Equilibrium and Kinetic Studies of the Biosorption of Dissolved Metals on *Bacillus drentensis* Immobilized in Biocarrier Beads

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**Abstract**

Biocarrier beads with dead biomass, *Bacillus drentensis*, immobilized in polymer polysulfone were synthesized to remove heavy metals from wastewater. To identify the sorption mechanisms and theoretical nature of underlying processes, a series of batch experiments were carried out to quantify the biosorption of Pb(II) and Cu(II) by the biocarrier beads. The parameters obtained from the thermodynamic analysis revealed that the biosorption of Pb(II) and Cu(II) by biomass immobilized in biocarrier beads was a spontaneous, irreversible, and physically-occurring adsorption phenomenon. Comparing batch experimental data to various adsorption isotherms confirmed that Koble-Corrigan and Langmuir isotherms well represented the biosorption equilibrium and the system likely occurred through monolayer sorption onto a homogeneous surface. The maximum adsorption capacities of the biocarrier beads for Pb(II) and Cu(II) were calculated as 0.3332 and 0.5598 mg/g, respectively. For the entire biosorption process, pseudo-second-order and Ritchie second-order kinetic models were observed to provide better descriptions for the biosorption kinetic data. Application of the intraparticle diffusion model showed that the intraparticle diffusion was not the rate-limiting step for the biosorption phenomena. Overall, the dead biomass immobilized in polysulfone biocarrier beads effectively removed metal ions and could be applied as a biosorbent in wastewater treatment.

**Keywords:** Adsorption isotherm, Biosorption, Immobilized biomass biocarrier beads, Kinetic, Thermodynamics

1. **Introduction**

Heavy metals such as lead and copper are often found in industrial wastewaters. The acute toxicity of heavy metals can cause various damages to vital internal organs or the central nervous system and lower energy levels. Long-term exposure to heavy metals may result in slowly progressing physical, muscular, and neurological degeneration. Due to the concern regarding the potential risks of heavy metals in aquatic environments, immense attention has been placed on finding technical solutions for removing heavy metals from wastewater.

Various physical and/or chemical treatment technologies such as adsorption, precipitation, complexation, chelation, membrane filtration, ion exchange, reverse osmosis, solvent extraction, etc., have been proposed and applied. However, in many cases, these techniques have been ineffective or impractical due to the low removal efficiency or high operating costs, especially in treating wastewaters with relatively low metal concentrations [1]. As a promising alternative, the application of biologic materials such as bacteria, algae, fungi, seaweeds, and sawdust as a sorbent has been studied over the past few decades [2, 3]. The “biosorption” refers to the passive uptake of pollutants from aqueous solutions, often, by the use of non-growing or non-living biomass [4], and has been known to be highly selective, efficient, relatively cost-effective, and non-hazardous [5-7]. The use of dead or inactive biomass as a biosorbent has many advantages compared to living or active biomass. The dead biomass is not affected by toxic or oligotrophic conditions in wastewaters and is easy to store, operate, and reuse [8, 9]. Furthermore, it has been reported that dead biomass can uptake more heavy metals than living biomass [8, 10].

In addition to sorption capacity, the biosorbents need to be equipped with mechanical strength, chemical resistivity, and hydraulic permeability for practical applications such as packed or fluidized bed reactors. These requirements can be achieved by the imprisonment of the powdered biomass in a distinct phase with proper size, shape, and rigidity. There are several immobilization techniques reported in the literature, which include...
adsorption on inert mineral or organic supports such as clay, aluminum oxide, starch, etc.; 2) entrapment in polymeric matrix such as calcium alginate, polyacrylamide, polysulfone, etc.; 3) covalent bonds in vector compounds such as silica gel; or 4) cross-linking with agents such as formaldehyde, divinyl sulfone, formaldehyde, etc. [11]. Among these techniques, immobilization of biomass in a polymer matrix has drawn great attention mainly due to its mechanical and chemical stability. In addition, granule-shaped polymer sorbents can be easily manufactured with customized specifications such as size or biomass contents to meet the requirements of a changing environment. The biomass immobilization can also provide additional advantages such as efficient and effective regeneration for the reuse of the biomass, easier solid-liquid separation, and minimal clogging in continuous flow systems [8].

This study aimed to investigate the thermodynamics, adsorption mechanisms, and kinetics of Pb(II) and Cu(II) biosorption by the immobilized biomass biocarrier beads. For this purpose, the biocarrier beads were fabricated with *Bacillus drentensis* and batch experiments were conducted to monitor the metal removal efficiency of the biosorbents in aqueous solutions. A thermodynamic analysis was also performed to identify the nature of the biosorption phenomena. Nonlinear regression analysis was applied to the comparison of the experimental data with theoretical models to search for the optimum sorption kinetics, isotherms, and for the estimation of the model parameters.

### 2. Materials and Methods

#### 2.1. Preparation of Dead Biomass for Immobilized Biocarrier Beads

Indigenous microorganisms were isolated from soil samples collected at a military base contaminated by oils and heavy metals in Daegu, Korea. Out of 16 microbial species, a strain of microorganisms dominant in the colony population, identified as *Bacillus drentensis* LMG 21831T by 16S rRNA sequencing was selected for use as a biosorbent in biocarrier beads [12]. After a series of massive cultivation processes, the biomass cells were collected through centrifugation (ASM 260PL; Tomoe Engineering Co. Ltd., Tokyo, Japan) and were vacuum freeze dried. The dried biomass was deactivated by autoclaving at 121°C and 1 atm for 20 min. The dead biomass was powdered and sieved through a 100-mesh sieve. Polysulfone (Sigma-Aldrich, St. Louis, MO, USA) a widely applied polymeric material, has mechanical, thermal, and hydrolytic stability. A 10% polysulfone solution was prepared by dissolving 10 g of polysulfone in 90 g of N,N-dimethylformamide (DMF) solvent for 16 hr on a rotary shaker at 125 rpm. Powdered biomass was homogeneously blended into the polysulfone solution on a stirrer. The resulting slurry was dripped into 80% methanol solution through a peristaltic pump with an 18-gauge needle and spherical beads were formed by phase inversion. The beads were incubated in distilled water on a rotary shaker for 1 hr to remove the remaining solvent and dried for 48 hr at room temperature. In preliminary experiments, various recipes and doses were examined. The results showed that the removal efficiency of the beads for dissolved heavy metal ions increased significantly when biocarrier beads with a biomass content of higher than 5% was applied and more than 2 g of beads added in 50 mL of contaminated solution. The optimized conditions were applied to fabricate the biocarrier beads and to conduct batch experiments [12].

The beads, displayed in Fig. 1, appeared yellowish-white in color and had a roughly spherical form with an approximate diameter of 2 mm. The biocarrier beads also appeared insoluble and mechanically stable in water. The particle density of a biocarrier bead was measured to be 0.288 g/cm³, which may be undesirable for application in column reactors because of the beads tendency to float in water. The porosity and the hydraulic conductivity of the beads were determined to be 0.370 and 1.455 cm/sec, respectively. Fig. 2(a) shows the scanning electron micrograph (SEM, S-2700; Hitachi, Tokyo, Japan) image of the surface of a resultant polysulfone biocarrier bead. The magnified...
image \((\times 70)\) revealed that the bead surface appeared irregular with some rough-splot scattered over the surface. No clear pattern for biomass immobilization was observed. The SEM image of the cross-section of the biocarrier in Fig. 2(b) clearly shows that the bead had a highly porous structure which is beneficial for the adsorption of metal ions. A thin skin-type outer layer was observed to cover the irregularly shaped pore structure, and the inner-most layer was composed of relatively large pore space and walls. The creation of the characteristic inside of the beads can be attributed to the precipitation of polysulfone and the diffusive flux of DMF solvent oozing out of the beads while they were rinsed [13]. Due to the highly porous structure, the specific surface area and pore volume of the biocarrier beads were measured by Brunauer-Emmer-Teller (BET) analysis to be 2.65 \(\text{m}^2/\text{g}\), which is 250 times larger than the external surface area, and 0.0067 \(\text{cm}^3/\text{g}\). However, it was difficult to visually distinguish polysulfone and biomass because of similar organic properties in the SEM images. In order to distinctively visualize the organic matters on the beads, transmission electron micrograph (TEM) (JEM-1210EX II; JEOL Ltd., Tokyo, Japan) analysis was also conducted. In Fig. 3, the TEM produced detailed surface images for the internal structure of a biocarrier bead at a magnification of 2,500. It revealed that the powdered debris of inactive Bacillus drentensis cells were tightly conjoined with the polysulfone matrix, suggesting that the polysulfone beads could be recycled for multiple use by keeping biomass stable during the desorption process.

### 2.2. Preparation of Trace Metal Solution

1,000 mg/L stock solutions of lead and copper were prepared by using commercial standard solutions (AnApex Ltd., Daejeon, Korea). All working solutions for each batch experiment at a specified concentration were prepared from the stock solutions by successive dilution with distilled water. The pH of the solution was carefully monitored with a pH meter and was adjusted with dilute HNO\(_3\) and NaOH.

### 2.3. Biosorption Experiments

For the thermodynamic modeling and equilibrium isotherm fitting analyses, a series of batch experiments were performed by adding 2 g of biocarrier beads with 5% biomass content into 50 mL of metal solution at specified aqueous concentrations, which was established as optimized conditions in preliminary experiments. After approximately 24 hr of agitation on a rotary shaker at 120 rpm, the solution was separated from the biocarriers by a filter paper (Whatman No. 40, retention 8 \(\mu\text{m}\); Whatman, Maidstone, Kent, UK) and the filtrates were analyzed by inductively coupled plasma-optical emission spectrometry (ICP/OES) (Optima 7000DV; PerkinElmer, Waltham, MA, USA) for the residual metal ions in the solutions. Various initial concentrations of Pb(II) and Cu(II) (0.01 to 100 mg/L) and different temperature conditions (from 293 to 313 K) were applied for the batch experiments. For kinetic analysis, biosorption batch experiments for Pb(II) and Cu(II), were performed with 2 g of biocarrier beads in 50 mL solutions with initial concentrations of 10 mg/L. These experiments were repeated for different contact times: 5, 10, 15, 20, 25, 30, 60, 180, 300, 480, 720, and 1,440 min. Solution samples were taken following the prescheduled sampling scheme for the residual metal concentration in the solution.

The amount of metal adsorbed at equilibrium, \(q_{eq}\) (mg/g), which represents the metal uptake by the unit mass of biocarriers, for each sample was calculated from the difference of the dissolved concentration regarding the solution before and after the biosorption as follows:

\[
q_{eq} = \frac{(C_i - C_{eq})V}{m}
\]

where \(C_i\) and \(C_{eq}\) (mg/L) are the initial and equilibrium concentrations of a dissolved metal, respectively; \(V\) (L) is the volume of solution; \(m\) (g) is the mass of dry biocarrier beads. The percent removal efficiency was calculated using the following equation:

\[
\text{removal efficiency} (\%) = \frac{C_i - C_{eq}}{C_i} \times 100\%
\]

All the batch experiments were conducted in duplicate and the mathematical mean values of two replicate measurements were applied to further analyses.

### 3. Results and Discussion

#### 3.1. Biosorption of Metals by Bacillus drentensis Immobilized in Biocarrier Beads

To identify the change in the structure after biosorption experiments for Pb(II), the surface and the inside of a biocarrier bead were analyzed by SEM coupled with energy dispersive spectroscopy (EDS, EX-250; Horiba Scientific, Kyoto, Japan). Fig. 4(a) and (b) are the SEM images (\(\times 10,000\)) of the bead surface and the internal pore wall from a cutting cross-section, respectively. Tiny plaque-type solid crystals with a size of less than 1 \(\mu\text{m}\) were scattered on the bead surface and the inside pore wall. The EDS analysis focused on the crystals confirmed that this phenomenon resulted from adsorption of Pb(II) in a solid state. The distinct Pb peaks in the EDS spectra of the cluster on the surface and inside of the biocarrier bead were observed after the experiments. The porous structure of the biocarrier bead appeared to increase its sorption capacity by uptaking metal ions diffused
ship between $\Delta G_0$ and $T$ in Eq. (4), which are presented as the intercept and the slope of the regression line in Fig. 5. The thermodynamic parameters determined from the relationships are given in Table 1.

### Table 1. Thermodynamic parameters for biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta S^0$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>198.30</td>
<td>-68.32</td>
<td>-9.534</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>258.40</td>
<td>-79.86</td>
<td>-3.842</td>
</tr>
</tbody>
</table>

Fig. 5. Gibbs free energy changes ($\Delta G^0$) versus temperature for the biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads.
3.3. Equilibrium Isotherm

With underlying physical, chemical, or mathematical assumptions, the adsorption isotherms can provide information on biosorption mechanisms and surface properties and affinity of the biosorbents. In this study, a series of biosorption batch experiments for 2 g of biocarrier beads at 20°C and different metal concentrations (from 0.01 mg/L to 100 mg/L) were conducted and the equilibrium distribution of Pb(II) and Cu(II) was respectively plotted in Fig. 6(a) and (b). It was observed that the amount of metal adsorbed at equilibrium by the unit mass of biocarriers \( (q_{eq}) \) increased with the increase in initial concentration. It was due to the enhanced adsorption resulting from the increased concentration gradient between the bulk liquid and sorbent surface. While the initial concentration was too low to provide sufficient sorbate to saturate available sorption sites on biosorbents, the initial concentration could have a significant effect on both the aqueous and solid phase concentrations at equilibrium. After the initial concentration increased beyond 5 mg/L for Pb(II) and 10 mg/L for Cu(II), the equilibrium state had been established between the phases and the increase in initial concentration did not affect the biosorption processes.

For further analyses, the results were fitted by five widely applied adsorption isotherms including Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan and Temkin isotherm models as follows.

- **Langmuir isotherm model:**
  \[
  q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (5)
  \]

- **Freundlich isotherm model:**
  \[
  q_{eq} = K_F C_{eq}^{1/n} \quad (6)
  \]

- **Redlich-Peterson isotherm model [17]:**
  \[
  q_{eq} = \frac{K_P C_{eq}^{n_F}}{1 + a_{ad} C_{eq}^{n_F}} \quad (7)
  \]

- **Koble-Corrigan isotherm model [18]:**
  \[
  q_{eq} = \frac{K_C C_{eq}^{a KC}}{1 + a_{ad} C_{eq}^{n F}} \quad (8)
  \]

- **Temkin isotherm model [19]:**
  \[
  q_{eq} = B_1 \ln K_F + B_1 \ln C_{eq} \quad (9)
  \]

where \( q_{max} \) (mg/g) is the maximum adsorption capacity; \( K_L \) (L/mg) is the Langmuir constant; \( K_F \) (L/mg)\(^{1/n} \) and \( n \) (mg/g) are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively; \( K_P \) (L/mg), \( a_{ad} \) (L/mg)\(^{1/n_F} \), and \( n_F \) are the Redlich-Peterson constants. The exponent \( n_F \) should lie between 0 and 1. \( K_C \) (mg/g), \( a_{ad} \) (L/mg)\(^{1/n_F} \), and \( n_F \) are the Koble-Corrigan constants. \( K_F \) (L/mg) and \( B_1 \) (mg/g) are the Temkin constants which are the equilibrium binding constant corresponding to the maximum binding energy and the constant related to the heat of adsorption. The isotherm constants along with the correlation coefficients \( R^2 \) were evaluated by nonlinear regression analysis using SOLVER in MS Excel and the results are presented in Table 2.

Fig. 6(a) and (b) show the amount of Pb(II) and Cu(II) adsorbed onto the unit mass of biocarrier beads at equilibrium at different initial concentrations and adsorption isotherms fitted to the experimental data. The sorption increased as the equilibrium concentration of Pb(II) and Cu(II) in the aqueous phase increased. The comparison of the correlation coefficients in Table 2 confirmed that the equilibrium biosorption data of Pb(II) and Cu(II) fit very well to the Koble-Corrigan, Redlich-Peterson and Langmuir isotherms compared to the Freundlich or Temkin isotherm. Despite the mathematically good fit and high correlation with experimental data, the Redlich-Peterson isotherm, which was originally suggested as a combined form of Langmuir and Freundlich isotherms, was not found suitable to describe the biosorption of Cu(II) because of its innate constraint of 0 < \( \beta < 1 \). The applicability of the Koble-Corrigan and Langmuir isotherm implied that the biosorption system was likely to be monolayer sorption onto a homogeneous surface and that the adsorption was a cooperative process due to adsorbate-adsorbent interactions [18]. In the Langmuir isotherm, a constant \( q_{max} \) is an esti-
mate of the maximum amount of heavy metals that the biocarrier surfaces can hold. The other constant \( K_i \) is related to binding energy of adsorption and its high value indicates the strong sorption bonding of the biocarriers for metal ions. According to the Langmuir isotherm constants in Table 2, at specified conditions, the maximum adsorption capacities of the immobilized biomass biocarrier beads for Pb(II) and Cu(II) were estimated as 0.3332 and 0.5598 mg/g, respectively. Compared to other biosorbents reported in the literature, the sorption capacities of bead-type biosorbents are significantly low (e.g., 0.29 mg/g for Pb(II) and 0.90 mg/g for Cu(II) by polyacrylonitrile bead [20]). It is because the capacities are calculated based on the mass of beads which are mainly composed of the polysulfone matrix. The polymer matrix functions to safely hold tiny pieces of inactive biomass to sorb heavy metal ions, not as a sorbent itself. Although only the mass of biomass in a biocarrier bead is not easily measurable, it is regarded to weigh less than a few percent in mass of a biocarrier bead. For an effective application, biosorbents should have a large sorption capacity with a strong bonding. In an isotherm curve, the high values of \( q_{max} \) and \( K_i \), respectively appears as a high plateau and a steep initial slope. It was supposed that the biocarrier beads proposed in this study would uptake more Pb(II) than Cu(II). However, the sorption binding between the beads and Pb(II) was weaker than that of Cu(II). A dimensionless separation factor \( R_s \) can also explain the essential characteristics of a Langmuir-type sorption process [21]:

\[
R_s = \frac{1}{1 + K_i C_0}
\]

where \( C_0 \) (mg/L) is the initial concentration; The value of \( R_s \) indicates the shape of the isotherms to be either unfavorable (\( R_s > 1 \)), linear (\( R_s = 1 \)), favorable (0 < \( R_s < 1 \)) or irreversible (\( R_s = 0 \)). For an initial concentration of 10 mg/L for Pb (II) and Cu (II), respectively in the batch experiments, the values of \( R_s \) were calculated as 0.04 for Pb(II) and 0.44 for Cu(II), which indicated that the biosorption of Pb(II) and Cu(II) onto the immobilized biomass biocarrier beads was favorable. Having a lower \( R_s \) value at higher initial concentrations implied that the biosorption was more favorable at higher concentrations. The degree of favorability generally ranges between 0 and 1 (complete irreversible sorption to complete reversible sorption). Due to the stronger binding of Pb(II) adsorbed on biocarrier beads Pb(II) had significantly lower desorption tendencies compared to Cu(II).

### 3.4 Kinetic Modeling

Results from batch experiments were fitted by five widely applied kinetic models including pseudo-first-order, pseudo-second-order, Ritchie second-order, intraparticle diffusion, and the Elovich kinetic model. The nonlinear forms of the tested kinetic models are as follows.

#### Table 2. Adsorption isotherm parameters for biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads

<table>
<thead>
<tr>
<th>Equilibrium models</th>
<th>Lead</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>Lead</td>
<td>Copper</td>
</tr>
<tr>
<td>q_{max} (mg/L)</td>
<td>0.3332</td>
<td>0.5598</td>
</tr>
<tr>
<td>K_i</td>
<td>2.2329</td>
<td>0.3622</td>
</tr>
<tr>
<td>Freundlich isotherm model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_F )</td>
<td>0.1535</td>
<td>0.1260</td>
</tr>
<tr>
<td>( n_F )</td>
<td>2.8716</td>
<td>1.6665</td>
</tr>
<tr>
<td>Redlich-Peterson isotherm model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{RP} )</td>
<td>0.5611</td>
<td>0.1526</td>
</tr>
<tr>
<td>( a_{RP} )</td>
<td>1.0788</td>
<td>0.00003</td>
</tr>
<tr>
<td>( \beta )</td>
<td>1.2181</td>
<td>5.4983</td>
</tr>
<tr>
<td>Koble-Corrigan isotherm model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{KC} )</td>
<td>0.3616</td>
<td>0.4141</td>
</tr>
<tr>
<td>( a_{KC} )</td>
<td>1.6892</td>
<td>0.6012</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.9368</td>
<td>1.9981</td>
</tr>
<tr>
<td>Temkin isotherm model</td>
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<td></td>
</tr>
<tr>
<td>( K_T )</td>
<td>28.2970</td>
<td>19.4860</td>
</tr>
<tr>
<td>( B_T )</td>
<td>0.0602</td>
<td>0.0734</td>
</tr>
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</table>

#### Table 3. Kinetic parameters for metal biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Lead</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Lead</td>
<td>Copper</td>
</tr>
<tr>
<td>k_{1,ad} (mg/min)</td>
<td>0.1154</td>
<td>0.1590</td>
</tr>
<tr>
<td>q_{a0} (mg/g)</td>
<td>0.1809</td>
<td>0.1430</td>
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<tr>
<td>Pseudo-first-order kinetic model</td>
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<tr>
<td>k_{2,ad} (mg/min)</td>
<td>0.8845</td>
<td>1.5515</td>
</tr>
<tr>
<td>q_{a0} (mg/g)</td>
<td>0.1994</td>
<td>0.1577</td>
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<tr>
<td>Pseudo-second-order kinetic model</td>
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<tr>
<td>k_{2,ad} (mg/min)</td>
<td>0.1763</td>
<td>0.2447</td>
</tr>
<tr>
<td>q_{a0} (mg/g)</td>
<td>0.1994</td>
<td>0.1577</td>
</tr>
<tr>
<td>Ritchie-second-order kinetic model</td>
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<tr>
<td>k_{2,ad} (mg/min)</td>
<td>0.0603</td>
<td>0.0048</td>
</tr>
<tr>
<td>C (mg/L)</td>
<td>0.1170</td>
<td>0.1013</td>
</tr>
<tr>
<td>Intraparticle diffusion kinetic model</td>
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</tr>
<tr>
<td>( k_0 )</td>
<td>0.3625</td>
<td>0.8685</td>
</tr>
<tr>
<td>( \beta )</td>
<td>38.0228</td>
<td>54.7981</td>
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<td>Elovich kinetic model</td>
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http://dx.doi.org/10.4491/eer.2013.18.1.045
model, 96.7% and 95.7% of total Pb(II) and Cu(II) biosorption were accomplished within the initial 30 and 60 min, respectively. As the saturation or equilibrium state was approached, the biosorption proceeded slowly and became ineffective. In this later stage, the remaining vacant sorption sites on the surface were competitively occupied by the sorbates and intraparticle biosorption gradually continued as the metal ions were diffusing into the interior of the biosorbents. The total contact time of 40 min for Pb(II) and 124 min for Cu(II) were estimated to be required to reach near equilibrium (99% of maximum biosorption).

Comparing the correlation coefficients for the applied kinetic models to experimental data, the pseudo-first-order kinetic produced the best fit for Pb(II), while the pseudo-second-order and the Ritchie second-order kinetics produced the best fit for Cu(II). The second-order kinetics and the Elovich kinetic also fit the experimental data for Pb(II) and Cu(II) relatively well, respectively. In these nonlinear regressions, the pseudo-second-order and the Ritchie second-order kinetics generated almost identical fits. The intraparticle diffusion kinetic could not represent biosorption of both Pb(II) and Cu(II) by the biocarrier beads. In general, first-order kinetic models are reported to be applicable to the initial stage of a sorption process, but not over the entire range of adsorption processes [26]. However in this study, the pseudo-first-order kinetic model generated the best representation for biosorption of Pb(II) with the process proceeding in a very short time. In less than 1 hr, equilibrium had been reached and no further changes occurred. Overall, the biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads could be represented by the pseudo-second-order and Ritchie second-order kinetics over the entire biosorption process.

Biosorption by granular porous sorbents is a multi-step process which consists of bulk diffusion in bulk liquid, external film diffusion between the bulk liquid and sorbent surface, intraparticle diffusion inside a particular sorbent, and interaction between sorbates and sorption sites over the interior pore structure [27]. In order to investigate the contribution of intraparticle diffusion in the multi-step sorption mechanism, the intraparticle kinetic model proposed by Weber and Morris [24] have been widely applied [23, 25, 28]. According to the Weber-Morris model, the plot of experimental data for \( q_t \) vs. \( t^{1/2} \) shows linearity if intraparticle diffusion has a significant role in the sorption process. Intraparticle diffusion is the sole rate controlling step if the regression line passes through the origin. Fig. 8 shows that the

\[
q_t = q_{ad} \left( 1 - \exp \left( -k_{ad} t \right) \right)
\]

where \( q_t \) (mg/g) is the amount of adsorbed metal ions on the biomass at time \( t \); \( k_{ad} \) (1/min) is the first-order rate coefficient for Lagergren model; \( K_{ad} \) (g mg\(^{-1}\) min\(^{-1}\)) and \( K_{ad} \) (1/min) are the second-order rate coefficients for Lagergren and Ritchie model, respectively; \( k_d \) (mg g\(^{-1}\) min\(^{-1}\)) is the intraparticle diffusion rate coefficient; \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) is the initial adsorption rate and \( \beta \) (g/(mg min\(^{1/2}\))) is the sorption constant. The same analytical procedure to the equilibrium isotherm was applied and kinetic parameters were estimated. The comparisons of kinetic experimental data to model simulations are shown in Fig. 7(a) and (b) and estimated model parameters are listed in Table 3.

Fig. 7(a) and (b) show the changes in the amount of adsorbed metal ion (\( q_t \)) for the experimental data and the model simulations over time. The sorption processes for Pb(II) and Cu(II) by immobilized biomass biocarrier beads proceed in two steps. In the initial step, the metal ions in the aqueous phase were rapidly adsorbed to vast unoccupied sorption sites on the surface of the biosorbents. Based on calculations using the best-fitted kinetic model, 96.7% and 95.7% of total Pb(II) and Cu(II) biosorption were accomplished within the initial 30 and 60 min, respectively. As the saturation or equilibrium state was approached, the biosorption proceeded slowly and became ineffective. In this later stage, the remaining vacant sorption sites on the surface were competitively occupied by the sorbates and intraparticle biosorption gradually continued as the metal ions were diffusing into the interior of the biosorbents. The total contact time of 40 min for Pb(II) and 124 min for Cu(II) were estimated to be required to reach near equilibrium (99% of maximum biosorption).

Comparing the correlation coefficients for the applied kinetic models to experimental data, the pseudo-first-order kinetic produced the best fit for Pb(II), while the pseudo-second-order and the Ritchie second-order kinetics produced the best fit for Cu(II). The second-order kinetics and the Elovich kinetic also fit the experimental data for Pb(II) and Cu(II) relatively well, respectively. In these nonlinear regressions, the pseudo-second-order and the Ritchie second-order kinetics generated almost identical fits. The intraparticle diffusion kinetic could not represent biosorption of both Pb(II) and Cu(II) by the biocarrier beads. In general, first-order kinetic models are reported to be applicable to the initial stage of a sorption process, but not over the entire range of adsorption processes [26]. However in this study, the pseudo-first-order kinetic model generated the best representation for biosorption of Pb(II) with the process proceeding in a very short time. In less than 1 hr, equilibrium had been reached and no further changes occurred. Overall, the biosorption of Pb(II) and Cu(II) by immobilized biomass biocarrier beads could be represented by the pseudo-second-order and Ritchie second-order kinetics over the entire biosorption process.

Biosorption by granular porous sorbents is a multi-step process which consists of bulk diffusion in bulk liquid, external film diffusion between the bulk liquid and sorbent surface, intraparticle diffusion inside a particular sorbent, and interaction between sorbates and sorption sites over the interior pore structure [27]. In order to investigate the contribution of intraparticle diffusion in the multi-step sorption mechanism, the intraparticle kinetic model proposed by Weber and Morris [24] have been widely applied [23, 25, 28]. According to the Weber-Morris model, the plot of experimental data for \( q_t \) vs. \( t^{1/2} \) shows linearity if intraparticle diffusion has a significant role in the sorption process. Intraparticle diffusion is the sole rate controlling step if the regression line passes through the origin. Fig. 8 shows that the
experimental data for Pb(II) and Cu(II) were not linearly aligned and their regression lines over the entire time range did not pass the origin. The nonlinearity, or multilinearity, indicated that the entire mechanisms of biosorption of Pb(II) and Cu(II) on biomass immobilized in biocarrier beads comprised of more than one sorption process. Having non-zero intercepts (0.14 mg/g for Pb(II) and 0.71 mg/g for Cu(II)) suggested that intraparticle diffusion and resulting intraparticle sorption were involved, but did not play a key role in the entire biosorption process. In addition, the relatively high values of non-zero intercepts implied that the biosorption largely depended on surface adsorption. The relatively small contribution of intraparticle sorption to entire sorption capacity may result from the interior pore structure of the biocarrier beads. Although the SEM image for the cross-section of the bead in Fig. 2(b) reveals its porous interior, the most highly porous inner layer appears to be approximately 0.3 mm thick beneath the outer shell and relatively large pore space and walls composes the inner-most space. In addition, the near-surface intraparticle sorption may not be easily distinguishable to exterior surface sorption. In order to increase the sorption capacity of the biocarrier beads, therefore, it is required to maximize internal surface area by creating a compact pore structure throughout the entire bead interior. The effects of the type of polymeric matrix, recipe for polymer solution, size of bead, etc., on the interior architecture of the biocarrier beads should be investigated for further improvement.

4. Conclusions

In this study, the dead biomass (Bacillus drentensis LMG 21831T) immobilized in polysulfone biocarrier beads were prepared and their biosorption mechanisms for Pb(II) and Cu(II) ions were investigated. The physical structure and sorption capability of the biocarrier beads were visualized and examined through SEM, TEM, and EDS analyses. The highly porous interior structure clearly implied that the biocarrier bead had the beneficial property of an effective biosorbent. Furthermore, dead biomass closely conjoined to the polysulfone matrix assuring the recyclability of the biosorbent. SEM-EDS analyses revealed that metal ions were successfully adsorbed as a form of plaque-type solid crystal over the surface and inside pore walls. The thermodynamic, equilibrium, and kinetic analyses were conducted as further tools quantitatively measured the intrinsic nature of the biosorption processes. Nonlinear regression analyses demonstrated that the equilibrium data fit the Kobler-Corragan and Langmuir isotherms well. This good fit suggested monolayer sorption of Pb(II) and Cu(II) onto a homogeneous surface of the immobilized biomass biocarrier beads. Pseudo-second-order and Ritchie second-order kinetic models were the best-fitting models for kinetic sorption data of the biosorption process. The intraparticle diffusion model was applied and confirmed that various rate controlling steps consisted of the entire biosorption process and that surface diffusion played the most significant role. The thermodynamic calculations suggested that the process was spontaneous and exothermic under the examined conditions. The observations and analyses of this study indicated that the immobilized dead biomass biocarrier beads have the potential as a promising biosorbent for the removal of hazardous metals from wastewaters.

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