Nickel Ion Adsorption Behavior of *Ceriporia lacerata* Isolated from Mine Tailings in Korea

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**ABSTRACT**

In the present study, surface of laccase producing *Ceriporia lacerata* was modified using 4-bromobutyryl chloride and polyethylenimine. The modified biomass was freeze dried and utilized as a biosorbent for the removal of Ni(II) from aqueous solution. The physicochemical properties of the biosorbent were analyzed using scanning electron microscopy and Fourier transform infrared spectroscopy. Batch experiments were carried out as a function of contact time (0-60 min), pH (2 to 8), adsorbent dosage (25-150 mg), and initial Ni(II) concentration (25-125 mg/L). The results indicate that surface modified biosorbent effectively adsorbed (9.5 mg/0.1 g biomass) Ni(II) present in the solution. The equilibrium adsorption data were modeled with different kinetic and isotherm models. The Ni(II) adsorption followed pseudo-first-order kinetics ($R^2 = 0.998$) and Langmuir isotherm ($R^2 = 0.994$) model. Hydroxyl and carbonyl functional groups present in biomass play a major role in the adsorption of Ni(II). The adsorbed Ni(II) from the biosorbent was successfully desorbed (85%) by 1 M HCl. The results of the study indicate that the surface modified *C. lacerata* biomass could be used for the treatment of Ni(II) contaminated ground waters.

**Key words :** Adsorption isotherm, *Ceriporia lacerata*, Heavy metal, Kinetics, Nickel

1. Introduction

Heavy metal pollution has been known to cause severe hazards to public health and ecosystems (Ngah et al., 2011). Ni(II) is one of the major threats to the environment due to its high utilization in developing countries and its recalcitrant nature. The major sources for Ni(II) are mining and metallurgy activities, various industrial activities and electronic equipments (Congeevaram et al., 2007). Strict regulations and restrictions have been established for Ni(II) effluent discharge into the ecosystems due to its serious threat to human health such as allergies, cardiovascular issues, gastrointestinal irritation, kidney disease, and lung fibrosis (Kasprzak et al., 2003). The acceptable discharge level of Ni(II) from industrial effluent into water bodies is 3 mg/L and the permissible level in drinking water for human consumption is less than 40 µg/L (Rodríguez and Quesada, 2006; Congeevaram et al., 2007). Consequently, it is essential to manage the levels of Ni(II) in industrial effluent before it enters into water bodies. Environmental engineers have been trying to develop innovative technologies in order to solve this problem. A variety of technologies including chemical reduction, precipitation, evaporation, coagulation, electrochemical, ion exchange, and membrane processes have been studied for the removal of heavy metals from wastewater (Fu and Wang, 2011). Nevertheless, additional research and broader validation are still needed in order to solve this problem for field application with cost effective techniques that are also eco-friendly. The adsorption process has been proven as one of the best treatment technologies for heavy metal contamination (Gupta and Bhattacharyya, 2011; Sukumar et al., 2014). In particular, biosorption is an attractive treatment method due to its operational flexibility and also the fact that the treated efflu-
ent is reusable. In addition, the regeneration of the adsorbent may be possible with economical operation, because adsorption is generally reversible.

Fungi have been used extensively in several industrial processes in order to produce enzymes, flavorings, and antibiotics. During the industrial fermentation process large amount of residual biomass is generated, which is not suitable for use as agricultural fertilizer due to low nutrient value and high levels of cellulose, chitin, and glucans that make digestion or degradation difficult (Shroff and Vaidya, 2011). These characteristics make the fungi biomass waste difficult to dispose off in the environment and, hence, could be obtained free of charge. The use of fungi biomass as an adsorbent for removing toxic metal ions can generate extra revenue for industries and, at same time, it can ease the disposal problem. However, fungi have limited metal adsorption potential because of weak adsorbing functional groups, hydrophobic and hydrophilic characters of the cell wall. Thus, several approaches have been made to modify the surface characteristic of the fungal biomass in relation to their metal adsorption mechanism (Deng and Ting, 2005; Arica and Bayramoglu, 2007; Song et al., 2015). This may be in terms of activating the available sites for enhanced metal adsorption or ion exchange.

Polyethyleneimine (PEI), a cationic polymer, has wide application in different scientific fields including water treatment. Several adsorbents have been modified with PEI and reported to have good adsorption potential for metals and dyes. However, only limited studies have been reported on surface modification of fungal biomass using PEI (Deng and Ting, 2005). Thus, the objective of the present study were to (i) modify the fungi, Ceriporia lacerata, biomass using PEI, (ii) evaluate the potential of surface modified fungi for Ni(II) adsorption, (iii) assess the experimental variables affecting the adsorption process, and (iv) explore adsorption isotherms and kinetic models to identify the possible mechanism of Ni(II) removal.

2. Materials and Methods

2.1. Adsorbate and Adsorbent

A stock solution of Ni(II) was prepared by dissolving 4.4786 g of Nickel(II) sulfate hexahydrate (AR grade) in 100 mL of deionized water to obtain a concentration of 10,000 mg/L. The stock solution was then appropriately diluted to create the desired Ni(II) concentration for the test solution.

The fungi were isolated from the mine soil. Briefly, 1 mg of the soil sample was serially diluted using autoclaved water and 0.1 mL of dilution was plated using the spread plate technique onto Potato Dextrose Agar. Plates were incubated at 25°C for 7 days and observed for the fungal growth. Morphologically distinct colonies were purified and used for the laccase production (Palvanan and Sathishkumar, 2010). The C. lacerata biomass was collected from the laccase production media after laccase production and used as an adsorbent for Ni(II) removal.

The biomass was washed and dried in an oven at 50°C. The dried biomass was modified as follows: 10 g of dried biomass was mixed with pyridine (2.5 mL) and chloroform (95 mL) in a 500 mL glass bottle and 4-bromobutyryl chloride was added to the mixture by dropwise addition. The reaction mixture was gently stirred at 25°C for 12 hours. The acylated biomass was rinsed with chloroform in order to remove any unreacted 4-bromobutyryl chloride, and it was then treated with a mixture of PEI (10 g; 10 kDa) and KOH (0.1 g) in 90 mL of tert-amyl alcohol at 75°C for 24 hours. Then, the modified biomass was rinsed with methanol (50%), freeze-dried at −80°C and used for the adsorption studies.

2.2. Physicochemical Characterization

The surface morphology of modified C. lacerata biomass was observed using a scanning electron microscope (SEM, GSM-5900, Jeol, Japan). Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer, USA) was used in order to determine the surface functional groups on the biosorbent by vibrational frequency changes in the functional groups, which were obtained by averaging the results of 32 scans in the range of 400-4000 cm⁻¹ at a 4 cm⁻¹ resolution.

2.3. Batch Adsorption Experiments

Batch experiments of Ni(II) adsorption studies were studied with respect to well-established, effective parameters including contact time, pH, adsorbent dosage, and initial concentration of Ni(II) at a constant speed of 160 rpm at
room temperature. The adsorption equilibrium experiment was carried out by agitating 50 mL of Ni(II) solution at various concentrations (25-125 mg/L). The effect of pH on Ni(II) adsorption was studied over a range of 2 to 8. The pH of the Ni(II) solution was adjusted by adding diluted HCl or NaOH (0.1 M). Fifty mL of Ni(II) solution was mixed with 25-150 mg of biosorbent until equilibrium was reached in order to study the effect of the biosorbent dosage. The effect of the initial Ni(II) concentrations (25-125 mg/L) and the contact time up to equilibrium was studied under optimized conditions described above. The samples were collected at a predetermined time and filtered with Whatman grade 1 filter paper in order to minimize the interference of fine biomass particles. The Ni(II) concentration in the resulting filtrates was analyzed using inductively coupled plasma (ICP, Leemans Labs Inc., USA). The percentage of Ni(II) adsorption was calculated using the following equation (1) (Arulkumar et al., 2012):

\[
\text{Adsorption (\%) = } \frac{C_0 - C_{eq}}{C_0} \times 100
\]

where \( C_0 \) is the initial concentration (mg/L) and \( C_{eq} \) the equilibrium concentration (mg/L). Blanks were also performed simultaneously without biosorbent. All of the experiments were performed in duplicates, and the mean values are presented here.

2.4. Adsorption Isotherm

The adsorption isotherms Langmuir and Freundlich models were used in order to explain the equilibrium relationship between the Ni(II) adsorbed onto the surface modified \( C. lacerata \) biomass and Ni(II) that was left in the aqueous solution. The Langmuir isotherms is based on sorption on a homogeneous surface by monolayer sorption without interaction between sorbed species (Langmuir, 1918). The theoretical basis of the Langmuir isotherm equation relies on the hypothesis that there are a finite number of binding sites, which are homogeneously distributed over the biosorbent surface and which have the same affinity for adsorption of a single molecular layer. In addition, it is assumed that there is no interaction between the adsorbent and the adsorbate (Şahin and Öztürk, 2005; Aryal et al., 2010). The theory can be represented using the following linear form (Arulkumar et al., 2012):

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}
\]

where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) is the amount adsorbed at equilibrium (mg/g), and \( Q_0 \) (mg/g) and \( b \) (L/mg) are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively. The essential characteristics of Langmuir isotherms can be explained in terms of an equilibrium parameter, \( R_L \), which is defined as (Arulkumar et al., 2012):

\[
R_L = \frac{1}{1 + bC_0}
\]

where \( C_0 \) is the initial Ni(II) concentration (mg/L). The value of \( R_L \) indicates whether the shape of the isotherm is unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\), or irreversible \((R_L = 0)\).

The Freundlich isotherm (Freundlich, 1906) provides a more realistic description of heavy metal adsorption by an organic biosorbent, because it accounts for different binding sites. This adsorption isotherm model is an empirical model that takes into consideration the heterogeneous adsorptive energies on the adsorbent surface, and it is expressed as follows (Arulkumar et al., 2012):

\[
q_e = K_F C_e^n
\]

where \( q_e \) is the amount of solute adsorbed, \( C_e \) is related to the equilibrium concentration of the solute in solution, and \( K_F \) and \( n \) are parameters affecting the adsorption process including adsorption capacity and intensity, respectively. This expression can be linearized to give the following equation (Arulkumar et al., 2012):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \( K_F \) is a constant for the system that is related to the bonding energy. \( K_F \) can be defined as the adsorption or distribution coefficient and is related to the quantity of Ni(II) adsorbed onto the biosorbent for a unit equilibrium concentration (a measure of adsorption capacity, mg/g).
2.5. Kinetic Study and Intraparticle Diffusion Model

The kinetic modeling of the Ni(II) biosorption process was studied using the time dependent removal of Ni(II) under optimized conditions at a constant pH of 8.0 with an initial Ni(II) concentration of 100 mg/L and an adsorbent concentration of 100 mg/L at 40°C and 160 rpm. First and second-order kinetic equation models and intra-particle diffusion were used for kinetic modeling. The individual kinetic expressions for first-order reaction kinetics and second-order reaction kinetics were calculated as follows (Arulkumar et al., 2012):

\[ \frac{dC}{dt} = -k_1 C \]  \hspace{1cm} (6)
\[ \frac{dC}{dt} = -k_2 C^2 \]  \hspace{1cm} (7)

where \( C \) is the concentration of Ni(II); \( k_1 \) and \( k_2 \) represent the apparent kinetic rate constants of first- and second-order reaction kinetics, respectively; and \( t \) is the reaction time. By integrating Equations 6 and 7, the following equations can be obtained (Eqs. 8 and 9) (Arulkumar et al., 2012):

\[ C_t = C_0 e^{-k_1 t} \]  \hspace{1cm} (8)
\[ \frac{1}{C_t} = \frac{1}{C_0} + k_2 t \]  \hspace{1cm} (9)

where \( C_t \) is the concentration of Ni(II) at reaction time \( t \).

The most commonly used technique for identifying the mechanism involved in the sorption process is fitting the experimental data into an intraparticle diffusion plot. The mathematical expression for the intraparticle diffusion model is defined as follows (10) (Arulkumar et al., 2012):

\[ p_t = k_p t^{1/2} \]  \hspace{1cm} (10)

where \( p_t \) represents the intraparticle diffusion rate constant, \( k_p \) (mg/gm min\(^{1/2}\)) the fraction of adsorbate removed (mg/g), and \( t \) the contact time (min).

2.6. Desorption Studies

Desorption is a phenomenon where a substance is released from or through a surface. This study was performed in order to assess the regeneration capacity of the adsorbent for reuse in a more economic manner. The Ni(II) loaded biosorbent was separated from the adsorbent-water slurry by centrifugation and was brought into contact with various concentrations of acidic (0.1 M HCl) or basic (0.1 M NaOH) desorbents for 3 hours at 160 rpm in an orbital shaker. The remaining procedure was the same as that employed in the adsorption equilibrium experiments.

3. Results and Discussion

3.1. Physicochemical Parameters of Prepared Biomass

The study represents an attempt to assess the influence of surface modified \( C. lacerata \) biomass for the removal of Ni(II) from aqueous solution. The SEM image of the surface modified \( C. lacerata \) biomass is shown in Fig. 1. The image shows the rough and uneven surface with cross-linking between the mycelia, providing a good possibility for adsorption of Ni(II). Fig. 2 shows the FT-IR spectra of sur-
surface modified and Ni(II) loaded *C. lacerata* biomass. The peaks corresponding to the hydroxyl (–OH), alkyl C–H, carbonyl (C=O), nitrile (C≡N), and halogen (C–X) groups were observed in both the samples. The most significant difference between the two spectra was at an intensity of 3000-3600 cm\(^{-1}\), which represents the hydroxyl (O–H) group stretching band, and at an intensity of 1600-1700 cm\(^{-1}\), which represents the carbonyl (C=O) stretching band. It has been reported that the hydroxyl and carbonyl functional groups play a role in Ni(II) binding (Pandey et al., 2008; Amini et al., 2009). Significant changes were observed in the intensity of the hydroxyl and carbonyl bands of the Ni(II) loaded, surface modified *C. lacerata* biomass. These changes were due to the complexation of the carboxylate anions’ functional group through coordination with the Ni(II) (Lin et al., 2005).

### 3.2. Batch Experiments

The pH of the aqueous solution has been reported to have a significant effect on the adsorption of heavy metals due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the adsorbate molecule (Oliveira et al., 2008). It has been well established that most industrial wastewaters are acidic in nature. Thus, the experiments were conducted in between the pH 2 to 8 and the results are presented in Fig. 3. The maximum adsorption of Ni(II) on surface modified *C. lacerata* biomass was found to be at pH 8.0. Our results indicated that the pH level plays a critical role in the biosorption processes of Ni(II) on surface modified *C. lacerata* biomass. This could be due to the competition effect between the metal ions and the hydronium ions present in the active sites of the biomass surface (Ahalya et al., 2005). The functional groups were protonated due to the fact that they are closely associated with hydronium (H\(_3\)O\(^{+}\)) ions in acidic conditions, and therefore, the overall surface charge on the biomass became positive. As a result, the very low level of Ni(II) uptake at a pH 3.0. Moreover, competition between the Ni(II) and H\(_3\)O\(^{+}\) ions limits the interaction of the Ni(II) ions with the surface of the biomass due to repulsive forces from the surface functional groups (Xu et al., 2006; Zafar et al., 2007). The competing effect of the H\(_3\)O\(^{+}\) ions decreased when the pH was increased from acidic to alkaline conditions. This result would explain the rapid rise in the binding efficiency of Ni(II) on the surface modified *C. lacerata* biomass at pH 8.0. The pH range that is widely accepted as being optimal for metal uptake for almost all types of biomasses is between 4.0 and 8.0 (Blackwell et al., 1995). Therefore, further experiments in this study were carried out at pH 8.0.

The adsorbent dosage is a key factor in the sorption process, because it determines the adsorbent capacity for a specified initial concentration of the adsorbate. Our experiments were performed with an adsorbent dosage ranging from 25 mg to 150 mg at a fixed Ni(II) concentration of 100 mg/L and a pH level of 8.0. The effect of the surface modified *C. lacerata* biomass on the adsorption of Ni(II) is illustrated in Fig. 4. The maximum sorption of Ni(II) (99 mg/L) was observed at an adsorbent dosage of 100 mg. The results indicate that the adsorption of Ni(II) increased with an increase in the concentration of the adsorbent dosage up to a certain limit and then remained constant. An increase in the adsorption associated with the adsorbent dosage can be attributed to increased surface area and additional adsorption sites. However, the amount adsorbed per unit mass of the adsorbent decreased considerably. The decrease in the unit adsorption with an increase in the dose of the adsorbent may be due to the adsorption sites remaining unsaturated during the adsorption process (Thinakaran et al., 2008). Thus, further experiments were carried out with an adsorbent dose of 100 mg in 50 mL (w/v).
The metal ion concentration plays a significant role in the determination of the biosorption system feasibility and efficiency. Fig. 5 shows the effect of the initial Ni(II) concentration and the contact time on the maximum adsorption on the surface modified *C. lacerata* biomass. The adsorption percentage was found to decrease with an increase in the Ni(II) concentration. This result may be due to the saturation of the surface area and active sites on the adsorbent. Similar results were reported by Shroff and Vaidya for Ni(II) adsorption on the dead fungal biomass of *Mucor heimalis* (Shroff and Vaidya, 2011). Our results showed greater than 95% Ni(II) (100 mg/L) adsorption on 100 mg of surface modified *C. lacerata* biomass within 60 minutes. This result is very interesting, since high concentrations of adsorbate attained maximum adsorption even at a low adsorbent dosage. Therefore, the surface modified *C. lacerata* biomass is a better biosorbent for the removal of Ni(II) from aqueous solution. The percentage of Ni(II) uptake was rapid in the beginning. However, it gradually decreased with time until it reached equilibrium. It was reported that the rate of adsorption was higher in the beginning due to the larger surface area of the adsorbent (Janaki et al., 2014). After adsorption, the rate of metal ions uptake might be controlled by the rate of metal ions transported from the exterior to the interior sites of the biosorbent.

### 3.3. Kinetic Study and Intraparticle Diffusion

The kinetics of metal ion sorption is a key parameter for the design of sorption systems. The kinetic data generated under optimized conditions were modeled using pseudo-first-order and pseudo-second-order models for the biosorption of Ni(II) on surface modified *C. lacerata* biomass. In the case of the pseudo-first-order model, the correlation coefficient ($R^2$) was found to be 0.998, indicating that the model sufficiently fit the kinetic data for the adsorption system in the present study (Fig. 6a). In contrast, the pseudo-second-order ($R^2 = 0.819$) kinetics shown in Fig. 6b were unable to describe the sorption kinetics satisfactorily. Therefore, these results indicate that the adsorption kinetics of Ni(II) on surface modified *C. lacerata* biomass adequately followed the pseudo-first-order kinetics. It is possible that the transport of the adsorbate into the pores of the adsorbent is the rate controlling step in a batch reactor with rapid stirring (Weber and Morris, 1963; Poots et al., 1978). This possibility was examined in terms of a graphical relationship between the amount of Ni(II) adsorbed and the square root of time at different initial Ni(II) concentrations. The results of intraparticle diffusion are presented in Fig. 7. The plots obtained were of a general type, i.e. initial curved portion with a final linear portion. The initial curved portions could be attributed to the boundary layer diffusion effect, while the final linear portions might be due to the intraparticle diffusion effect (Chang et al., 2003). The straight line did not pass through the origin, which indicated that the...
intraparticle diffusion was not the only rate-controlling step (Özcan et al., 2004). In addition, this result clearly shows that the adsorption process of Ni(II) onto surface modified *C. lacerata* biomass follows both boundary layer diffusion and intraparticle diffusion.

### 3.4. Adsorption Isotherms

The Langmuir and Freundlich adsorption equilibrium isotherm models were used in this study in order to describe the experimental adsorption data. It is important to find the best-fit isotherm in order to evaluate the efficacy of the prepared adsorbent for the development of suitable industrial adsorption system designs. In the Langmuir isotherm model, the experimental data produced a straight line fit with a relatively good correlation coefficient ($R^2 = 0.994$), which indicated that the surface modified *C. lacerata* biomass adsorption system is acceptable (Fig. 8). The value of $R_L$ (0.007) was observed to be in the range of 0 to 1, which confirms that the adsorption process was favorable (Arivoli et al., 2008). These findings indicate that the surface binding was primarily caused by physical forces and implicit in its deviation was the assumption that all of the sites possessed identical affinity for the sorbate (Davis et al., 2003). Therefore, the Langmuir isotherm model results for the surface modified *C. lacerata* biomass adsorption system indicated that the surface of the sorbent could be homogenous. The Langmuir isotherm model showed that the maximum adsorption ($Q_0$) of Ni(II) on the surface modified *C. lacerata* biomass was 95 mg/g. The results are consistent with previous studies reported high Ni(II) adsorption potential of fungi biomass (Deng and Ting, 2005; Vijayaraghavan et al., 2008). The biosorption capacity of surface modified *C. lacerate* was superior compared with dead *M. heimalis* cells, which is reported in the Table 1.

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**Fig. 6.** The pseudo-first (a) and second order (b) kinetics patterns of the Ni(II) adsorption on the surface modified *C. lacerata* biomass.

**Fig. 7.** The intraparticle diffusion rate of the Ni(II) adsorption on the surface modified *C. lacerata* biomass.

**Fig. 8.** The Langmuir isotherm of the Ni(II) adsorption on the surface modified *C. lacerata* biomass.
The Freundlich isotherm model employed to determine the adsorption of Ni(II) on the surface modified Ceriporia lacerata biomass is illustrated in Fig. 9. The Freundlich isotherm exhibits slightly inferior correlation coefficient ($R^2 = 0.981$) for Ni(II) adsorption as compared to Langmuir isotherm. The Freundlich constant values of $K_f$ and $n$ were found to be 27.925 and 1.338, respectively. When the value of $n$, which is related to the distribution of the bonded metal ions on the biosorbent surface, is between 1 and 10, it represents beneficial adsorption (Ahalya et al., 2005) and the $K_f$ represents the adsorbent capacity of the biosorbent for the given adsorbate. The ‘$n$’ value and high ‘$K_f$’ clearly indicate high affinity and binding capacity between the adsorbent and adsorbate.

### 3.5. Desorption Studies

The reusability efficiency of biosorbent for Ni(II) remediation gives significant value to the proposed biosorption system for field application. Desorption is an important process, because it provides recovery of the biosorbent in a concentrated form, which makes disposal easy and, therefore, it restores the biosorbent for effective reuse. The Ni(II)-loaded surface modified Ceriporia lacerata biomass was subjected to desorption under acidic (0.1 M HCl) and basic (0.1 M NaOH) conditions. The 0.1 M HCl was highly effective during desorption; it released 84.8% of the metal ions from the biosorbent. On the other hand, only limited desorption 12.4% was observed in the case of the 0.1 M NaOH. The reason for this behavior can be explained as follows: under strong acidic conditions, the number of positively charged sites on the adsorbent may increase and cause the elution of Ni(II) ions due to electrostatic repulsion (Suhasini et al., 1999).

### 4. Conclusions

In this study, surface modified Ceriporia lacerata biomass was used for the removal of Ni(II) from aqueous solutions. The results of the study identified surface modified Ceriporia lacerata biomass as a highly efficient and effective reusable biosorbent for the removal of Ni(II) from water. Therefore, this process may be the solution for the cleansing of the fungal biomass generated in the bio-based industries and its reutilization, as well as for protecting the environment from Ni(II) pollution. Further studies address the potential of selected fungi on mobilization of Ni in contaminated soil.

### References


Arca M.Y. and Bayramoğlu G., 2007, Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fun-


