

# Removal of $Pb^{2+}$ , $Ag^+$ , $Cs^+$ and $Sr^{2+}$ from aqueous solution by brewery's waste biomass

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## Abstract

Heavy metal pollution is becoming a more and more serious environmental problem, posing threat to biota life. Biosorption is an alternative technology for the treatment of wastewater containing metal ions. In this paper, the removal of four metal ions, i.e.,  $Pb^{2+}$ ,  $Ag^+$ ,  $Sr^{2+}$  and  $Cs^+$  by waste biomass of brewery was studied. The experimental results showed that metal uptake is a rapid process, which can be described by pseudosecond order kinetic model. The Langmuir adsorption isotherm was applied to correlate the equilibrium data and fitted quite well. The maximum biosorption capacities for four metal ions were 0.413 mmol  $Pb^{2+}$ /g, 0.396 mmol  $Ag^+$ /g, 0.091 mmol  $Sr^{2+}$ /g and 0.076 mmol  $Cs^+$ /g, respectively. The binding of metals was also discussed in term of several factors. The order of accumulated metal ions at equilibrium state on the molar basis was as follows:  $Pb^{2+} > Ag^+ > Sr^{2+} > Cs^+$ , which positively correlated with their covalent index and electronegative and reversely correlated with dissociation constant.

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## 1. Introduction

Heavy metal pollution has become one of the most serious environmental problems today. Heavy metal means the metal ion whose specific weight is usually more than 4 or 5  $g\ l^{-1}$  [1]. The toxic characteristics of heavy metals are displayed as follows: (1) the toxicity can last for a long time in nature, (2) some heavy metals even could be transformed from relevant low toxic species into more toxic forms in a certain environment, mercury is such a case, (3) the bioaccumulation and bioaugmentation of heavy metal by food chain could damage normal physiological activity and endanger human life finally, (4) metals can only be transformed and changed in valence and species, but cannot be degraded by any methods including biotreatment, (5) the toxicity of heavy metals occurs even in low concentration.

Heavy metal containing wastewater which is mainly discharged from some industrial waste-process streams like electroplating has posed great damage to human being and environment because of its self-properties like lasting toxicity,

conversion from one form to others which might cause greater toxicity like mercury, bioaccumulation and bioaugmentation through food chain and cannot be degraded in substance [1]. Because of the reasons listed above and the increasing application of heavy metal, heavy metal containing wastewater has earned great concern recently.

Traditional technologies applied to treat heavy metal containing wastewater such as precipitation, ion exchange, membrane methods (reverse osmosis, electro-dialysis, ultra-filtration) and adsorption by activated carbon are often limited by their several disadvantages, e.g., ineffective, expensive when used for treatment of low concentration heavy metal solution [1,2] and large-amount sludge creation. Because of the shortages of traditional technologies, new alternative methods should be extensively studied.

Biosorption is regarded as a cost-effective biotechnology for the treatment of high volume and low concentration complex wastewaters containing heavy metal(s) in the order of 1–100  $mg\ l^{-1}$ . Among the promising biosorbents for heavy metal removal which have been researched during the past decades, *Saccharomyces cerevisiae* has received increasing attention. Biosorption is referred to the pollutants uptake by non-living biomass and bioaccumulation is offered to remove

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via living biomass [3]. These two methods both use various natural materials to sequester heavy metal ions from wastewater solutions and decrease the concentration of heavy metal ions in solution greatly.

A variety of biological materials like bacteria, algae, yeasts, and fungi have been used as biosorbent and studied extensively. Kratochvil and Volesky [4] and Veglio and Beolchini [5] reviewed the advances in the biosorption of heavy metals by various sort of biosorbents in recent years, while Davis et al. [3], Goodyear and McNeill [6], Wang and Chen [1] and Kapoor and Viraraghavan [7] reviewed the biosorption of heavy metal by algae, brown algae, *S. cerevisiae* and fungi, respectively. All the works done by these researchers showed that biosorption and bioaccumulation offer an ideal alternative method for the treatment of heavy metal pollution.

Of the many sort of biosorbents recently investigated for the biosorption ability of heavy metals, *S. cerevisiae* has proven to be the most promising as well as reliable and effective one in the removal of heavy metal ions from large volume and low concentration solutions, because it is easy to get from fermentation industry as a by-product, safe, helpful to identify the molecular mechanism of biosorption and can be produced in large quantities [1].

Uptake capacity of biomass is always affected by many factors like pH, temperature, initial concentration of biomass and metal ions, culture conditions and some others like presence of various ligands and metal ions, etc. While all the culture conditions are the same, the biosorption capacity of a biomass mainly depends on the chemical characters of the metal ion and its preference to form ionic or covalent bonds. To understand the interaction between the metal ions and the biomass, the hard and soft principle of metal ions proposed by Nieboer and Richardson [8] has been widely used. According to this theory, metal ions can be separated to three groups on the basis of magnitude of complex formation constant. Class A metals have the preference sequence for metal-binding donor atoms in biological ligands: O > N > S and are described as non-polarizable hard metals, because their metal-ligand bonds are predominately ionic, while Class B metals have the opposite preference and are described as polarizable soft metals because their bonds have a more covalent character with ligands [8–10].

The objective of this work was to investigate the biosorption of four metal ions (one toxic metal ion-Pb, one precious metal ion-Ag and two radionuclides-Cs and Sr) by waste biomass of brewery, including the biosorption kinetics and the sorption equilibrium isotherm equation, as well as to correlate the biosorptive capacity of metal ions with their ionic characteristics.

## 2. Material and methods

### 2.1. Biomass and metal ions solution

Yeast powder was provided by a local brewery, and it was ground in a mortar and pestle, and passed through a screener with the order of 150  $\mu\text{m}$ . Then the yeast cells were stored in desiccators for future use.

Metal ions stock solutions of  $10 \text{ mmol l}^{-1}$  were made by dissolving analytical grade  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ ,  $\text{CsNO}_3$  and  $\text{Sr}(\text{NO}_3)_2$  into the deionized water, respectively. The series of metal solution used in these experiments were made by diluting their stock solutions to the desired concentrations.

### 2.2. Kinetic studies

Kinetic studies were carried out by mixing 50 ml metal ions' solution ( $1 \text{ mmol l}^{-1}$ ) with 0.1 g biomass in several 100 ml conical flasks and shaken on a rotary-shaker at 150 rpm with constant temperature of  $30^\circ\text{C}$ . Flasks were taken at appropriate time intervals and centrifuged immediately (10,000 rpm) for 10 min.

### 2.3. Equilibrium studies

A series of flasks containing 50 ml of  $0.16\text{--}8 \text{ mmol l}^{-1}$  metal solutions at pH 4.0 were prepared. When the experiment began, 0.1 g biomass ( $X=2 \text{ g/l}$ ) was added to each flask and the systems were shaken at 150 rpm for 3 h with constant temperature of  $30^\circ\text{C}$ . After that, the biomass was separated from the metal solutions by centrifugation (10,000 rpm for 10 min) and the supernatants were analyzed for metal concentrations by atomic absorption spectrometry (AAS6 VARIO) and pH values by pH meter (HANNA223).

The equilibrium metal uptake  $q$  ( $\text{mmol g}^{-1}$  dry weight) was calculated from the metal concentrations in the solution before and after the equilibrium,  $C_i$  and  $C$  ( $\text{mmol l}^{-1}$ ):

$$q = \frac{(C_i - C)V}{m} \quad (1)$$

$V$  is the volume of suspension of biomass and metal solution (l) and  $m$  is the dry weight of biomass (g).

### 2.4. Isotherm study

Adsorption is a well-known equilibrium separation process. There are many isotherm equations used for modeling the adsorption equilibrium, such as Langmuir, Freundlich, linear and Redlich–Peterson equation, etc. [11] Among all of these, the Langmuir model is the most popular used equation, because its coefficients have some real meanings. Langmuir equation is valid for monolayer sorption on to a surface with a finite number of identical sites and its expression is given by Eq. (2):

$$q_e = \frac{q_{\max} b C_e}{(1 + b C_e)} \quad (2)$$

Where  $q_{\max}$  and  $b$  are the Langmuir coefficients.  $q_{\max}$  is the maximum amount of the pollutant per unit weight of adsorbent to form a complete monolayer on the surface bound at high  $C_e$  ( $\text{mmol g}^{-1}$ ), and  $b$  is a constant related to the affinity of the binding sites ( $1 \text{ mmol}^{-1}$ ).  $q_{\max}$  and  $b$  can be determined from the slope and intercept of  $C_e/q_e$  versus  $C_e$  linear plot.

## 2.5. Pseudosecond-order model

In order to examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data.

The pseudosecond order equation is most widely used by many researchers to express the kinetic of metal ions' biosorption on biomass because it always provided a more appropriate description than the first order equation [12]. It can be expressed in a linear form:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (3)$$

where  $q_t$  the amount of sorbate on sorbent at time  $t$  ( $\text{mmol g}^{-1}$ ),  $k_2$  is the equilibrium rate constant of pseudosecond order sorption kinetics ( $\text{g mmol}^{-1} \text{min}^{-1}$ ), and  $q_e$  the equilibrium uptake ( $\text{mmol g}^{-1}$ ). These two parameters can be obtained from the intercept and slope of Eq. (3).

## 3. Results and discussion

### 3.1. Kinetic study of biosorption process

The variation of biosorption uptake values of four metal ions, that is,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  with contact time was studied using solutions of metal ions with initial concentration of  $1 \text{ mmol l}^{-1}$  at pH 4.0 and yeast concentration of  $2 \text{ g l}^{-1}$  (pH 4 was selected in this study to make sure the selected four metal ions not precipitate at that stage and the appropriate metal removal). The shaking time was varied from 10 min to 24 h. The results were shown in Fig. 1.

Fig. 1 showed that the equilibrium reached very quickly. More than 90% of metal ions were bound to biomass within 30 min of contact, and there was a slight increase in biosorption amounts until a plateau was reached after about 3 h. This result was in accordance with the findings of many researchers. Jalali-Rad et al. [13] found that most of the cesium ions were bound to FASs1 (FASs1 means ferrocyanide algal sorbents type 1 that derived from *Sargassum glaucescens* and *P. australis*) in less than 2 min and equilibrium reached within the first 30 min of contact. Al-Saraj et al. [14] studied the biosorption of some hazardous metals ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ )

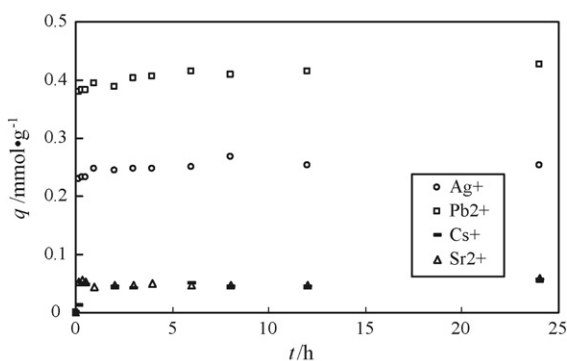


Fig. 1. Biosorption uptake values of four metal ions- $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  vs. time ( $C_0 = 1 \text{ mmol l}^{-1}$ ,  $X = 2 \text{ g l}^{-1}$ , pH 4, 150 rpm,  $30^\circ \text{C}$ ).

Table 1

Parameters of pseudo-second order sorption kinetics ( $C_0 = 1 \text{ mmol l}^{-1}$ ,  $X = 2 \text{ g l}^{-1}$ , pH 4, 150 rpm,  $30^\circ \text{C}$ )

Metal ions	$q_e$ ( $\text{mmol g}^{-1}$ )	$k_2$ ( $\text{g mmol}^{-1} \text{min}^{-1}$ )	$R^2$
$\text{Ag}^+$	0.255	1.769	0.999
$\text{Pb}^{2+}$	0.423	0.292	0.999
$\text{Cs}^+$	0.054	0.472	0.989
$\text{Sr}^{2+}$	0.058	0.461	0.983

on *S. cerevisiae* and found that the maximum accumulation of metal ions by yeast cells was observed to take place within 3 h. Özer et al. [15] found that the adsorption equilibrium of  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  on *S. leibleinii* was established in 15–20 min and the adsorbed amount did not change with time. Arica et al. [16] and Tüzün et al. [17] found the biosorption equilibrium time of  $\text{Pb}^{2+}$  on *Phanerochaete chrysosporium* and *Chlamydomonas reinhardtii* was 1 h. So, 3 h shaking time was taken as the biosorption time of metal ions needed to reach equilibrium on dry yeast in later experiments.

The pseudosecond order sorption kinetics was used to fit the experiment data in order to analyze the sorption of metal ions on yeast. The values of  $q_e$  and  $k$  were calculated and tabulated in Table 1. The values of the theoretical  $q_e$  for all sorbents were in good agreement with those obtained experimentally. These results indicated that the sorption process of metal ions onto yeast followed a pseudosecond order kinetic, which meant that the external mass transfer and intraparticle diffusion together were involved in the sorption process [1].

### 3.2. Biosorption equilibrium

The result of the equilibrium metal uptake ( $q$ ) versus equilibrium concentration ( $C_e$ ) data was shown in Fig. 2.

Fig. 2 indicated that the amount of adsorbed metal increased with the equilibrium concentration in solution and had a tendency of reaching the saturated level. The removal percentage was high with the low concentration of metal ions in solution. The removal percentage was 89.9, 82.8, 22.7 and 6.3%, respectively when the concentration was  $0.064 \text{ mmol Pb}^{2+} \text{ l}^{-1}$ ,  $0.055 \text{ mmol Ag}^+ \text{ l}^{-1}$ ,  $0.208 \text{ mmol Sr}^{2+} \text{ l}^{-1}$  and  $0.157 \text{ mmol}$

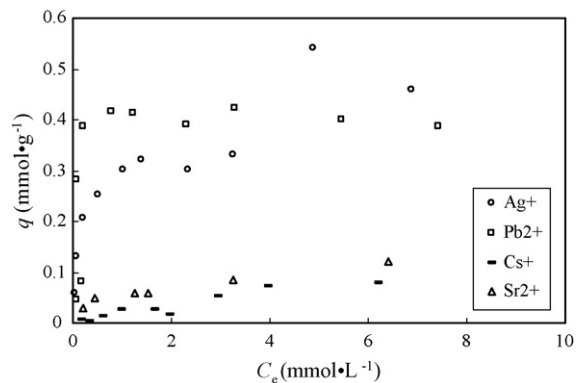


Fig. 2. The equilibrium metal uptake ( $q$ ) vs. equilibrium concentration ( $C_e$ ) ( $C_0 = 0.16\text{--}8 \text{ mmol l}^{-1}$ ,  $X = 2 \text{ g l}^{-1}$ , pH 4, 150 rpm,  $30^\circ \text{C}$ ).

Table 2  
Langmuir adsorption isotherm equation ( $C_0 = 0.16\text{--}8\text{ mmol l}^{-1}$ ,  $X = 2\text{ g}^{-1}$ , pH 4, 150 rpm,  $30\text{ }^\circ\text{C}$ )

Metal ions	Equations	$q_{\max}$ (mmol g <sup>-1</sup> )	$b$ (l mmol <sup>-1</sup> )	$R^2$
Ag <sup>+</sup>	$1/q = 0.442/C_e + 2.524$	0.396	5.706	0.922
Pb <sup>2+</sup>	$1/q = 0.068/C_e + 2.424$	0.413	35.701	0.917
Cs <sup>+</sup>	$1/q = 28.397/C_e + 13.117$	0.076	0.465	0.986
Sr <sup>2+</sup>	$1/q = 4.518/C_e + 10.968$	0.091	2.427	0.917

Cs<sup>+</sup> 1<sup>-1</sup>, respectively. While the percentage was reduced to 9.47%, 11.8%, 3.68% and 2.5% when the concentration was 7.422 mmol Pb<sup>2+</sup> 1<sup>-1</sup>, 6.840 mmol Ag<sup>+</sup> 1<sup>-1</sup>, 4.229 mmol Sr<sup>2+</sup> 1<sup>-1</sup> and 6.189 mmol Cs<sup>+</sup> 1<sup>-1</sup>, respectively. The reduction removal of these four metal ions by increasing initial concentration was the result of occupation of available binding sites on cell walls. So yeast could be used to treat heavy metal wastewater with low concentration.

Langmuir adsorption isotherm is the most widely used model for the description of biosorption equilibrium. To investigate the maximum uptake capacity of metal ions onto dried yeast biomass, the Langmuir isotherm equation was used to fit experimental data. The results were listed in Table 2.

It can be seen from Table 2 that the maximum biosorption capacities ( $q_{\max}$ ) of metal ions onto yeast were in the range of 0.076 mmol g<sup>-1</sup> dry weight for Cs<sup>+</sup> to 0.413 mmol g<sup>-1</sup> dry weight for Pb<sup>2+</sup>. The order of accumulated metal ions at an equilibrium state was in the following order (on the molar basis): Pb<sup>2+</sup> > Ag<sup>+</sup> > Sr<sup>2+</sup> > Cs<sup>+</sup>. The sequence of the metal ions showed that the Class A metal (Sr<sup>2+</sup> and Cs<sup>+</sup>) had the lower equilibrium capacities than the other two metal ions in the same range of equilibrium concentration. This result was in accordance with the findings of Kogej and Pavko. [10], who found that alkali metal ions Li<sup>+</sup> was adsorbed to *R. nigricans* to a lesser extent than other metal ions. While Pb<sup>2+</sup> and Ag<sup>+</sup> as a Class B metal had the greatest adsorption capacities, which had also been proven by many other researchers. Arica et al. [16] found that the maximum uptake capacity of Pb<sup>2+</sup> was always greater than Zn<sup>2+</sup> by algae beads, no matter immobilized live *P. chrysosporium* or heat inactivated fungus. The biosorption of three metal ions (Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>) onto *C. reinhardtii* conducted by Tüzün et al. [17] also showed that, the maximum uptake capacities increased in the order of Pb<sup>2+</sup> > Hg<sup>2+</sup> > Cd<sup>2+</sup>, and Pb<sup>2+</sup> had the greatest equilibrium capacity when compared with the other two metal ions.

The equilibrium capacity results got by different researchers were summarized in Table 3 and compared with the results of this work. The biosorption uptake capacities of *S. cerevisiae* for Pb<sup>2+</sup> and Ag<sup>+</sup> in this paper were in the range of data reported in other literatures. As for Sr<sup>2+</sup> and Cs<sup>+</sup>, their biosorption data on other biomass were listed in Table 3 because their biosorption data on *S. cerevisiae* were absent. The results of Sr<sup>2+</sup> and Cs<sup>+</sup> in this paper were lower than those in literatures, which might be mainly caused by the difference of the type of biomass. Table 3 also showed that there were no great differences between *S. cerevisiae* and other biomaterials in the magnitude of metal uptake capacity, which meant that *S. cerevisiae* had the mediocre metal biosorption capacity, this results were in accordance with the

conclusion drawn by Wang and Chen [1]. In spite of its normal uptake capacity, still *S. cerevisiae* was a promising biosorbent for heavy metal removal because of its several advantages.

### 3.3. Factors affecting uptake capacity

Metal ions uptake capacities are affected by many factors, e.g., surface character of biomass, properties of metal ions and solution. The binding capacities of different biomass result in different equilibrium biosorption order of metal ions. Bayramoğlu et al. [22] found that the uptake values of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> onto immobilized *Trametes versicolor* increased in the order of Cu<sup>2+</sup> > Zn<sup>2+</sup> > Pb<sup>2+</sup>, which were different with the results of many other researchers.

Property of metal ions is one of the most important factors affecting the biosorption capacity. To explain the difference of

Table 3  
Comparison of the results in this paper with those in literatures

Metal ions	Biomass	pH	$q_{\max}$ (mmol l <sup>-1</sup> )	References
Pb <sup>2+</sup>	<i>S. cerevisiae</i>	5	1.304	[18]
	<i>S. cerevisiae</i> (Ethanol treated)	5	0.291	[19]
	<i>S. cerevisiae</i>	6	0.236	[14]
	<i>S. cerevisiae</i> (Dried)	4.5	0.880	[20]
	<i>S. cerevisiae</i>	4	0.413	This study
	<i>S. cerevisiae</i>	5	0.211	[10]
	<i>Rhizopus nigricans</i>	5	0.403	[10]
	<i>P. chrysosporium</i>	5	0.419	[10]
	<i>A. terreus</i>	5	0.201	[10]
	<i>M. purpurea</i>	5	0.279	[10]
	<i>Streptomyces clavulgerus</i>	5	0.140	[10]
	<i>M. inyoensis</i>	5	0.159	[10]
	<i>U. lactuca</i>	4.5	0.603	[21]
	<i>C. glomerata</i>	4.5	0.362	[21]
	<i>G. corticata</i>	4.5	0.241	[21]
	<i>G. canaliculata</i>	4.5	0.174	[21]
<i>S. hystrix</i>	4.5	1.279	[21]	
<i>S. natans</i>	4.5	1.081	[21]	
<i>P. violacea</i>	4.5	0.483	[21]	
<i>P. pavonia</i>	4.5	1.014	[21]	
Ag <sup>+</sup>	<i>S. cerevisiae</i> (Dried)	4.5	0.140	[20]
	<i>S. cerevisiae</i>	4	0.396	This study
	<i>Rhizopus nigricans</i>	5	0.452	[10]
	<i>A. terreus</i>	5	0.233	[10]
Sr <sup>2+</sup>	<i>Rhizopus nigricans</i>	5	0.278	[10]
	<i>S. cerevisiae</i>	4	0.091	This study
Cs <sup>+</sup>	<i>P. australis</i>	5.5	0.122	[13]
	<i>S. cerevisiae</i>	4	0.076	This study

Table 4  
The covalent index and  $q_{\max}$  values of metal ions

Metal ions	Pauling electronegativity	$X_m^2 r$	$q_{\max}$ (mmol g <sup>-1</sup> )
Ag <sup>+</sup>	1.93	4.25	0.396
Pb <sup>2+</sup>	2.33	3.29	0.413
Cs <sup>+</sup>	0.79	1.04	0.076
Sr <sup>2+</sup>	0.95	1.05	0.091

metal ions' adsorption capacities and to elucidate the mechanism of metal ions binding on the ligands, a lot of work has been done. The studies conducted by Şatiroğlu et al. [23] and Arıca et al. [24] showed that, the equilibrium uptake capacities of Hg<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> onto *Polyporus versicolor* and immobilized *Funalia trogii* increased in the order of Hg<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup>, which was positively correlated with electronegativity of metal ions. The same result was drawn by Sadowski [25], who also found that the uptake capacities of metal ions increased with increasing of the electronegativity values of metal ions for the biosorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> onto *Nocardia* sp. In this paper, the order of equilibrium uptake values of Pb<sup>2+</sup>, Ag<sup>+</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> on the dry yeast was Pb<sup>2+</sup> > Ag<sup>+</sup> > Sr<sup>2+</sup> > Cs<sup>+</sup>, the uptake values of these four metal ions could be ordered by the electronegativity of the metal ions where the electronegativity values of Pb<sup>2+</sup>, Ag<sup>+</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> were 2.33, 1.93, 0.79 and 0.95 (listed in Table 4), respectively. But this theory needs to be proven further when applied to more elements.

Except for electronegativity, equilibrium uptake capacities of metal ions are also correlated with some other factors, such as atomic number, ionic potential and ionic radius etc. Özer et al. [18] found that the biosorption capacities of Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup> onto *S. cerevisiae* increased in the order of Pb<sup>2+</sup> > Ni<sup>2+</sup> > Cr<sup>3+</sup>, which increased with the atomic number's increasing. Benguella and Benaissa [26] investigated the biosorption characters of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> onto chitin, the results indicated that the biosorption capacity was correlated with ionic potential and ionic radius. While the complex ion effect on biosorption of lead conducted by Sekhar et al. [27] indicated that the complex interactions of several factors, such as ionic charge, ionic radius and electrode potential would account for the differences in the metal removal capacity of the biomass in multicomponent systems. As a result, ordering of the metal ions based on a single factor is very difficult. The functional groups in the sorbent have been studied previously [28], and the binding mechanism to remove might mainly correlate with the carboxylic and amine groups, which play important role in the biosorption of metal ions.

Because it is difficult to order the metal ions based on a single factor as described above, a concept of covalent index was proposed by Nieboer and Richardson [8], which is a complex parameter computed using the following expression:  $X_m^2 r$ , where  $X_m$  is electronegativity and  $r$  is ionic radius. Many researchers found that the metal uptake capacity was correlated with covalent index. By the report of Brady et al. [9], the sorption capacities of metal ions (Sr<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>) at an equilibrium state were directly correlated with covalent index

values. Kogej and Pavko [10] also drew the same conclusion after studying the biosorption of metal ions (Li<sup>+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>) by *Rhizopus nigricans* biomass.

The covalent index and  $q_{\max}$  values were listed in Table 4.

It is evident that the uptake of metal ions by yeast is higher for metals of class B (Pb<sup>2+</sup> and Ag<sup>+</sup>), while the uptake of class A ions (Sr<sup>2+</sup> and Cs<sup>+</sup>) is lower. From the Table 4, an increasing trend between maximum biosorption capacities of yeast for metal ions and the covalent index of the element can be observed. Metal ions with higher covalent index (Pb<sup>2+</sup> and Ag<sup>+</sup>) were bonded to a greater extent than metal ions of typical ionic character (Sr<sup>2+</sup> and Cs<sup>+</sup>). Because the main structural components of yeast are glucans, mannans and proteins, the result indicated that metal ions form bonds of predominately covalent character with glucans, mannans and proteins as biomass binding sites.

Dissociation constant,  $K$ , is the reciprocal of constant  $b$  of Langmuir equation, could be used to predict the affinity between the sorbate and sorbent. According to Kogej and Pavko. [10], the extent to which a metal ion would bind to a ligand was reversely correlated with the dissociation factor. The binding of metal ions to *R. nigricans* biomass could be lined up in the order of magnitude of their dissociation factor,  $K$ : Li<sup>+</sup> > Cu<sup>2+</sup> > Sr<sup>2+</sup> > Zn<sup>2+</sup> > Al<sup>3+</sup> > Ni<sup>2+</sup> > Ag<sup>+</sup> > Cd<sup>2+</sup> > Fe<sup>2+</sup> > Fe<sup>3+</sup> > Pb<sup>2+</sup>. In this paper, the dissociation factor order of metal ions to yeast was Cs<sup>+</sup> > Sr<sup>2+</sup> > Ag<sup>+</sup> > Pb<sup>2+</sup>, which was opposite with the uptake capacities of metal ions.

#### 4. Conclusions

Biosorption is a most promising alternative method for the treatment of heavy metal pollutant that studied widely. Among the biomaterials used in the biosorption studies, *S. cerevisiae* is a unique one because of its great properties and the mediocre metal biosorption capacity.

This paper studied the biosorption of four metal ions—Pb<sup>2+</sup>, Ag<sup>+</sup>, Sr<sup>2+</sup> and Cs<sup>+</sup> by waste biomass of brewery including kinetic studies and equilibrium studies in order to investigate the biosorption mechanism and the factors correlated with uptake capacities of metal ions.

The results of kinetic studies showed that biosorption of four metal ions by brewery's yeast could well be described by pseudo-second order kinetic model ( $R^2 > 0.99$ ), which meant that the external mass transfer and intraparticle diffusion together were involved in the sorption process.

The sorption equilibrium studies conformed to Langmuir adsorption isotherm. The maximum biosorption capacity was 0.413 mmol Pb<sup>2+</sup> g<sup>-1</sup>, 0.396 mmol Ag<sup>+</sup> g<sup>-1</sup>, 0.091 mmol Sr<sup>2+</sup> g<sup>-1</sup> and 0.076 mmol Cs<sup>+</sup> g<sup>-1</sup>, respectively. *S. cerevisiae* could be used to treat heavy metal pollutant with low concentration. Comparison of uptake capacities between yeast and other biomasses showed that the metal uptake capacity of *S. cerevisiae* was in the middle in comparison with other biomass and *S. cerevisiae* was a unique biomaterial because of its great advantages although it had the normal metal biosorption capacity.

The order of accumulated metal ions at equilibrium state on the molar basis was as follows: Pb<sup>2+</sup> > Ag<sup>+</sup> > Sr<sup>2+</sup> > Cs<sup>+</sup> and the

extent of metal ions binding to yeast was predominantly due to covalent index, electronegative and dissociation constant.

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