,19–21]. The aim of this study was to use waste beer yeast for the adsorption of heavy metals ions from wastewater. The objective of the present work was to study the influence of the uptake of Cu(II) and Pb(II) by waste beer yeast in different adsorptive conditions and to compare the biosorption behavior of a single-metal system and two-system in batch mode.

2. Materials and methods

2.1. Preparation of biomass

Waste beer yeast, taken from Aoke Beer Company in Zhengzhou, Henan province, China, was in suspended in 1% (v/v) hydrochloric acid for one hour. This process removed the adsorbed nutrient ions. Then it was centrifuged and the acid solution was discarded. The acid-washed biomass was rinsed using deionized water. This process was repeated three times and the rinsed yeast is again centrifuged and the remaining biomass was dried at 333 K for four hours. The drying yeast was ground and screened through a set of sieves to get different geometrical sizes 100–120 mesh. This produced a uniform material which was stocked in the refrigerator.

2.2. Metal solution

The chemicals used for the study were analytical grades of lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate ($\text{Cu}(\text{NO}_3)_2$), nitric acid, hydrochloric acid, hydrochloric sodium and hydrochloric calcium all supplied by Luoyang Chemical reagent company (China).

All chemicals and reagents used for experiments and analyses were of analytical grade. Stock solutions of 1000 mg L^{-1} Pb(II) and Cu(II) were prepared from $\text{Cu}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ in distilled, deionized water that contained a few drops of 0.1 mol L^{-1} HNO_3 to prevent the precipitation of Cu(II) and Pb(II) by hydrolysis. The solutions were diluted as required to obtain working solutions. The initial pH of the working solutions was adjusted

to 5.0 by addition of HNO_3 or NaOH solution, except the experiment examining the effect of pH. Fresh dilutions were used for each sorption study.

2.3. Methods of adsorption studies

Batch adsorption experiments were carried out by shaking the flasks at 120 rpm for a period of contact time using a water bath mechanical shaker. Following a systematic process, the adsorption uptake capacity of Cu(II) and Pb(II) in batch system was studied in the present work.

The data obtained in batch mode studies was used to calculate the equilibrium metal adsorptive quantity. It was calculated for each sample of Cu(II) and Pb(II) by using the following expression:

$$q_e = \frac{v(c_0 - c_e)}{m} \quad (1)$$

where q_e is the amount of heavy metal ions adsorbed onto per unit weight of beer yeast in mmol g^{-1} , v the volume of solution treated in L, c_0 the initial metal ion concentration in mmol L^{-1} , c_e the equilibrium metal ion concentration in mmol L^{-1} , and m is the dry weight of the biomass in g.

2.3.1. Effect of contact time on biosorption

Batch biosorption tests were done at different contact time at the initial concentration of $0.315 \text{ mmol L}^{-1}$ for Cu(II) and $0.393 \text{ mmol L}^{-1}$ for Pb(II), respectively, and waste beer yeast dose concentration is 8 g L^{-1} in 10 mL solution. The temperature was controlled with a water bath at the temperature of 293 K. The samples were then collected at different intervals and were centrifuged. The concentration of metal ions in the supernatant solution was analyzed using flame atomic absorption spectrometry (AAAnalyst 300, Perkin-Elmer). Each determination was repeated three times and the results given were the average values. The deviation is less than 5%.

2.3.2. Effect of yeast concentration on biosorption

Batch sorption tests were done at different yeast concentrations 3 to 15 g L^{-1} at pH 5.0, for a contact time (60 min), and 293 K. The initial concentrations of Cu(II) and Pb(II) were $0.315 \text{ mmol L}^{-1}$ and $0.393 \text{ mmol L}^{-1}$, respectively. Agitation was made for 60 min. The samples were then centrifuged and the left out concentration in the supernatant solution was analyzed as said before.

2.3.3. Effect of solution pH on biosorption

The effect of pH on the adsorption capacity of beer yeast (particle size 100–120 mesh) was investigated using solutions of $0.315 \text{ mmol L}^{-1}$ Cu(II) and $0.393 \text{ mmol L}^{-1}$ Pb(II) for a pH range of 0.8–6.0 at 293 K. An aliquot of yeast (8.0 g L^{-1}) was added to 10 mL of Cu(II) and Pb(II) solutions. Experiments could not be performed at higher pH values due to hydrolysis and precipitation of the lead ions. Flasks were agitated on a shaker for 60 min to ensure that equilibrium was reached. Then the mixture was centrifuged and the concentration of metals in the supernatant solution was measured.

2.3.4. Effect of NaCl and CaCl₂ concentration on biosorption

The effects of salt concentration on the values of q_e for copper and lead ions were analyzed over the NaCl and CaCl₂ concentration range from 0 to 0.15 mol l⁻¹, respectively.

2.3.5. Effect of temperature on biosorption

Keeping the beer yeast dose 8.0 g L⁻¹, pH 5.0, and the initial concentration of 0.315 mmol L⁻¹ for Cu(II) and 0.393 mmol L⁻¹ for Pb(II), respectively. The relative conical flasks was then shaken at a constant speed of 120 rpm in a shaking water bath with temperatures 293, 298, 303, 313, 323 K, respectively. The samples were then centrifuged and analysis was performed as said before.

2.3.6. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.08 g of yeast with 10 mL of metal solution of different initial concentration, 0.05–0.7 mmol L⁻¹. A series of such conical flasks was then shaken at a constant speed of 120 rpm in a shaking water bath with temperatures 293 K. The samples were then centrifuged and analysis was performed as said before.

2.3.7. Competitive adsorption in binary metal system

In this group of experiments, competitive adsorption of Cu(II) and Pb(II) ions from their binary solutions was investigated by following a similar procedure as described above. These studies were performed at a initial pH of 5.0 at 293 K. The experiments of competitive adsorption of Cu(II) and Pb(II) included two parts: (i) the competitive adsorption of Cu(II) and Pb(II) in the total metal concentration was fixed (0.386 mmol L⁻¹); (ii) in a series of two metal ions solution, the initial concentration of Cu(II) was fixed to 0.315 mmol L⁻¹, whereas, the concentration of Pb(II) were varied from 0 to 0.491 mmol L⁻¹. In another binary system, the initial concentration of Pb(II) was constant in 0.386 mmol L⁻¹, and the concentration of Cu(II) were varied from 0 to 0.472 mmol L⁻¹.

3. Result and discussion

3.1. The effect of contact time

The effect of contact time on copper and lead biosorption on beer yeast was studied and the results were shown in Fig. 1.

From Fig. 1, it was found that the adsorptive quantity of both copper and lead ions on beer yeast increased as the contact time increased. The biosorption of Cu(II) and Pb(II) onto waste beer yeast was rapid for first 10 min and equilibrium was nearly reached after 60 min. Hence, in the present experiment, 60 min was chosen as the equilibrium time.

3.2. The effect of yeast dose on biosorption

The influence of adsorbent dosage in equilibrium uptake was shown in Fig. 2.

The effect of biomass dose on Cu(II) and Pb(II) biosorption was similar. With the dose of biosorbent increasing, the values

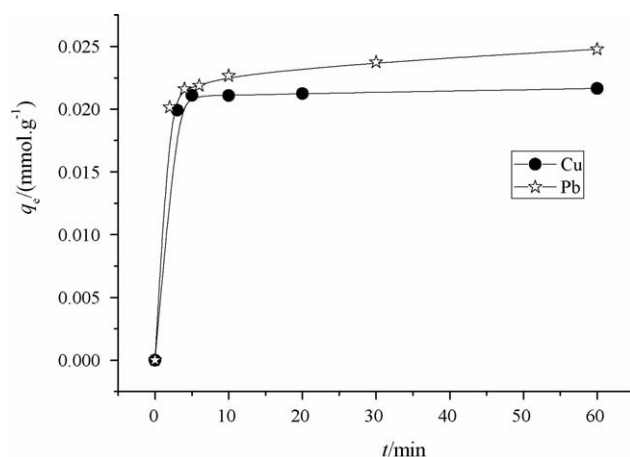


Fig. 1. The effect of contact time on biosorption.

of q_e were both decreased. Increasing adsorbent dosage can be attributed to increased adsorbent surface area and the availability of more adsorption sites. But the values of q_e decreased with increasing the adsorbent dosage. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [22].

3.3. The effect of solution pH

The pH of the solution is perhaps the most important parameter for adsorption. The charge of the adsorbate and the adsorbent often depends on the pH of the solution. To understand the adsorption mechanism, the adsorption of Cu(II) and Pb(II) as a function of pH was measured, and the results are shown in Fig. 3.

There was an increase in biosorption capacity of biomass with increasing pH from 2.0 to 6.0 for both metal ions. The lowest metal uptake values were determined at pH < 2.0 for both metal ions. At pH values above the isoelectric point, there is a net negative charge on the cell wall components and the ionic state of ligands such as carboxyl, phosphate and amino groups will

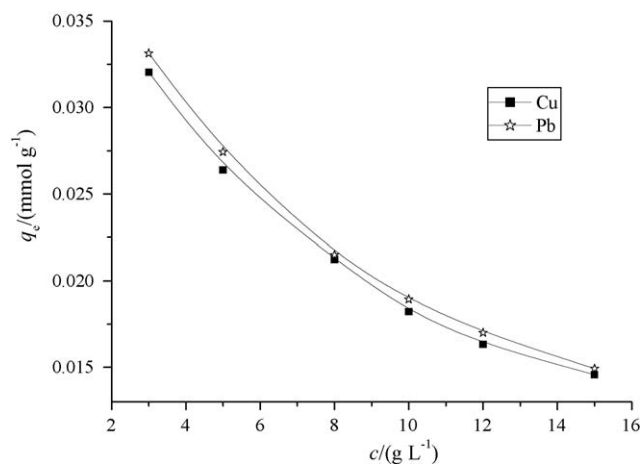


Fig. 2. The effect of yeast dose on biosorption.

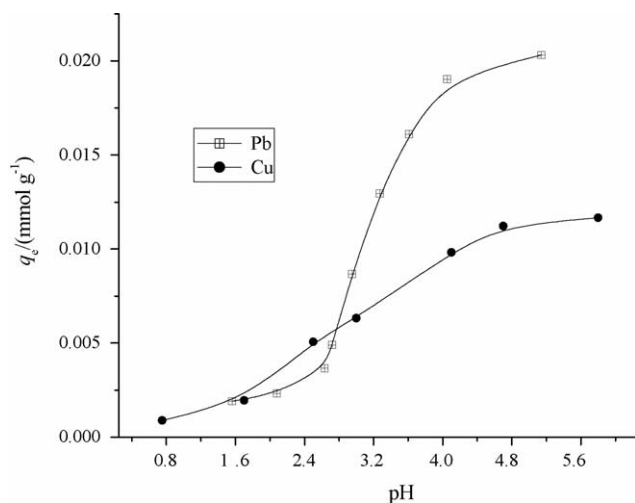


Fig. 3. The effect of solution pH on biosorption.

be as such to promote reaction with metal cations. As the pH is lowered, however, the overall surface charge on the cells will be positive, which will inhibit the approach of positively charged metal cations [15].

As the pH increases, more ligands will be exposed, i.e. carrying negative charges, to the subsequent attraction of metallic ions with positive charges and adsorption to the cell surface. When pH increasing, the cell–wall ligands will be associated with hydronium or other positive ions, such as Na^+ , K^+ , Ca^{2+} , then the ion exchange process may be one of mechanism adsorbing Cu(II) and Pb(II) . During adsorptive process, it was observed that that value of pH is lower than the original solution, but the difference is smaller as the adsorptive quantity is smaller. This result also explained that the ion exchange is one of adsorptive mechanisms.

Several researchers have also investigated the effect of pH on biosorption of heavy metals by using different biomass and found similar results with this study. Say et al. [23] investigated the biosorption of Cd(II) , Pb(II) and Cu(II) ions by filamentous fungus *Phanerochaete chrysosporium* and determined the optimum pH for biosorption as 6.0. Yin et al. [24] found the optimum pH for Cd(II) uptake as 6.0 for pretreated fungal biomass. Han et al. [6,25] used cereal chaff for Pb(II) and Cu(II) adsorption and found that Pb(II) uptake increased with increase in medium pH and had a optimum value at pH 5.0–6.0, but the maximum pH for Cu(II) uptake is 5.0.

3.4. The effect of NaCl and CaCl_2 concentration on biosorption of copper and lead by beer yeast

Na^+ and Ca^{2+} ions, as common ions existed in solution, can influence Cu(II) and Pb(II) adsorption onto yeast. The effect of different NaCl and CaCl_2 concentration on Cu(II) and Pb(II) was shown in Fig. 4, respectively.

At equilibrium state, the adsorbing quantity of copper and lead ions by the materials was dependent on ionic strength. This phenomenon can be explained by two factors. First, the metal ions form out-sphere complexes with the solids sites, which

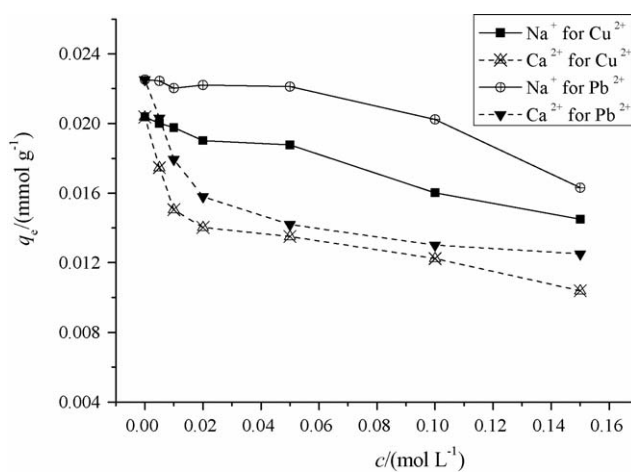


Fig. 4. Effect of salt concentration on biosorption.

favor the adsorption when the concentration of the competing salt is decreased. This might indicate that the adsorption between the functional groups of the adsorbent and the metal cations was mainly of ionic interaction nature, which is consistent with an ion exchange mechanism. The second factor is the influence of the great ionic strength on the activity coefficient of copper and lead ions, which limit their transfer to the solid surface [26]. As CaCl_2 solution has more than ionic strength than the same concentration of NaCl solution, it had great influence on biosorption quantity. But even in the same ionic strength, such as 0.15 mol L^{-1} NaCl and 0.05 mol L^{-1} CaCl_2 existed in solution, the adsorptive quantity (q_e) about biomass is still bigger as NaCl existed than CaCl_2 , this results showed that the competitive adsorption is the main reason for the decrease of q_e as the concentration of Ca(II) is great bigger than Pb(II) in the system. Villaescusa et al. studied the removal of copper and nickel ions from solutions by grape stalks wastes and concluded that the ion exchange be the main mechanism of removing heavy metal ions [27]. But when CaCl_2 existed in solution with higher concentration, beer yeast still had the capacity for binding heavy metals. This result showed that complexation may be other mechanism to adsorb heavy metals except ion exchange. Fungal cell surfaces have different functional groups, such as carboxyl ($-\text{COOH}$), amide ($-\text{NH}_2$), hydroxide ($-\text{OH}$), and these groups played great role in biosorption of lead and copper ions [12,20,21]. The interaction between amide group and heavy metal ions should be through complexation during biosorption process.

3.5. The effect of temperature on biosorption of copper and lead by beer yeast

The effect of temperature on biosorption of Cu(II) and Pb(II) by beer yeast was shown in Table 1.

From Table 1, it was found that effects of temperature on biosorption of copper and lead ions by beer yeast were different. In the experimental temperature range, with the temperature rising, the adsorptive quantity of copper ions by beer yeast was increasing, but for lead it was decreasing. So the process of copper is endothermic and the process of lead is exothermic. About

Table 1

The biosorption quantity of Cu(II) and Pb(II) biosorption onto beer yeast at different temperature (mmol g^{-1})

	T (K)				
	293	298	303	313	323
q_e for Cu(II)	0.00809	0.009055	0.0111	0.0143	0.0206
q_e for Pb(II)	0.0213	0.0209	0.0190	0.0165	0.0148

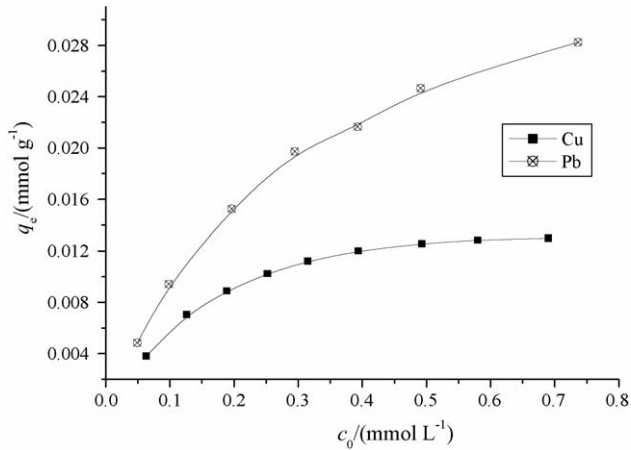


Fig. 5. Equilibrium uptake quantity of Cu(II) and Pb(II) at different initial concentrations.

effect of temperature on metal ions adsorption, the similar results were observed about copper and lead ions adsorbed on cereal chaff [6,25].

3.6. The effect of initial concentration of copper and lead ions

The metal ion equilibrium level of beer yeast is presented as a function of the initial concentration of copper and lead ions in the aqueous solution in Fig. 5. From Fig. 5, equilibrium uptake increased with the increasing of initial metal ions concentrations at the range of experimental concentration. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial metal ion concentrations. In the same conditions, if the concentration of metal ions in solution was bigger, the active sites of beer yeast were surrounded by much more metal ions, the process of adsorption would carry out more sufficient. So the values of q_e increased with the increasing of initial metal ions concentrations.

Adsorption isotherms show the distribution of solute between the liquid and solid phases equilibrium conditions. Many different isotherm models have been proposed for the adsorption

of solutes in a liquid solution onto a solid surface. Langmuir model is probably the most popular isotherm models due to its simplicity and its good agreement with experimental data. The Langmuir model, the saturated monolayer isotherm, can be described by the linear form [28]:

$$\frac{1}{q_e} = \left(\frac{1}{c_e K_L q_{\max}} \right) + \frac{1}{q_{\max}} \quad (2)$$

where c_e is the equilibrium metals concentration in aqueous phase (mmol L^{-1}); q_m is the q_e for a complete monolayer (mmol g^{-1}), a constant related to sorption capacity (the maximum amount of metal ion per unit weight of adsorbent); and K_L is a constant related to the affinity of the binding sites and energy of adsorption (l mmol^{-1}). By plotting $1/q_e$ versus $1/c_e$, q_{\max} and K_L can be determined.

The equilibrium established between the adsorbed metal ions (q_e) and that remained free in the solution (c_e) was also represented by the Freundlich adsorption isotherm, the linear equation as following [29]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (3)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

The equilibrium data of copper and lead ions adsorption by beer yeast obtained at 293 K was applied to Langmuir and Freundlich models. The relative parameters and correlation coefficients (R) and residual standard deviations (S.D.) were listed in Table 2.

The mono-component Langmuir constant, q_{\max} , represents the monolayer saturation at equilibrium or the total capacity of beer yeast for copper and lead ions. From Table 2, the maximum loading capacities of beer yeast was obtained as $0.0228 \text{ mmol g}^{-1}$ for copper and $0.0276 \text{ mmol g}^{-1}$ for lead. So the ability of Pb(II) adsorption on beer yeast is bigger than Cu(II). The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of metal-biosorbent system. The values q_m about some microorganisms adsorbing Cu(II) and Pb(II) from the Langmuir constant were listed in Table 3.

Compared to other biosorbents in Table 3, the adsorptive capacity of Cu(II) and Pb(II) adsorption onto beer yeast is smaller, but as it is cheap, it is still considered as adsorbent to remove heavy metals from solution.

From Table 2, the values of K_F showed easy uptake of metal ions with high adsorptive capacity of beer yeast. As $0.1 < 1/n < 1$, indicating that copper and lead ions are favorably adsorbed by beer yeast at the temperatures studied [39].

Table 2

Parameters for the application of Langmuir and Freundlich model to the biosorption of Cu(II) and Pb(II) on beer yeast using linear regression

Model	Langmuir				Freundlich			
	K_L (L mmol^{-1})	q_{\max} (mmol g^{-1})	R	S.D.	K_F	$1/n$	R	S.D.
Cu	9.12	0.0228	0.997	0.09	0.0223	0.4738	0.971	0.05
Pb	21.2	0.0276	0.998	0.03	0.0429	0.4338	0.981	0.05

Table 3
Pb(II) and Cu(II) biosorption by microorganism: a selection of the Langmuir constant, q_m of various related biosorbents from the literature

No.	q_m (mmol g ⁻¹)		Biosorbent	References
	Cu ²⁺	Pb ²⁺		
1		0.3	Ethanol treated yeast	[15]
2	0.54	0.37	Bacterial cells	[30]
3	0.976	0.35	Rhizopus arrhizus(funugs)	[31]
4	0.318	0.34	Filamentous fungus	[32]
5	0.042	0.04	the NaOH-treated fungus <i>Aspergillus niger</i>	[33]
6		0.18	Streptomyces noursei	[34]
7	0.217	0.19	<i>S. subspicatus</i> (algae)	[35]
8	0.026	0.01	<i>P. tricornutum</i> (algae)	[35]
9	0.414	0.18	<i>C. cryptica</i> (algae)	[35]
10		0.31	A green alga	[36]
11	0.537	0.4	<i>Zoogloea ramrgera</i> (bacteria)	[37]
12	1.301	1.63	Pre-treated marine algae	[38]
13	0.0228	0.0276	Waste beer yeast	This study

The biosorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The apparent equilibrium constant (K'_c) of the biosorption is defined as [6,40]:

$$K'_c = \frac{c_{ad,e}}{c_e} \quad (4)$$

where $c_{ad,e}$ is the concentration of metal ion on the adsorbent at equilibrium. The value of K'_c in lowest experimental lead concentration can be obtained. The K'_c value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG°) [6,39].

$$\Delta G^\circ = -RT \ln K'_c \quad (5)$$

where ΔG° is standard Gibbs free energy change (kJ mol⁻¹), R the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K).

The free energy changes for Cu(II) and Pb(II) sorption onto beer yeast were determined at 293 K and pH 5.0, are -0.921 and -2.93 kJ mol⁻¹, respectively. The negative values of ΔG° validate the feasibility of the biosorption process, and the spontaneity of biosorption.

3.7. The effect of coexistence ions on the biosorption of copper and lead ions on beer yeast

3.7.1. The effect on biosorption of copper ion with the presence of lead ion in the solution

The effect on biosorption of copper ion was studied when lead ion in existence. The result was shown in Fig. 6 (down curve). With increasing Pb(II) concentration, the biosorption quantity of Cu(II) decreased.

From Fig. 6, the adsorptive quantity of Cu(II) decreased with the increasing of Pb(II) initial concentration. The biosorption quantity of copper ion decreased from 0.0188 to 0.0130 mmol g⁻¹ when the concentration of lead ion ranged from 0 to 0.491 mmol L⁻¹. Thus it can be seen that the existence of lead has great effect on the biosorption of copper on

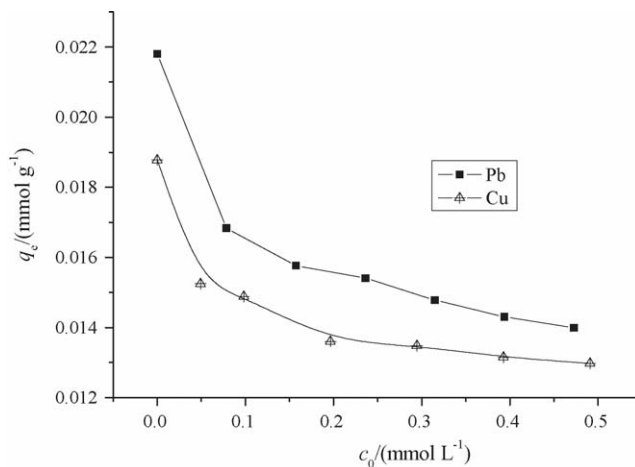


Fig. 6. The effect on biosorption of copper when lead in existence (down curve) and the effect on biosorption of lead when copper in existence (upper curve).

beer yeast. When the lead ions existence in the solution, it will be adsorbed by beer yeast and compete to the copper ions, and it will hold some activated sites on beer yeast, hence the adsorption capacity of copper will decrease. So when the ions of lead existence, it will be a disadvantage condition to the biosorption of copper ions on beer yeast. Furthermore, the concentration of lead is more, the effect is serious.

3.7.2. The effect on biosorption of lead ion with the presence of copper ion in the solution

The effect on biosorption of lead ion was also studied when copper ion in existence. The result was also shown in Fig. 6 (upper curve). With increasing the copper ion concentration, the biosorption quantity of lead ion decreased.

From Fig. 6, the adsorption quantity of Pb(II) decreased with the increasing of Cu(II) concentration. The biosorption quantity of Pb(II) decreased from 0.0218 to 0.0140 mmol g⁻¹ when the concentration of Cu(II) ranged from 0 to 0.472 mmol L⁻¹. As the copper ions existence in the solution, similarly, it will be adsorbed by beer yeast and compete to the lead ions. So when the ions of copper existence, it will be a disadvantage condition to the biosorption of lead ion on yeast, too. Furthermore, the concentration of copper is higher, the effect is also serious.

3.7.3. The competitive adsorption of Cu(II) and Pb(II) in the total concentration fixed

The objective of this part work was to study the effect of two metal ions coexistence on the total adsorptive capacity of yeast. Keeping the total mol-concentration of copper and lead ions changeless (0.386 mmol L⁻¹), one metal concentration reduced, and in the same time, the other increased. The result was shown in Fig. 7.

From the three-dimensional Fig. 7, it was observed that when increased the concentration of copper, reduced the concentration of lead, the quantity increased for binding copper while decreasing for lead. Furthermore, the total quantity also decreased. At the port of the adsorptive curve both copper and lead, when there was single metal ions existence, the value of q_c about lead was bigger than copper, so the binding ability for lead is stronger

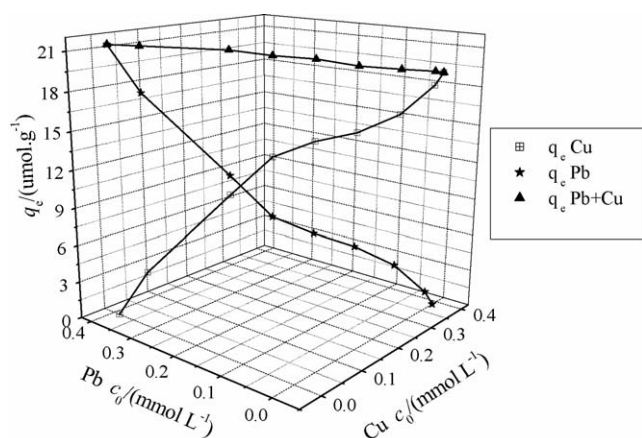


Fig. 7. Keeping the total mol-concentration of copper and lead ions fixed, the equilibrium level of copper and lead ions onto beer yeast.

than copper. Other studies have the similar results using other biosorbent, such as fungus and alga [30,32,38]. But from Fig. 7, waste beer yeast can be used to remove copper and lead ions in solution when there was two-metal ions coexistence. The results were similar to those in Fig. 6.

Above all, competitive biosorption of two metals was investigated in terms of sorption capacity and found that the biosorption capacity of biomass decreased with increasing the competing metal ion concentration. But from Fig. 7, it can be concluded that the total capacity for adsorbing copper and lead ions be insignificantly changed.

Lower binding capacity of copper ions over lead ions on the biomass could be explained by comparing the covalent index of Pb(II) (11.1) with Cu(II) (5.67) ions. The covalent index of metal ions can be calculated by Eq. (6), taking into accounts of electronegativity (X) and ionic radius (r) of the metal ions. The value of 0.85 in Eq. (6) represents an appropriate constant assumed to reflect the radius of O and N donor atoms [41]. The high value of the covalent index shows the high degree of binding capacity of the metal ions to the biological ligands:

$$\text{covalent index} = X^2(r + 0.85) \quad (6)$$

Pb(II) is classified as a class b ion, while Cu(II) are classified as borderline ions, so the behavior of adsorption is not full same [42], and the binding capacity is difference. Similar results were found using different biosorbents by other research [42–46].

4. Conclusion

The results of experiment showed that the beer yeast has some ability to adsorb Cu(II) and Pb(II) from solution. Different variables, such as contact time, adsorbent dose, solution pH and temperature influenced the adsorptive quantity. The process of biosorption has nearly reached equilibrium in 30 min and the optimum pH is near 5.0. Increasing the initial concentration of Cu(II) and Pb(II) results in higher adsorptive quantity, respectively. The experimental data of adsorbing Cu(II) and Pb(II) are fit well to Langmuir and Freundlich model and the maxi-

imum adsorptive quantity of beer yeast were $0.0228 \text{ mmol}\cdot\text{g}^{-1}$ for Cu(II) and $0.0276 \text{ mmol}\cdot\text{g}^{-1}$ for Pb(II) according to Langmuir model, respectively. The adsorptive process for Cu(II) and Pb(II) is spontaneous. Waste beer yeast can simultaneously adsorb Cu(II) and Pb(II) from solution. The competitive results show that the adsorptive quantity for one metal is significantly decreased as other metal existence, but the total capacity for binding heavy metals changes little. It was referred that ion exchange be one of main mechanism during adsorptive process.

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