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Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system

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HIGHLIGHTS

- ▶ Utilisation of rice straw as a cheap and effective sorbent for the removal of Cu and Pb ions.
- ▶ Incorporation of selectivity factor of solute for the modification of extended-Langmuir model.
- ▶ Representation of binary adsorption data and the model fittings in 3D plots.
- ▶ Application of biosorption study using real effluent from a wastewater treatment plant.
- ▶ Regeneration study of biosorbent for industrial practice.

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ABSTRACT

The single and binary biosorption of copper and lead ions from aqueous solution using a low cost agro-based resource (i.e. rice straw) has been demonstrated in this work. The biosorption experiments were performed in a static mode. Experimental parameters affecting the sorption process namely biosorbent dose, pH, and temperature were studied. Two empirical adsorption models (i.e. Langmuir and Freundlich) were used for the evaluation of biosorption equilibrium data in single system. Both models were able to correlate experimental data satisfactorily. The adsorptivity of solute (K_L) and maximum sorption capacity of the solid (q_m) were increased at higher temperatures. For binary metal system, we modified the adsorption parameters of extended-Langmuir model (i.e. $K_{L\text{-bin}}$ and $q_{m\text{-bin}}$) by introducing selectivity factor of the solute (S). It was found that the modified extended-Langmuir model with incorporation of solute's selectivity factor gave good correlation results against binary adsorption data with reasonable fitted parameter values. The feasibility and biosorption performance of rice straw in sequestering copper and lead ions was also tested using real effluent along with its regeneration possibility.

1. Introduction

Heavy metals are a type of pollutants that are generated from various industrial activities such as metal plating, mining, metallurgical, leather tanning, batteries, alloy, and electronic goods manufacturing. Despite of their importance for economic growth in most countries including Indonesia, the discharged wastewater containing considerable amounts of heavy metal ions is of a major concern to the environment. The contamination of heavy metals in the surface waters, groundwater, and soil causes deterioration of soil and water qualities and gives adverse impacts on the growth of terrestrial and aquatic organisms [1–3]. Moreover, the distribution and accumulation of this substance in food chains often pose serious threats to public health [4,5]. Copper (Cu) and lead (Pb) are two kinds of heavy metals that are widely used since ancient times and their negative effects on human health have been assessed [6]. The Indonesian government has set the regulation for maximum levels of Pb and Cu ions in industrial effluents discharged into inland surface waters (Table 1). To obey this regulation, the industries have to treat their effluents properly before discharge into environment.

Many conventional methods are available for the treatment of metal-bearing effluent such as electrochemical [7], biological treatment [8], membrane separation [9], coagulation [10], chemical precipitation [11], reverse osmosis [12], solvent extraction [13], and ion exchange [14]. However, the application of such methods is often limited, particularly in handling effluents containing trace amounts of heavy metal ions (1–100 mg/l) due to incomplete metal removal, energy-intensive, economically expensive, and generation of secondary waste products (e.g. toxic sludge) that require proper disposal techniques without creating any problem to the environment. To this end, adsorption has proven as a cost-effective and high efficiency method that produced high quality effluents with

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Table 1
The maximum levels of lead and copper heavy metals in industrial effluents discharged into inland surface waters.

Category	Target of uses	Lead[a]	Copper[a]
A	Drinking water (direct-consumed)	0.05	1
B	Bottled drinking water	0.1	1
C	Fishery and livestock	0.03	0.02
D	Agricultural, urban business, industry, and hydro power-plant	1	0.2

[a] In the unit concentration of mg/l.

minimum environmental impacts [15]. One of the key successes of adsorption process in removing heavy metal ions from water and wastewater lies in the selection of the adsorbing material (or adsorbent). To ensure the effectiveness and economic feasibility of the process, the adsorbents should have the following criteria: (1) high loading capacity; (2) cheap; (3) abundant availability; and (4) regenerable. Out of criteria above, commercial activated carbons may satisfy the first and the fourth criteria while the second and the third become the main limitations for large-scale use of this adsorbent in water and wastewater treatment processes.

Recently, the lignocellulosic solid wastes generated from agricultural and forestry sectors have been highlighted as potential adsorbents for the removal of heavy metal ions from water and wastewater [16]. Among the aforesaid criteria, the lignocellulosic-based adsorbents may satisfy three or all criteria although their adsorption capacities are lower than activated carbons. Rice straw that produced from harvesting process of paddy can be utilised as a low cost and effective biosorbent for such purpose. This crop waste mainly composed of natural polymer materials such as lignin, cellulose, and hemicelluloses, which are known to be the binding sites of heavy metal ions [16]. The availability of rice straw in Indonesia is huge with total production reached eighty millions tons in 2011. Of this amount, 30–40% have been used as cattle feeds, 7–15% have been used for handicrafts making, and the rest (about 50%) ends up as a waste [17]. A common method to reduce excess quantities of rice straw is by incineration, which not only causes an air pollution but also waste of natural resources. Therefore, an advantageous waste management process for unused rice straw is by utilising them as a biosorbent for purifying metal-bearing effluents.

This work deals with the evaluation of biosorption performance of rice straw for the removal of copper and lead ions in single and binary component systems. Although biosorption studies of heavy metal ions in single system using pristine or chemically-modified rice straw have been well reported in the last few years [18–21], however, the adsorption equilibria aspect of multicomponent system and its modeling still needs to be explored. Several adsorption models such as extended-Langmuir, extended-Freundlich, and ideal adsorption solution theory (IAST) models (e.g. Fast-IAS theory, real adsorption solution theory) have been developed to describe multicomponent adsorption equilibria. Despite of their reasonable success, the applications of IAST and its modified forms are restricted due to their complex algorithm and the use of an elaborate computer programming for solving the model. In other hand, extended-Langmuir is the most extensively used model featuring its simple approach in describing multicomponent adsorption equilibria. The correlation of adsorption equilibrium data by extended-Langmuir model is mostly performed through a comparison between experimental and theoretical amounts of q_e (i.e. the equilibrium concentration of adsorptive in the adsorbed state). However, this procedure lacks of theoretical sounds and often fails to describe experimental data satisfactorily because it does not address the competitive adsorption in the system. To respond this problem, we propose modification on the adsorption parameters of extended-Langmuir model that incorporates selectivity factor of the solute (S). To the best of our knowledge, there is no report in the literature regarding the incorporation of solute's selectivity factor for the modification of extended Langmuir parameters (i.e. $q_{m\text{-bin}}$ and $K_{L\text{-bin}}$) and its model fitting against binary adsorption equilibrium data of heavy metals-biomass system. The regeneration and metal recovery studies of spent biosorbent were also conducted in order to evaluate the feasibility and reliability of rice straw for practical applications.

2. Experimental sections

2.1. Chemicals

Analytical grade $CuSO_4{\cdot}5H_2O$ and $Pb(NO_3)_2$ as metal ion sources were purchased from Sigma–Aldrich, Singapore. Deionized water was used throughout all experiments in this work.

2.2. Preparation of biosorbent

Rice straw in this work was collected from a rice field located near the border of Lumajang city, East Java, Indonesia. After the collection, the straw was cut into a size of 1 × 1 cm and boiled with deionized water for 2 h to remove color materials. The decolorized straw was then washed with deionized water three times and dried in an oven at 80 °C for 24 h. The biomass was then crushed with an IKA-Labortechnick grinder and sieved to obtain particle size of 150–180 μm. Finally, the product was kept in airtight plastic bag for further experimental use.

2.3. Characterizations of biosorbent

The surface morphology of rice straw was visualized in a JEOL JSM-6300F field emission scanning electron microscopy. Prior to scanning, the sample was coated with a conductive film of platinum using an Eiko IB-5 sputter-coater operated at 6 mA for 4 min in argon atmosphere. The surface scanning was performed at an electron acceleration voltage of 20 kV, four aperture, eight spot size, and 9 mm working distance.

The pore structure of rice straw was analyzed by a Quadrasorb SI sorption analyzer using nitrogen as the adsorbate at 77.15 K and relative pressure (p/p^0) ranging from 0.005 to 0.995. The specific surface area of biosorbent was obtained by means of the BET method applied at p/p^0 range of 0.06–0.3.

The surface functional groups of biosorbent were identified by infrared spectroscopy technique, using a Shimadzu FTIR-8400S spectrophotometer. The analysis was conducted based on the KBr disk method with 200 cumulative scans in a scanning range of 4000–500 cm^{-1}.

The pH of point of zero charge (pH_{pzc}) of rice straw was determined by pH-drift method [22] and found to be 3.2.

Han and Rowell method [23] was applied for quantification of the percentage composition of lignin, cellulose, and hemicellulose in rice straw (wt%, dry matter) and it was found to be 17.4%, 38.2%, and 20.6%, respectively.

The composition of inorganic matters (minerals) in rice straw such as Na, K, Mg, and Ca was analyzed by a MiniPal QC energy dispersive X-ray fluorescence spectrometer (PANalytical) and the results are given as follows: Na = 0.09%; K = 1.87%; Mg = 0.23%; and Ca = 0.52%.

2.4. Static biosorption experiments

The stock solutions of copper and lead ions at initial concentration of 100 mg/l (1.57 mmol/l – Cu(II) and 0.48 mmol/l – Pb(II)) were prepared by dissolving a known amount of $CuSO_4{\cdot}5H_2O$ and $Pb(NO_3)_2$ into 500 ml deionized water. The single and binary biosorption isotherm experiments were performed by adding a prescribed amount of biosorbent ranging from 1 g to 20 g into a series of stoppered conical flasks containing 100 ml metal solution. The flasks were then placed in a Memmert thermostatic shaker water-bath and shaken at desired temperature (30 °C, 40 °C, 50 °C, and 60 °C) with a shaking speed of 100 rpm. Preliminary experiments show that biosorption equilibrium time was reached within 3–4 h. Subsequently, the flasks were removed from the bath and the mixture was filtered pass through a Whatman filter paper to remove solid particles. The residual concentration of metal ions in the filtrate was analyzed using a Shimadzu AA-6200 atomic absorption flame emission spectrophotometer. The measurements were performed at a wavelength corresponding to the maximum absorbance of each metal ion species, i.e. 324.4 nm for copper and 216.7 nm for lead.

The effect of pH on the biosorption of Cu(II) and Pb(II) ions in single and binary component systems was investigated at pH range of 1–6 since the formation of metal hydroxide precipitates, i.e. $Cu(OH)_2$ and $Pb(OH)_2$, occurs at pH higher than 6. The pH of metal solutions was adjusted by the addition of 0.1 M HCl solution as per required.

2.5. Calculations

The amounts of Cu(II) and Pb(II) ions adsorbed onto rice straw in single solute system were calculated by following equation:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions in the liquid phase (mmol/l), V is the volume of metal solution (l), q_e is the amount of metal ions adsorbed per unit of biosorbent mass (mmol/g), and m is the mass of biosorbent (g). The equilibrium concentration of metal i species ($C_{e,i}$) in binary mixture can be calculated by the same manner using following mass balance equation:

$$q_{e,i} = \frac{(C_{0,i} - C_{e,i})}{m} \times V \quad (2)$$

where $q_{e,i}$ is the equilibrium amount of solute i in the adsorbed phase (mmol/g), $C_{0,i}$ and $C_{e,i}$ are the initial and equilibrium concentrations of solute i in the liquid phase (mmol/l), respectively. For reproducibility test, all experiments were repeated three times with averages used as the results.

3. Results and discussion

3.1. Characterizations of biosorbent

The surface morphology of rice straw, as visualized by SEM at magnifications of 5000× and 10000× is depicted in Fig. 1. It was found that rice straw belongs to a nonporous solid material with respect to its surface smoothness. This surface characteristic was also revealed from the N_2 adsorption–desorption isotherm results (figure not shown). The specific surface area of rice straw (S_{BET}) is fairly low (40.7 m^2/g) with total pore volume (V_T) of 0.11 cm^3/g at STP. Low N_2 sorption capacity of rice straw may be ascribed to the low porosity in the solid matrices.

The presence of natural heteropolymer materials like lignin, cellulose, and hemicelluloses in biosorbent was evidenced from FTIR results (spectra not shown). Several strong absorption bands were noted at wavenumbers of 3618 cm^{-1}, 2941 cm^{-1}, and 1127 cm^{-1}. These bands correspond to the O—H stretch of phenol groups, C—H stretch of alkanes groups, and C—O stretch of carboxylic acids, alkoxy groups, or fiber carbonaceous that presented in the lignocellulosic structure. The presence of aromatic C—C stretch and aliphatic C═C stretch was observed at wavenumbers of 1596 cm^{-1} and 1671 cm^{-1}, respectively. Two moderate bands at wavenumbers of 1082 cm^{-1} and 464 cm^{-1} reflected the vibration of silicaeous groups, associated with Si—O stretch and Si—O bend, respectively.

After biosorption, several absorption bands namely O—H stretch and C—O stretch were altered. The reduced peak energy and the shifting of O—H stretch from 3618 cm^{-1} to 3583 cm^{-1} were due to the deformation of this band after metal ions binding. Another shifting was observed in C—O stretch from 1127 cm^{-1} to 1079 cm^{-1} and Si—O stretch from 1082 cm^{-1} to 1051 cm^{-1}, indicating the involvement of these functional groups in the metal sorption process. Moreover, two new peaks at around 1400 cm^{-1} and 1600 cm^{-1} were observed, associated with the vibration bands of metal-carboxylate functional groups (COO-M) where M refers to lead or copper ions. This result implies that the binding of metal ions onto rice straw takes place via complexation or chelating mechanism with hydroxylate and carboxylate surface groups as the main adsorption sites and silicaeous groups in lesser extent through unidentate or bidentate coordination types.

In order to investigate whether ion exchange plays a major role in the metal sorption process, the concentrations of inorganic matters such as Na, K, Ca, and Mg in the solid before and after biosorption were analyzed. It was found that the concentrations of these minerals in pristine and metal-loaded biosorbents were slightly different and can be regarded essentially unchanged. This denotes that the binding of metal ions onto rice straw predominantly occurred by surface complexation or chelation mechanism (as evidenced from FTIR results) and ion exchange in lesser extent. For the latter mechanism, it was found to be predominant in the biosorption using algae or seaweed biomass, as verified in several studies [24–26].

3.2. Effects of pH

The adsorption behavior of heavy metal ions and other contaminants such as dyes, natural organic matters, etc. in aqueous phase strongly depends on pH and may be different for each solute-sorbent interaction. The pH-dependence of metal biosorption has been verified by many researchers, which are relevant to the ionic state of surface functionalities on the adsorbent and the metal chemistry in the solution. The effect of pH on the removal of Cu(II) and Pb(II) ions by rice straw from single and binary mixture was investigated in a pH range of 1–6 and the results are shown in Fig. 2. It can be seen that the percentage removal of both metal ions steeply increased with increasing pH from 3 to 5, continued by a slight increase with increasing pH from 5 to 6. For binary component system, the highest percentage removal of metal ions was observed at pH about 6. Hence, pH 6 was selected as the optimum point and used throughout single and binary biosorption experiments in this work.

At pH value below the pH_{pzc} of biosorbent (i.e. pH 1–3), the surface functional groups on the solid (primarily carboxylic acids) were protonated by hydronium ions (H^+) hence the overall surface charge on the solid was positive. The protonation of carboxylic acid surface groups by H^+ ions occurred as follows:

$$\text{R-COOH} + H^+ \rightarrow \text{R-COOH}_2^+ \quad (3)$$

As the result, an electrostatic repulsion force was generated between metal ions and positively charged solid surface that retards metal binding process. In addition, high concentrations of H^+ ions in the solution also competed with metal species for the adsorption sites on the solid surface.

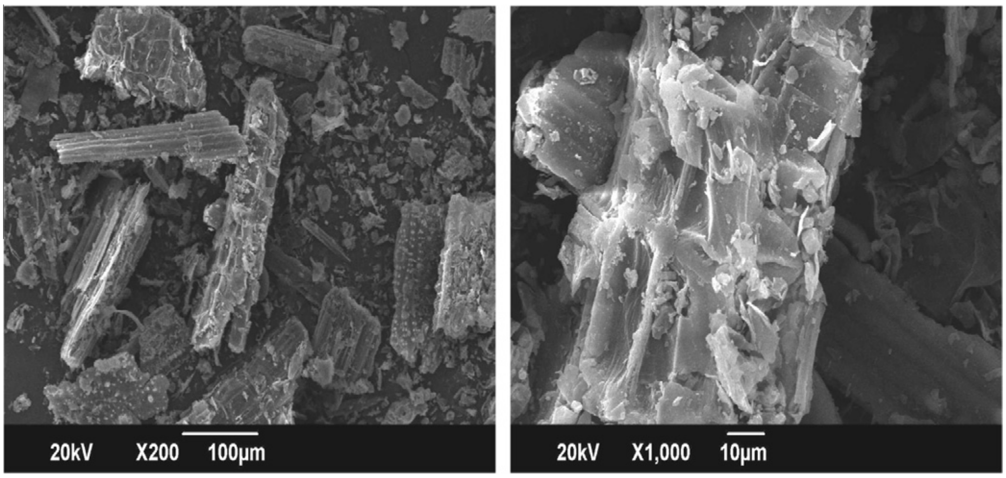

Fig. 1. SEM micrographs of rice straw at magnifications of 200× and 1000×.

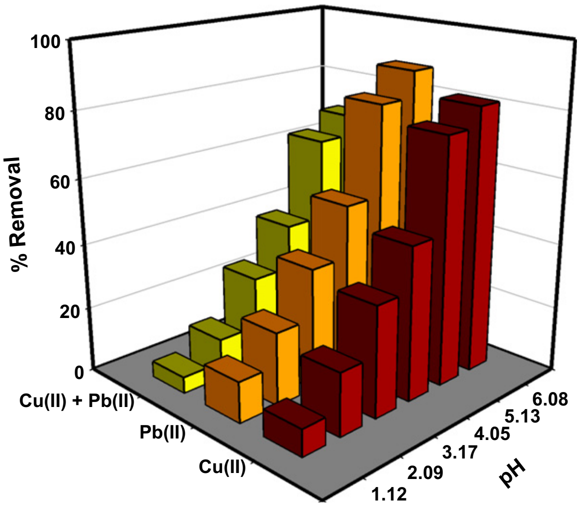

Fig. 2. Effect of pH on the removal of Cu^{2+} and Pb^{2+} ions from single and binary solutions.

Increasing pH of the solution above the pH_{pzc} of the solid facilitated the sorption process. This is due to the increased negative charge density on the biosorbent surface because of the dissociation of carboxylic acids to carboxylate anions (R-COO^-) that took place in a pH range between 3.5 and 5.5, which is the range of acid dissociation value (p*K*a) of carboxylic acids. Hence, an electrostatic attraction force between the deprotonated solid surface and metal ions occurred and facilitated biosorption process. Furthermore, the occurring competitions between metal ions and H+ for the adsorption sites become weaker with increasing pH of the solution.

3.3. Biosorption mechanism of Cu(II) and Pb(II) ions onto rice straw

When dealing with the investigation of adsorption mechanism of adsorbate onto the adsorbent surface, the information regarding the shift of functional groups and the presence of new absorption bands can be used as valuable hints. The main constituents of rice straw namely lignin, cellulose, and hemicelluloses are known to be associated, in part, hydroxyl, carboxyl, and phenol functional groups, which are responsible in providing the adsorption sites for metal ions. These oxygen-containing surface groups are pH-dependent hence the change in pH would affect the chemical state and charge density of these functionalities. As explained above, when pH of the solution was above pH_{pzc} of the biosorbent, the surface functional groups of biosorbent were deprotonated and negatively charged ligands were formed. Conversely, the surface groups were protonated by hydronium ions when pH of the solution was below the pH_{pzc} of biosorbent, bearing a positive charge on the solid surface which tends to repulse the cationic-type adsorbates.

The first stage of metal biosorption process was the deprotonation of hydroxyl group in carboxyl and phenol functionalities to form negatively charged hydroxylate and carboxylate sites. The next stage was the release of hydration waters from the hydrated metal ions, leaving the non-solvated cationic species in the solution. The last stage was the uptake of non-solvated metal ions through electrostatic attractive forces between these species and negatively charged carboxyl or phenol oxygen atoms. Among the three stages above, the role of pH was remarkably important in the first stage because it governed the protonation and deprotonation of surface functionalities and the chemistry of metal species. Meanwhile, the sorption mechanism of copper and lead ions onto rice straw surface in binary mixture was essentially similar to that of single component system, except for the occurring competition between each metal species for the adsorption sites.

3.4. Modeling of adsorption isotherms

3.4.1. Single component system

The information of the equilibrium relationship between the concentration of adsorbate in the liquid phase and adsorbed phase, also known as the adsorption isotherms is of great importance in the adsorption studies, not only for the design purpose, but also in understanding the adsorption equilibria, kinetics, and thermodynamics of single and multicomponent systems. In this regard, two adsorption models namely Langmuir and Freundlich were used to evaluate adsorption equilibrium data of single component system. Langmuir developed an adsorption theory based on the kinetic principle and proposed the monolayer surface adsorption on the ideal solid with definite localised sites that energetically identical [27]. This model further assumes that the adsorbate molecules can only accommodate one localised site without lateral interactions between the adsorbed molecules, even on the adjacent sites. Graphically, Langmuir isotherm is characterized by a plateau curve, which means that no further adsorption can be occurred when equilibrium established. Originally, this empirical model was developed for describing adsorption phenomena in the gas phase but it had been extensively used for the correlation of adsorption equilibrium data of various solute-sorbent interactions in the liquid phase [19–21]. The mathematical form of Langmuir isotherm model is given as follows:

$$q_e = q_m \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

where q_m is the maximum adsorptive capacity of the solid (mmol/g), corresponds to the monolayer surface coverage (i.e. the adsorbate layer is one molecule in thickness) and K_L is Langmuir constants of adsorption affinity (l/mmol). As the value of C_e becomes lower, the term of $K_L{\cdot}C_e$ is much less than unity and Langmuir isotherm will obey Henry's law behavior. In contrast, when the value of C_e getting higher, the saturation point of adsorption will be reached and the concentration of solute on the solid surface will be equal to the maximum sorption capacity. The essential characteristic of Langmuir isotherm on the adsorption nature can be assessed by following equation [28]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (5)$$

where R_L is a dimensionless equilibrium parameter or the separation factor and C_0 is the initial concentration of metal solution (mmol/l). The value of R_L denotes the adsorption nature to be unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), or linear ($R_L = 1$).

The second adsorption model used was Freundlich. Freundlich [29] proposed an empirical adsorption model on the solid with non-ideal nature, i.e. the adsorption energy and affinity are varied over the surface. This isotherm is not restricted to only monolayer surface adsorption and can be used adequately for describing the adsorption behavior in heterogeneous systems, particularly for the adsorption of organic matters by activated carbons, molecular sieves, and other solids with a complex structure. Freundlich isotherm model has a mathematical form as follows:

$$q_e = K_F \times C_e^{1/n} \quad (6)$$

Here, K_F and n are Freundlich constants of adsorption affinity ((mmol/g) (mmol/L)$^{-n}$) and degree of heterogeneity of the system, respectively. Higher value of n indicates a greater degree of heterogeneity and the system increasingly deviated from linear isotherm. When n value was higher than about 10, the system approached a rectangular or non-reversible isotherm [30]. Generally, Freundlich isotherm agreed well in a narrow range of adsorption data, typically at moderate concentrations because this isotherm does not have Henry's law limit at low concentration and saturation limit at high-end concentration. Moreover, this isotherm assumes that an infinite amount of adsorption can be occurred (i.e. the concentration of solute on the solid surface continues to rise with increasing concentration in the liquid phase), which means that no saturation limit at high-end concentration.

The plots of biosorption equilibrium data of Cu(II) and Pb(II) ions at various temperatures are displayed in Fig. 3. The parameter values of the models were determined by nonlinear regression fitting using SigmaPlot software (Version 12.3, Systat Software Inc.) and the results are given in Table 2. In Fig. 3, it can be seen that both Langmuir and Freundlich models can correlate experimental data satisfactorily with coefficient of determination (R^2) approaching unity. However, a deeper analysis of the model, associated with justification of the physical meaning of the model parameters should be conducted. The affinity constants of solute toward the solid surface (i.e. K_L and K_F) were increased at higher temperatures, indicating that high temperature facilitated the sorption process. This is due to greater kinetic energy in the system that caused the molecules to move around faster and increase the adsorptivity

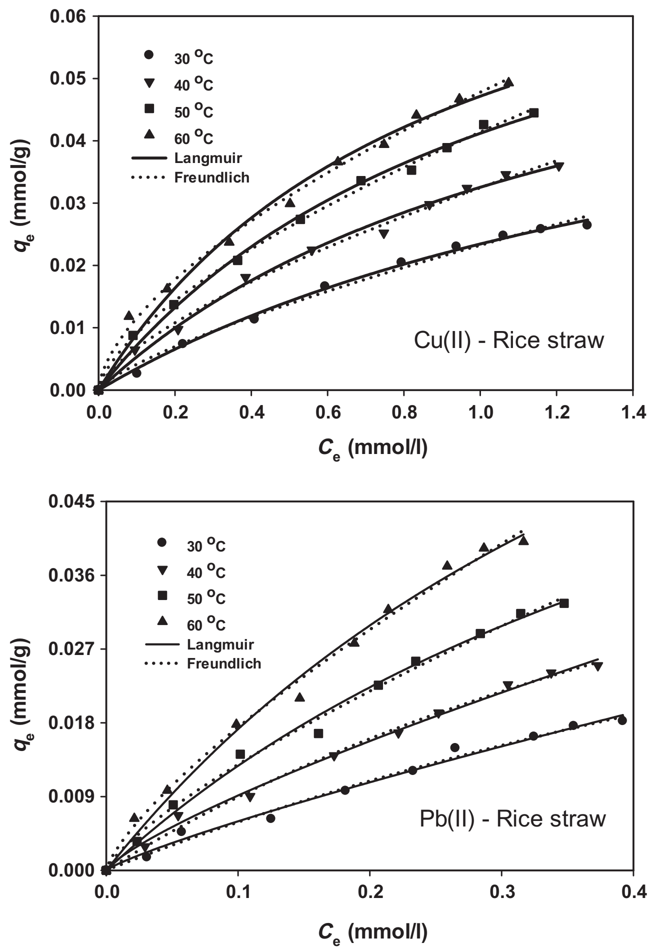

Fig. 3. Biosorption isotherm plots of Cu^{2+} and Pb^{2+} ions at various temperatures.

of solute. Because the Pauling electronegativity of Pb^{2+} ion is greater than Cu^{2+} ion (i.e. 2.33 vs. 1.95) and the ionic size of the former is larger than the latter (i.e. 1.19 Å vs. 0.73 Å) [31], a stronger electrostatic interaction between Pb^{2+} ion and deprotonated carboxyl and hydroxyl surface functionalities was expected hence Pb^{2+} ion was preferentially adsorbed than Cu^{2+} ion. Similar behavior was observed for the maximum uptake capacity of the solid at higher temperatures. The q_m values for Cu^{2+} and Pb^{2+} ions at 60 °C were 0.0891 mmol/g (5.66 mg/g) and 0.1127 mmol/g (23.35 mg/g), respectively. As comparison, the maximum sorption capacities of several biomass-based sorbents for sequestering copper and lead ions from water and wastewater are listed in Table 3 [32–39]. With respect to R_L values, all systems exhibit favorable biosorption nature. Moreover, the magnitude of all isotherm parameters obtained in this work agreed well with those reported previously in the literature for metal ion-biomass sorption systems [19–21,32,40].

As explained above, the movement of the molecules becomes faster at higher temperatures that increased the randomness degree of the system. This behavior was consistently described by Freundlich model, associated with the increasing value of n with temperature. Interestingly, it was also noted that the heterogeneity degree of Pb(II)-rice straw is lower than Cu(II)-rice straw at all temperatures. Through all analyses above, it can be concluded that the Langmuir and Freundich models were able to correlate biosorption equilibrium data satisfactorily from both graphical and parameter justification point of view along with reasonable values of the fitted parameters.

Table 2
The fitted Langmuir and Freundlich adsorption parameters for Cu(II)-rice straw and Pb(II)-rice straw at various temperatures.

Ion	T (°C)	Langmuir			Freundlich			
		q_m (mmol/g)	K_L (l/mmol)	R^2	R_L	K_F (mmol/g) (mmol/l)$^{-n}$	n	R^2
Cu^{2+}	30	0.0659	0.5515	0.99	0.53	0.0232	1.33	0.99
	40	0.0753	0.7618	0.99	0.46	0.0325	1.46	0.99
	50	0.0873	0.8945	0.99	0.42	0.0414	1.52	0.99
	60	0.0891	1.1244	0.98	0.36	0.0478	1.62	0.99
Pb^{2+}	30	0.0740	0.8646	0.98	0.71	0.0417	1.18	0.98
	40	0.0777	1.3014	0.99	0.62	0.0560	1.27	0.99
	50	0.0899	1.6526	0.99	0.56	0.0746	1.31	0.99
	60	0.1127	1.8046	0.99	0.54	0.0985	1.33	0.99

3.4.2. Binary component system

In the present work, the biosorption equilibrium data of Cu(II) and Pb(II) ions from binary solution were evaluated by selectivity extended-Langmuir model. Before moving further on the proposed model, it is necessary to discuss first the classical extended-Langmuir model that has a mathematical form as follows [30]:

$$q_{e,i} = q_{m,i}\frac{K_{L,i}\cdot C_{e,i}}{1+\sum_{j=1}^{n}K_{L,i}\cdot C_{e,i}} \quad (7)$$

For binary component system, Eq. (7) becomes:

$$q_{e,1} = q_{m,1}\frac{K_{L,1}\cdot C_{e,1}}{1+K_{L,1}\cdot C_{e,1}+K_{L,2}\cdot C_{e,2}} \quad (8)$$

$$q_{e,2} = q_{m,2}\frac{K_{L,2}\cdot C_{e,2}}{1+K_{L,1}\cdot C_{e,1}+K_{L,2}\cdot C_{e,2}} \quad (9)$$

where $q_{m,1}$, $q_{m,2}$, $K_{L,1}$ and $K_{L,2}$ are the Langmuir adsorption parameters for single component system. In most cases, the evaluation of binary adsorption data by extended-Langmuir model was conducted by comparing experimental and theoretical amounts of q_e where the latter was calculated from Eqs. (8) and (9) by introducing the adsorption parameters for single system. Although this procedure can give satisfactory fitting results visually, however, it is lack of theoretical sounds since the adsorption behavior in single and binary systems are completely different. This can be explained by considering that the adsorptivity of solute and maximum surface coverage on the solid in single system are derived from pure component adsorption equilibria without any sorption interference from other solutes. Meanwhile, adsorption in binary component system involves the competition between adsorbate species for the active functional groups on the adsorbent surface. Such phenomenon leads to the surface coverage on the solid by each adsorbate at certain fractional loadings. Hence, the adsorption parameters for single system can no longer be used to describe binary adsorption data. For binary adsorption system, the aforesaid behaviors should be included in the correlation of experimental data. To address this point, we propose modification on the parameters of extended-Langmuir model (i.e. $q_{m\text{-bin}}$ and $K_{L\text{-bin}}$) that incorporates selectivity factor of the solute to describe the competitive adsorption in the system. The proposed q_m and K_L parameters of extended-Langmuir model for binary adsorption system are as follows:

$$q_{m\text{-bin}} = q_{m,1\text{-sin}}(C_{0,1}\cdot S_{21}/C_{0,1}\cdot S_{21}+C_{0,2}\cdot S_{12}) + q_{m,2\text{-sin}}(C_{0,2}\cdot S_{12}/C_{0,1}\cdot S_{21}+C_{0,2}\cdot S_{12}) \quad (10)$$

$$K_{L,1\text{-bin}} = K_{L,1\text{-sin}}\cdot\exp(-S_{21}) \quad (11)$$

$$K_{L,2\text{-bin}} = K_{L,2\text{-sin}}\cdot\exp(-S_{12}) \quad (12)$$

where S is a dimensionless constant called selectivity factor or the ratio of affinity of each solute towards the solid surface and $C_{0,i}$ is the initial concentration of solute i in the mixture (mmol/l). The symbol S_{12} denotes the affinity of solute 1 (b_1) relative to the affinity of solute 2 (b_2) towards the solid surface and vice versa. Here, Cu and Pb ions were designated as solute 1 and solute 2, respectively. The exponential term was purposely used in order to describe the Langmuirian plots of adsorption isotherms (C_e vs. q_e) in which the concentration of adsorbate on the solid surface rose exponentially with declining concentration in the liquid phase and tend to be constant when equilibrium is getting closer to be reached. The mathematical relationship between K_L and S can be explained by considering the competitive adsorption between solute 1 and solute 2 in the system. Accordingly, the adsorptivity of each solute towards the solid surface in binary adsorption system should be weaker than that in single system. This behavior also applies to the maximum sorption capacity of the solid which is the sum of maximum sorption capacity of each solute multiplied by the mole fraction of solute adsorbed. By introducing the proposed mathematical forms of $q_{m\text{-bin}}$ and $K_{L\text{-bin}}$ (Eqs. (10)–(12)) into Eq. (7), the selectivity extended-Langmuir model for binary adsorption system was obtained:

$$q_{e,1} = \frac{(q_{m,1\text{-sin}}(C_{0,1}\cdot(b_2/b_1)/C_{0,1}\cdot(b_2/b_1)+C_{0,2}\cdot(b_1/b_2))+q_{m,2\text{-sin}}(C_{0,2}\cdot(b_1/b_2)/C_{0,1}\cdot(b_2/b_1)+C_{0,2}\cdot(b_1/b_2)))K_{L,1\text{-sin}}\exp(-b_2/b_1)C_{e,1}}{1+K_{L,1\text{-sin}}\exp(-b_2/b_1)C_{e,1}+K_{L,2\text{-sin}}\exp(-b_1/b_2)C_{e,2}} \quad (13)$$

$$q_{e,2} = \frac{(q_{m,1\text{-sin}}(C_{0,1}\cdot(b_2/b_1)/C_{0,1}\cdot(b_2/b_1)+C_{0,2}\cdot(b_1/b_2))+q_{m,2\text{-sin}}(C_{0,2}\cdot(b_1/b_2)/C_{0,1}\cdot(b_2/b_1)+C_{0,2}\cdot(b_1/b_2)))K_{L,2\text{-sin}}\exp(-b_1/b_2)C_{e,2}}{1+K_{L,1\text{-sin}}\exp(-b_2/b_1)C_{e,1}+K_{L,2\text{-sin}}\exp(-b_1/b_2)C_{e,2}} \quad (14)$$

Table 3
The maximum uptake capacity of several biomass-based sorbents for Cu^{2+} and Pb^{2+} ions.

Biomass	Conditions		q_m (mg/g)		Reference
	pH	T (°C)	Cu^{2+}	Pb^{2+}	
Rice straw	6	60	5.66	23.35	This study
Barley straw	6	30	4.64	23.2	[32]
Galaxaura oblongata	5	25	–	88.6	[33]
Ulva lactuca	5	20	–	34.7	[34]
Banana peel	5.5	30	–	7.97	[35]
Crab shell	3	25	38.62		[36]
	5.5		19.83		
Pine Cone Shell	5	25	6.81	–	[37]
Tea fungal	4	25	4.64	–	[38]
Garden grass	na[a]	Ambient	58.34	–	[39]

[a] na = Not available.

In the case of single component system, i.e. $C_{0,2} = 0$ in Eq. (13) and $C_{0,1} = 0$ in Eq. (14), both equations will reduce to single Langmuir isotherm. To test the validity of the proposed model, the fitting results between original and selectivity extended-Langmuir models against experimental data were compared as shown in Fig. 4-I–III. In these figures, the circle and triangle symbols represented the concentrations of copper and lead ions in binary solution, respectively. For binary adsorption system, the plot of the isotherm model should fit both experimental data points because the concentrations of both solutes in the liquid phase are in dynamic balance with those in the adsorbed state at equilibrium.

Fig. 4-I shows the fitting result between experimental (solid symbols) and theoretical amounts of q_e (wire-mesh plots). As clearly seen, this procedure fails to give good correlation result, revealing the invalid use of Langmuir adsorption parameters of single system for the evaluation of binary adsorption equilibrium data. To give more evidence on this, the evaluation of experimental data by original extended-Langmuir model by nonlinear regression fitting is depicted in Fig. 4-II. It was found that the fitted parameter values ($K_{L,1}$, $K_{L,2}$, $q_{m,1}$, and $q_{m,2}$) obtained for binary adsorption system deviate away than those in single system. In other hand, the proposed selectivity extended-Langmuir model with two fitted parameters (i.e. b_1 and b_2) satisfactorily representing experimental data in this work (Fig. 4-III).

The fitting of selectivity extended-Langmuir model against adsorption equilibrium data of copper and lead ions from binary solution at various temperatures is displayed in Fig. 5. It can be

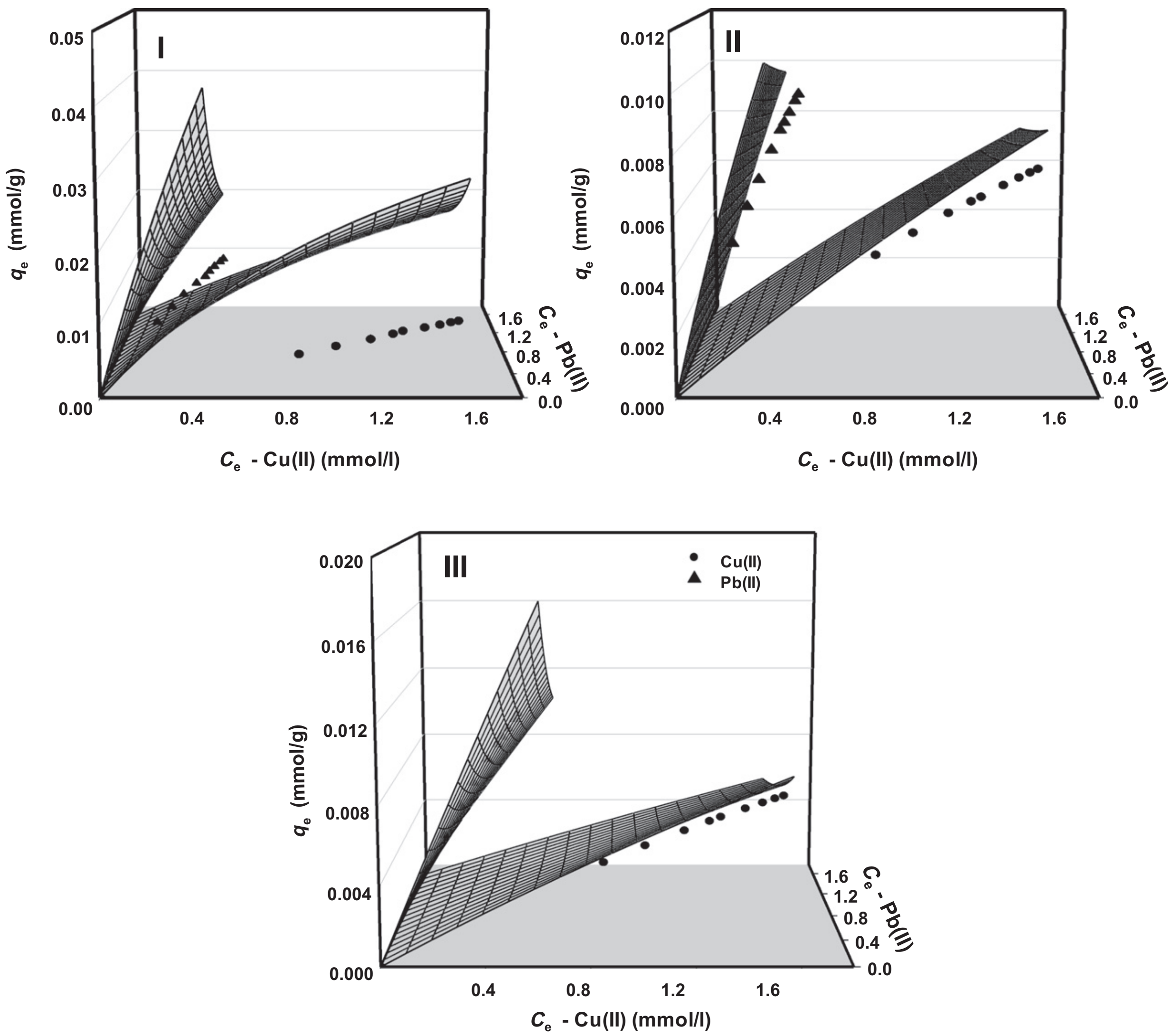

Fig. 4. Comparison of the fitted models between original extended-Langmuir (I and II) and selectivity extended-Langmuir (III) against biosorption data of Cu^{2+} and Pb^{2+} ions in binary solution at 30 °C.

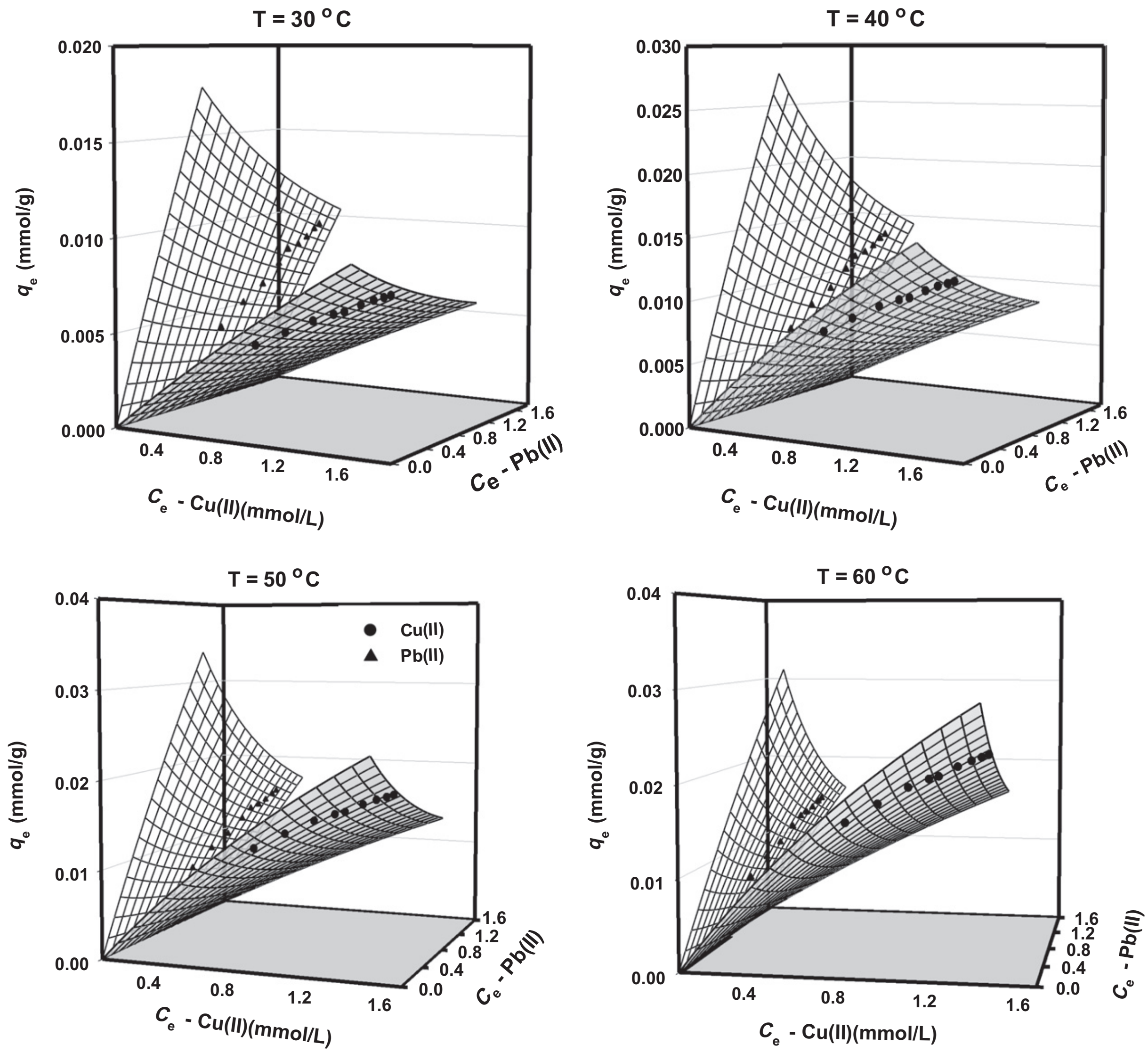

Fig. 5. The fitted model of selectivity extended-Langmuir against biosorption data of Cu^{2+} and Pb^{2+} ions in binary solution at various temperatures.

Table 4
The fitted selectivity extended-Langmuir model parameters for the biosorption of Cu^{2+} and Pb^{2+} ions from binary solution at various temperatures.

T (°C)	Fitted parameters		Adsorptivity[a]		$q_{m\text{-bin}}$[b] (mmol/g)	R^2
	b_1	b_2	$K_{L,1\text{-bin}}$ (l/mmol)	$K_{L,2\text{-bin}}$ (l/mmol)		
Synthetic effluents						
30	0.0168	0.0276	0.1069	0.4698	0.0667	0.95
40	0.0210	0.0309	0.1752	0.6593	0.0756	0.94
50	0.0273	0.0341	0.2563	0.7426	0.0877	0.96
60	0.0311	0.0367	0.3455	0.7713	0.0934	0.95
Real effluent						
30	0.0019	0.0032	0.1024	0.5523	0.0667	0.71

[a] Calculated from Eqs. (11) and (12).
[b] Calculated from Eq. (10).

seen that the model can correlate experimental data satisfactorily with coefficient of determination (R^2) ranged between 0.94 and 0.96. The parameter values of b_1 and b_2 were determined by non-linear regression fitting until convergence and minimum standard error of the estimate achieved. From Table 4, it can be seen that the values of $K_{L,2\text{-bin}}$ are higher than $K_{L,1\text{-bin}}$ at all temperatures, indicating that Pb(II) ion is more readily adsorbed onto rice straw surface than Cu(II) ion and the order of ion's affinity for the adsorption sites is consistent with the behavior in single system. At higher temperatures, the metal uptake process was more favorable due to enhanced affinity of each cation towards the biosorbent surface. Toward this end, the adsorptivities of both adsorbates in binary solution were lower than those in single system, revealing the competitive adsorption in the system.

3.5. Application of biosorption studies in real effluent

The feasibility of rice straw for removing heavy metal ions was also tested using real effluent. The effluent was collected at the influent point from a wastewater treatment plant (WWTP) located in Rungkut Industrial area that contained various heavy metal ions with initial concentrations given in Table 5. Other components such as phenols, chlorides, nitrogen and sulfur compounds were also found in trace to moderate concentrations (1–100 mg/L). The pH of the effluent was measured by a Schott CG-825 digital pH-meter and found to be 4.31. Total dissolved solids (TDS) and total solids (TS) in the effluent were determined by following APHA standard methods [41] and found to be 1527 mg/L and 1912 mg/L, respectively.

The biosorption experiments were conducted in a 250 mL stoppered conical flask containing 100 ml effluent at room temperature (around 30 °C) and pH 6 using biosorbent mass of 10 g. The mixture was then shaken at 100 rpm for 24 h to reach equilibrium. The characteristics of untreated and treated real effluents are listed in Table 5. It was found that the concentration of TDS in untreated effluent was unchanged after pH adjustment, indicating that the formation of metal hydroxide precipitates did not occur. The formation of metal hydroxide precipitates is essentially undesirable because it diminishes the concentration of free metal ions in the solution, leading to a lesser metal removal and physically change the characteristic of the effluent with respect to the increase of TSS (total suspended solids) and decreased TDS. By comparing the percentage removal of Cu and Pb ions from synthetic (Cu + Pb + water) and real effluents, the latter gave lower value for the same experimental conditions (68.4% vs. 48.7%). This is likely due to a more intensive competition of solutes for the active binding sites on the solid because more solute species are presented in the adsorption system. Lower percentage removal of copper and lead ions from real effluent also attributed to the reduced affinity of both adsorbates toward the biosorbent surface. The adsorptivity of copper ($K_{L,1}$) and lead ($K_{L,2}$) metal ions in the multicomponent system (i.e. real effluents) should be lower than those of single and binary sorption systems. However, it was found that the affinity of Pb(II) ions in real effluent (see Table 4) was higher than that of binary effluent (Cu + Pb + water), which verifies that the proposed model failed to describe experimental data from theoretical viewpoint. The inadequacy of the proposed model was also seen in Fig. 6, associated with a fairly poor value of the coefficient of determination (R^2 = 0.71) of the fitted model against experimental results. Taking into account all of these, it can be concluded that the proposed selectivity extended-Langmuir model cannot correlate experimental adsorption data of Cu(II) and Pb(II) ions in real effluent satisfactorily. A plausible explanation to this point is that the currently proposed model only considers the competitive adsorption between two adsorbates in the solution while in the real effluent; more than two adsorbates existing and a greater extent of the sorption competition occurred. Hence, a different mathematics model or further modification of the selectivity factor concerning *n*-components should be used in order to obtain a better correlation result.

With regard to the percentage removal, the adsorptivity of metal ions toward the solid surface can be arranged from the highest to the lowest as follows: Pb > Hg > Cd > Zn > Cu > Ni > Fe > Mn > Cr. After biosorption, the concentration of total dissolved solids in untreated effluent declined from 1522 mg/L to 1296 mg/L because of the removal of some amounts of metal ions by rice straw. The pH of untreated effluent became more acidic after metal ions uptake (from 6.07 to 5.21), which may be ascribed to the release of protons into the solution from the dissociation of carboxylic acids (R-COOH) into carboxylate anions (R-COO$^-$). This phenomenon acts as a preliminary stage in the metal binding process onto rice straw.

Table 5
The characteristics of untreated and treated real effluents.

Parameters	Untreated		Treated		
	Original	After pH adjustment			
TDS (mg/l)	1527	1522	1296		
TS (mg/l)	1912	1908	1658		
pH	4.31	6.07	5.21		
Concentration of metal ions (mmol/l)				% Removal	
				Synthetic	Real
Pb	0.35	0.35	0.32	40.8	9.1
Cu	1.26	1.26	1.19	27.6	5.3
Cr	0.71	0.71	0.69	–	2.7
Mn	0.64	0.64	0.62	–	3.4
Zn	0.82	0.82	0.77	–	5.6
Cd	0.53	0.53	0.50	–	6.2
Hg	0.18	0.18	0.17	–	7.5
Ni	0.49	0.49	0.47	–	4.8
Fe	1.65	1.65	1.58	–	4.1
Total removal (%)				68.4	48.7

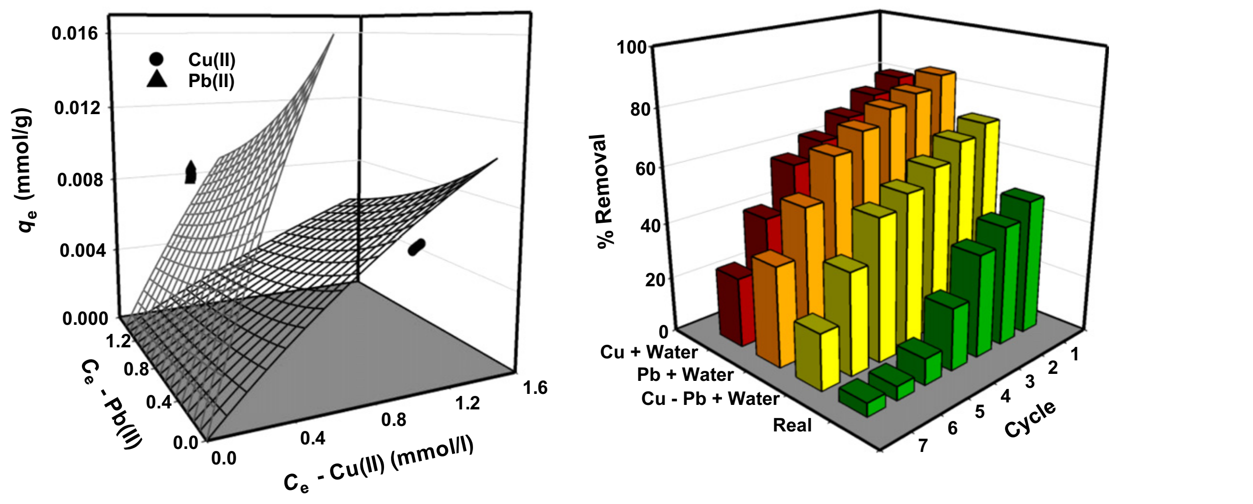

Fig. 6. The correlation of biosorption data of Cu^{2+} and Pb^{2+} ions from real effluent by selectivity extended-Langmuir model (left-hand side) and stability tests of spent biosorbent (right-hand side).

3.6. Desorption study of spent biosorbent

Regenerability is one of desired criteria of adsorbent in order to make the sorption process more economical, particularly for industrial practice and explore the possibility for recovering metal resources from the liquid phase. The regenerability of rice straw in this work was evaluated by subjecting the spent biosorbent to seven-successive adsorption–desorption cycles. Desorption experiments were performed at room temperature by mixing 1 g of metal-loaded rice straw with 50 mL eluent solution in a series of stoppered conical flasks for 24 h. The eluent solution used was dilute hydrochloric acid at initial concentration of 0.1 M. The effect of recycling time on the stability performance of rice straw in sequestering heavy metal ions from synthetic (Cu + water, Pb + water, and Cu + Pb + water) and real effluents is shown in Fig. 6.

Experimental results (Fig. 6) show that the repeated use of biosorbent in the case of synthetic wastewaters still feasible for five cycles with comparable percentage removal against the previous cycle. Meanwhile, the regenerated biosorbent can only be used three times for the effective removal of metal ions from real effluent. After third cycle, the adsorption capacity of biosorbent started to decline drastically and no further desorption at the sixth cycle. A shorter life time of regenerated biosorbent in this case may be ascribed to the difficulties in leaching some heavy metal ions that strongly bound in the solid matrices. Apart from this, all results above show the feasibility and potential application of rice straw for the treatment of metal-bearing effluents in large-scale operation.

3.7. Biosorption thermodynamics

In order to gain a complete understanding on the biosorption nature of Cu(II) and Pb(II) ions onto rice straw surface, thermodynamic aspects of the sorption process such as the standard enthalpy change ($\Delta H°$), the standard entropy change ($\Delta S°$), and the free energy change ($\Delta G°$) were studied. These thermodynamic parameters can be evaluated by considering the variation of apparent equilibrium constant or sorption distribution (K_D) with temperature. The mathematical relationship between the equilibrium sorption distribution and free energy change of adsorption can be expressed by the classical van't Hoff equation below:

$$\Delta G^{\circ} = -RT \ln K_D \tag{15}$$

where $\Delta G°$ is the Gibb's free energy change (kJ/mol) that measures the spontaneity of a chemical reaction and can be expressed as $\Delta G° = \Delta H° - T\Delta S°$, K_D is the thermodynamic distribution coefficient that defined as a ratio of concentration of the solute in the adsorbed phase (mmol/l) to that in the liquid phase (mmol/l) at equilibrium, R is the universal gas constant (8.314 J/mol K), and T is the operating temperature (K). The parameter K_D can be obtained by plotting a straight line of ln (q_e/C_e) vs. q_e and extrapolating q_e to zero according to the Khan and Singh method [42]. The standard enthalpy change and standard entropy change of an adsorption process can be determined by substituting $\Delta G° = \Delta H° - T\Delta S°$ into Eq. (15) to give the following van't Hoff equation:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{16}$$

The values of $\Delta H°$ (kJ/mol) and $\Delta S°$ (kJ/mol K) can be calculated from the slope and intercept of the linear plot of ln K_D vs. $1/T$, respectively. By evaluating these parameters, the nature of an adsorption process can be known whether it is endothermic ($\Delta H° > 0$), exothermic ($\Delta H° < 0$), spontaneous ($\Delta G° < 0$), or non-spontaneous ($\Delta G° > 0$).

The van't Hoff plots for the biosorption of copper and lead ions onto rice straw in single component system are depicted in Fig. 7 while the corresponding thermodynamic parameters are tabulated in Table 6. From Table 6, it can be known that the biosorption of Cu^{2+} and Pb^{2+} ions by rice straw are spontaneous and endothermic in nature with respect to the negative values of $\Delta G°$ and positive values of $\Delta H°$. Increasing temperature led to a more negative value of $\Delta G°$, indicating that higher temperatures energetically favor the feasibility and spontaneity of the biosorption process. This may be attributed to the faster mobility of solute molecules in the solution at elevated temperatures that enhanced their adsorptivity toward the biomass surface. By comparing the magnitude of $\Delta G°$ values for the biosorption of copper and lead ions at the same temperature, it can be known that the biosorption of the latter species was more favorable than the former, which is consistent with the adsorption isotherm results. The endothermic behavior of the removal of copper and lead ions by rice straw revealed that an energy input (heat) is required for conducting the process and the rise in temperature increased the removal effectiveness and maximum sorption capacity of the solute. In addition, the magnitude of $\Delta H°$ may also give an idea about the type of sorption process whether it is physisorption (i.e. 2.1–20.9 kJ/mol) or chemisorption (i.e. 80–200 kJ/mol). As seen in Table 6, the values of $\Delta H°$ for the biosorption of copper and lead ions using rice straw were 37.64 kJ/mol and 39.41 kJ/mol, respectively. These values do not fall into a range of pure physical or chemical adsorption process, which suggests a combination of physisorption and chemisorption where the latter serves as the controlling mechanism. The positive values of $\Delta S°$ were observed for copper-rice straw and lead-rice straw systems, which reflected high preference of metal cations towards the adsorption sites and a random state at the solid/solution interface with some structural changes in the adsorbate and biosorbent. Some explanations to this point were (1) the system gain more translational entropy from the displacement of adsorbed water molecules by metal cations; (2) the release of hydration waters during the transition of metallic species; (3) higher mobility of the adsorbate molecules at elevated temperatures; and (4) the distribution of translational and rotational energies during the self-orientation of adsorbate species in the adsorbed state. All these phenomena might be responsible, thus allowing for the prevalence of randomness in the system. For comparison purpose, the thermodynamic behavior of the biosorption of copper and lead ions using various kinds of biomass (besides rice straw) was given in Table 6 [34,43–45].

The thermodynamic behavior of biosorption of copper and lead ions from binary solution can be determined by the same approach as of single component system [46]. It was found that the

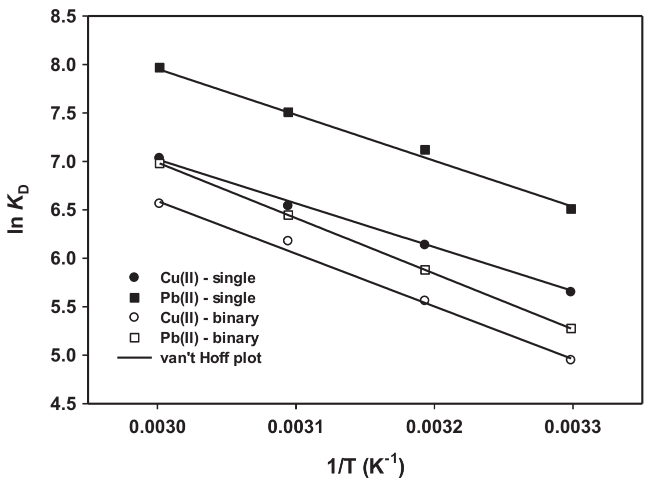

Fig. 7. The van't Hoff plot for biosorption of Cu^{2+} and Pb^{2+} ions from single and binary systems.

Table 6
Thermodynamic parameters for the biosorption of Cu^{2+} and Pb^{2+} ions by various biomass.

Biomass	Ion	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	Reference
Rice straw	Cu^{2+}	303.15	−14.29	37.64	171.29	This study
		313.15	−16.00			
		323.15	−17.71			
		333.15	−19.43			
	Pb^{2+}	303.15	−16.48	39.41	184.37	
		313.15	−18.33			
		323.15	−20.17			
		333.15	−22.01			
Ulva lactuca	Pb^{2+}	293.15	−16.7	−30.2	−45.8	[34]
		303.15	−16.4			
		313.15	−15.7			
		323.15	−15.4			
Tannin resin	Pb^{2+}	296	−5.43	31.84	127.02	[43]
		306	−6.63			
		326	−9.17			
		346	−11.54			
		366	−14.42			
Rubber leaf powder	Cu^{2+}	300	−3.38	−31.96	−95.94	[44]
		310	−2.17			
		320	−1.48			
Grafted chitosan bead	Cu^{2+}	303	−14.04	11.15	12	[45]
		313	−14.19			
		323	−14.23			

spontaneity of the sorption process for both heavy metals from binary solution at all temperatures was diminished likely due to the competitive adsorption occurring between the ionic species in the liquid phase. The ΔG° values for biosorption of Cu^{2+} and Pb^{2+} ions were ranged from −12.51 kJ/mol to −16.32 kJ/mol and −13.27 kJ/mol to −19.31 kJ/mol, respectively. Conversely, the values of entropy change for the removal of copper and lead ions from binary solution were higher that those of single metal removal (i.e. 190.52 J/mol K for Cu^{2+} and 201.20 J/mol K for Pb^{2+}), reflecting a more irregular state at the solid/solution interface which might be associated with the presence of competing ion so the vacant sites on the solid surface were occupied by both components. The biosorption of Cu^{2+} and Pb^{2+} ions from their mixture was endothermic with enthalpy changes of 45.24 kJ/mol and 47.72 kJ/mol, respectively. Higher values of ΔH° mean that more energy is required for the metal cations to be adsorbed onto biosorbent surface as a result of competitive biosorption in the system.

4. Conclusions

The utilisation and evaluation of rice straw for the removal of copper and lead ions from single and binary solutions have been demonstrated in this work. Some crucial implications of this study are listed below:

- The proposed selectivity extended-Langmuir model with two fitted parameters (b_1 and b_2) satisfactorily correlating biosorption equilibrium data of Cu(II)—Pb(II) mixture at all temperatures compared to the classical extended-Langmuir model.
- The biosorption performance of rice straw for sequestering heavy metals from real effluent was fairly good with percentage removal of 48.7%.
- The utilisation of rice straw as a natural sorbent for heavy metal ions show potential application for scale-up purpose due to its abundance in nature, low cost, and reusability.
- Thermodynamically, the biosorption of copper and lead metal ions by rice straw from single and binary solutions was spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$) with high preference of metal cations towards the biomass surface ($\Delta S^\circ > 0$).

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