CHAPTER THREE

KINETICS AND EQUILIBRIA OF COPPER BIOSORPTION
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3.1 General Background

Nonliving biomass immobilised on polymeric matrices has been identified as an effective biosorbent for the removal and recovery of metals from aqueous solutions. The main advantage of immobilised biomass is the possibility of using the biomass beads in column operations such as fixed or fluidised beds. In addition, immobilised biomass facilitates separation of the biomass from the aqueous solution in batch operation.

Evaluation of metal biosorption by immobilised biomass as a unit operation often focuses on two important physico-chemical aspects of the process, i.e. biosorption kinetics and equilibria.
In this chapter, the kinetic and equilibrium properties of a biosorption system comprising the biomass of a marine alga, *Sargassum baccularia*, immobilised on polyvinyl alcohol matrix, and copper as the model metal were investigated in detail.

Immobilisation parameters such as the concentration of the polymer, pH of the hardening agent and contact time between the immobilised beads and the hardening solution were studied to optimise the immobilisation conditions.

The kinetics of the metal sequestering process is a crucial process parameter which determines the time required for the biosorption system to attain equilibrium, commonly referred to as the contact time. The contact time is a critical factor especially in large-scale operations as it determines the size of the reactor which in turn affects the capital and operating costs of the process. A rapid metal binding process, i.e. short biosorbent-solution contact time is desirable. Kinetic studies using the immobilised algal biomass as well as native biomass were conducted in this work to investigate the effect of immobilisation on the kinetics of copper biosorption.

The pH of the metal solution has an important influence on the formation of metal-biosorbent complexes and exerts its effects in two ways (Kuyucak and Volesky, 1989a; Treen-Sears *et al.*, 1984; Zhou and Kiff, 1991). Firstly, pH variation influences the ionisation of functional groups on the cell walls which
are responsible for metal binding and secondly, pH regulates the solution chemistry affecting the chemical speciation of metal ions. This in turn determines the mobility and ability of the ions to adsorb onto the binding sites on biomass surface. The effect of solution pH on the equilibria of copper biosorption by the native as well as immobilised biomass was investigated in this work. The results were analysed in terms of equilibrium isotherms discussed in the next section.

3.2 Equilibrium Isotherms

Adsorption equilibrium is established when a certain amount of metallic species sequestered and bound by a solid phase, is in dynamic balance with the remaining dissolved metal in the solution. When a metal ion in solution collides with a solid surface, a limited number of outcomes are possible (Allen and Brown, 1995). They are as follows:

i) The metal ion may rebound from the surface.

ii) The metal ion may be adsorbed and the solid phase may preferentially concentrate specific metal ion species from solution onto its surface.

The adsorption process can be divided into two categories which are

- Physical adsorption, or physisorption, which is associated with the comparatively weak forces of physical attraction such as the Van de Waal's forces; and
Chemical adsorption, or chemisorption, which is associated with the exchange of electrons and the formation of a chemical bond between the adsorbed metal ion and the solid surface.

iii) Reaction may take place between the incoming cation and functional groups on the solid surface. This phenomenon is termed ion-exchange.

Positive adsorption in a metal ion-biosorbent system results in the transfer of the metal to the surface of the biosorbent where it increases in concentration until a dynamic equilibrium is reached between the biosorbent and the metal ions remaining in the liquid phase. At this equilibrium position there is a definite distribution of metal ions between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the biosorption process and is usually represented in the form of an equilibrium isotherm. This isotherm is a functional expression for the variation of adsorption with concentration of metal ion in the bulk solution at constant temperature. In other words, the isotherm plot is a graphical expression that represents metal adsorption by the biosorbent against the residual metal concentration in the contact solution.

Many researchers have used equilibrium isotherms to characterise the removal of heavy metals by biosorbents in the form of either immobilised or free biomass (Aksu and Kutsal, 1991; Ozer et al., 1994; Yang and Volesky, 1996). The isotherms can be used to evaluate the maximum adsorption capacities of
the biosorbents and to describe the equilibrium conditions for adsorption in different systems.

The two most commonly used equilibrium isotherms are the Langmuir isotherm model and the Freundlich isotherm model (Chang and Hong, 1994; Smith, 1981). The Langmuir isotherm has often been successfully used to evaluate metal biosorption on algal biomass (Holan and Volesky, 1994; Ozer et al., 1994). The Langmuir isotherm equation is as follows:

\[
q_{eq} = \frac{q_{\text{max}} k C_{eq}}{1 + k C_{eq}}
\]  

(3.1)

where

\[ q_{eq} = \text{solid phase equilibrium metal concentration (mmol/g biomass)}, \]
\[ C_{eq} = \text{liquid phase equilibrium metal concentration (mM)}, \]
\[ q_{\text{max}} = \text{maximum metal adsorption capacity (mmol/g biomass)}, \]
\[ k = \text{Langmuir equilibrium constant (mM}^{-1}). \]

The Langmuir model can be used to estimate the maximum metal adsorption capacity \(q_{\text{max}}\) of a biosorbent. The constant \(k\) is related to the energy of adsorption (Langmuir, 1918). The solid phase equilibrium metal concentration
which is the amount of metal adsorbed on the biomass surface in a batch system is calculated using the following mass balance equation:

\[
q_{eq} = \frac{V (C_i - C_f)}{M}
\]  

(3.2)

where

- \( V \) = volume of the metal-bearing solution (L),
- \( M \) = amount of the biomass (g),
- \( C_i \) = known initial metal concentration (mM), and
- \( C_f \) = final or equilibrium metal concentration (mM).

Since the equilibrium relationship between metal adsorption and residual metal is typically hyperbolic (Volesky, 1987), the Langmuir model is thus a very useful tool for the analysis of biosorption equilibria. The maximum adsorption capacity is an important feature of the biosorbent as it evaluates the performance of the biosorbent material at high residual concentrations. The shape of the equilibrium isotherm is also of interest. An isotherm which is steep from the origin is highly desirable as it indicates high affinity of the biosorbent for the adsorbed metal ions. Such biosorbent would be efficient at very low concentrations of the metal species in the solution.

In this study, the Langmuir equilibrium isotherm was employed as a method of characterising the biosorption of copper by the immobilised biomass of \( S. \)
**baccularia** at various pH values. Equilibrium studies were conducted in a series of batch experiments and the results were quantified using the Langmuir model. The Langmuir isotherm parameters which best fit the experimental equilibrium data reported in this chapter were determined by a non-linear regression analysis using a commercial software package (Coplot).

### 3.3 Materials and Methods

#### 3.3.1 Materials

Fresh samples of the biomass of a marine alga, **Sargassum baccularia**, were collected from Port Dickson, a beach located on the West Coast of Peninsular Malaysia. The location of the collection site on a Malaysia map is shown in Appendix I.

The freshly collected biomass was washed thoroughly with distilled deionised water to remove adhering sand and air dried overnight. The biomass was then further dried in an oven at 60 °C to constant weight. The dried biomass was ground in a blender and sieved to a size range of 250-500 μm using a Standard Testing Sieve (W. S. Tyler Inc., USA). The biomass was then stored in capped glass container at room temperature.

All glassware and plasticware were washed thoroughly with detergent and rinsed with distilled deionised water. To eliminate possible metal
contamination, all working containers and test flasks were soaked overnight in 10% nitric acid followed by rinsing with distilled deionised water.

Solution pH was measured by using a calibrated pH meter (Metrohm, Switzerland). pH adjustments were made by the addition of 1 M nitric acid or 1 M sodium hydroxide solutions. Analytical grade reagents were used in all experiments (Fluka, Switzerland). Polyvinyl alcohol (PVA) with a molecular weight of 72000 was used as the polymeric matrix in the immobilisation process. Stock solution of copper (1000 mg/L) was prepared by dissolving 3.80 g of Cu(NO$_3$)$_3$·3H$_2$O in 1.0 L of distilled deionised water according to the following equation:

\[
\text{Volume (L) x concentration (g/L) x molecular weight x } 10^4 \div \text{Atomic weight (g/mol) x purity (%) x normality (N)} = \text{Salt (g)} \quad (3.3)
\]

All working copper solutions were prepared by diluting the stock solution in distilled deionised water.

Copper concentration in aqueous solutions was determined by Inductively Couple Plasma Atomic Emission Spectrophotometry (ICP-AES) using a Baird ICP 2000 (Baird, Switzerland) instrument. ICP metal standard solutions were obtained from Fluka (Switzerland).
The surface area of the immobilised gel beads was determined by nitrogen adsorption using a BET porosimeter apparatus (Model ASAP 2010, Micromeritics Instrument Corp., USA).

3.3.2 Methods

The immobilisation procedures of Chen and Lin (1994) were adopted in this work. Approximately 150 g of S. baccularia biomass in the size range of 250-500 μm was thoroughly mixed with PVA aqueous solution (~15 %). The resulting mixture was extruded through a syringe into a gently stirred saturated boric acid to form spherical beads. The formed gel beads were then transferred to a sodium phosphate solution for hardening. Finally, the beads were washed with water to remove any boric acid or sodium phosphate residue. The average diameter of the beads produced was estimated to be 3.5 mm.

The kinetics of copper biosorption by the immobilised biomass was performed using the batch technique. The biosorption kinetics was studied by suspending 80 beads (ca. 0.11 g biomass) in 100 mL of a copper solution with an initial concentration of 0.8 mM (50 mg/L) of copper. The test flask was shaken at 200 rpm and 25 °C. Solution samples were drawn from the flask at fixed time intervals. The samples were filtered and analysed for their copper content. The kinetic experiment was conducted in duplicates. Average values of copper concentration in the samples were reported here.
The same experimental procedures were used to measure the kinetics of copper biosorption by the native biomass of *S. baccularia* (250-500 μm) as well as PVA gel beads without the algal biomass. All experimental conditions were maintained as previously.

Batch experiments were also carried out to determine the equilibrium isotherms of copper biosorption at initial pH values of 3.0 and 6.0. Similar experiments were conducted using the native *S. baccularia* biomass for comparison purposes. The Langmuir isotherm parameters, necessary in the mathematical modelling of biosorption systems, were obtained from representation of the equilibrium data as isotherm plots.

Copper solutions in the range of 0.3-4.7 mM (20-300 mg/L) were prepared from the stock solution. The initial pH values of the solutions prepared were in the range of 4.0 to 5.0. These pH values were adjusted to 3.0 or 6.0 using 1 M nitric acid or sodium hydroxide. Batch equilibrium experiments were performed by suspending 80 beads (about 0.11 g of biomass) in 100 mL of copper solutions with varying concentrations in 250 mL Erlenmeyer flasks. The flasks were agitated in a rotary shaker (ISF-1-V, Kuhner, Switzerland) at 200 rpm and 25 °C for a period of 24 hours.

At the end of the experiments, the beads were separated from the solutions. The solutions were then filtered using cellulose acetate membrane filters of 0.45 μm.
(Sartorius, Germany). The filtrate was diluted appropriately with distilled deionised water and analysed for its copper content.

3.4 Results and Discussion

3.4.1 Immobilisation of S. baccularia

It has been reported that the use of polyvinyl alcohol (PVA) as immobilisation matrix offers several advantages over other commonly used polymeric substances such as acrylamide, κ-carrageenan, alginate and agar (Hashimoto and Furukawa, 1987). For example, PVA is a cheap chemical and it possesses strong gel strength suitable for immobilisation of biomass.

A number of procedures for immobilising microbial cells using PVA as the polymeric matrix have been reported in the literature (Bauer et al., 1996; Chen and Lin, 1994; Hashimoto and Furukawa, 1987; Wu and Wisecarver, 1992). The PVA-boric acid method used in this work was first developed to entrap denitrifying activated sludge biomass (Chen and Lin, 1994). Spherical beads could easily be formed by instantaneous polymerisation of PVA-boric acid monodiol-type reaction which progresses according to the following equation:
However, the beads formed had a strong tendency to agglomerate into a mass of polymer which was very difficult to break up. The beads, therefore, could not be utilised in a fluidised-bed or a fixed-bed. Chen and Lin (1994) incorporated an additional hardening step in the immobilisation procedures which successfully eliminated this problem. A solidification process was carried out by esterification of formed PVA beads with phosphate. The PVA gel beads formed were strong and exhibited an elastic, rubber-like property.

*Immobilisation Conditions*

In the immobilisation process, boric acid is consumed during PVA gelling reaction. Thus, an excess amount of boric acid is required for a rapid
progression of PVA polymerisation. The solubilities of boric acid are 50.4, 66.0 and 87.2 g/L at 20, 30 and 40 °C, respectively (Perry and Green, 1984). Therefore, saturated boric acid solution was prepared by cooling a saturated boric acid solution at 40 °C to room temperature. PVA gelling reaction was carried out under the presence of undissolved boric acid crystals.

Upon contact with boric acid, gelling reaction occurred immediately at the surface of the beads. Subsequently, the gelling reaction inside the beads was accomplished with further diffusion of boric acid into the beads. In the immobilisation of S. baccularia, this process was completed after the beads were suspended in saturated boric acid for about 18 - 20 hours.

The formed gel beads were then transferred to a sodium phosphate solution for solidification which was accomplished by esterification of PVA with phosphate. The esterification reaction of PVA with phosphate was sensitive to pH changes. The pH effect was studied over the pH range of 5 - 9. It was found that pH 5.5 is most suitable for bead formation. The beads were not stable and easily dissolved at pH values greater than 8. Chen and Lin (1994) reported that the gel strength was very low for pH values lower than 4.

The variation of contact time with phosphate on bead stability was observed. With a contact time of less than 5 hours, the beads became very soft and were easily broken. Increase in contact time obviously resulted in an increase in gel
strength. However, there was no significant increase in gel strength for a contact time of more than 5 hours. Therefore, the immobilisation process was first carried out by polymerisation of PVA in boric acid for 20 hours followed by esterification reaction in a phosphate solution for another 5 hours. The hardened beads were then washed with large amounts of distilled water to get rid of any chemical residue.

Bead Production

PVA concentration is an important factor for the preparation of immobilised biomass by using this method. It was found that a solution containing less than 100 g of PVA/L did not have enough binder for the biomass and unattached biomass was observed. It was also reported by Hashimoto and Furukawa (1987) that the gel strength of immobilised activated sludge beads below 7.5 w/v % PVA final concentration was weak. In the present work, PVA solution of 15 w/v % was chosen for bead production.

Biomass is the active metal-adsorbing material in the beads and a highly concentrated biomass is desirable. However, there is a practical limit. Thus, 150 g of algal biomass/L of solution was chosen because of its ability to produce well-formed, mechanically strong beads.
Properties of Porous Beads

The size of the spherical beads was determined by averaging the diameter of 50 beads. The average diameter of the beads was found to be 3.5 mm with a standard deviation of 0.4 mm. A Micromeritics ASAP 2010 surface analysis instrument was used for both BET surface area and pore-size measurements. The freeze drying method was used to remove water from the beads because this method is able to preserve the porosity and porous structure of the beads from collapsing. The internal surface area of the beads determined by the BET method was 24.1 m²/g. This indicates that the beads have a porous internal structure. The average pore diameter calculated by this method is 181.6 Å.

3.4.2 Kinetics of Copper Biosorption

To determine the time required for the biosorption system to reach equilibrium, kinetic experiments were carried out for both the native algal biomass and immobilised biomass over a period of 48 hours and samples taken at regular intervals. The samples were filtered and analysed for copper concentration. The time profiles of copper biosorption by the native and immobilised biomass are shown in Figures 3.1 and 3.2, respectively.

It is clear that the uptake of copper by the native biomass was rapid and attained equilibrium within 1 hour of contact. Studies by Roy et al. (1993) and Ozer et al. (1994) using green microalga showed that metal biosorption by the algal
Figure 3.1: Kinetics of copper biosorption by the native biomass of *Sargassum baccularia*.
Figure 3.2: Kinetics of copper biosorption by the immobilised biomass of *Sargassum baccularia* and pure PVA beads.
biomass is a rapid process. The former concluded that the equilibrium binding of cobalt and nickel by the biomass of *Chlorella minutissima* was attained between 15 to 20 minutes. The latter found that the equilibrium of lead and chromium biosorption by *Cladophora crispata* was reached in 15 - 30 minutes following a rapid, physical adsorption. However, a study by Zhou *et al.* (1998) showed that uptake of copper by the brown macroalga, *Sargassum kjellmanianum*, required 8 hours to approach equilibrium.

On the other hand, a slower rate of copper uptake by the immobilised algal biomass was observed. About 20 hours were required for the system to reach equilibrium. Copper biosorption by the immobilised biomass beads is strongly affected by solute diffusion into the pores of the beads and to the binding sites on the surface of the biomass. Copper ions have to diffuse through the pores of the beads before reaching the binding sites of the biomass. Therefore, a slower rate of uptake was observed when compared to the algal biomass in native form.

Studies on uranium uptake by the immobilised biomass of a fungus, *Rhizopus arrhizus*, have concluded that beads with a size of 0.5 mm diameter required 40 hours to reach equilibrium while beads with a diameter of 1.0 mm took nearly 200 hours to reach equilibrium (Tsezos *et al*., 1988; Tsezos and Deutchmann, 1990). It is obvious that the kinetic profile of an immobilised biomass is a strong function of its bead size.
A kinetic study using pure PVA gel beads as control has also been conducted and the results are shown in Figure 3.2. It can be concluded that copper uptake by the pure PVA gel beads was negligible in comparison to copper uptake by the immobilised biomass beads.

Based on the kinetic results, subsequent biosorption equilibrium experiments were carried out for a period of 24 hours which was more than sufficient for the biosorption process to reach equilibrium.

3.4.3 Equilibria of Copper Biosorption

The pH of metal solution has been shown to play an important role in the biosorption process (Holan et al., 1993) as it bears a major influence on the formation of metal-biosorbent complexes and the chemistry of the binding sites. pH changes can modify the speciation of metal ions in the solution in four ways: as free ion, bound to a ligand in a complex, adsorbed on a solid surface or as a distinct precipitate. Free ions are usually easier to be adsorbed compared to complexes which could be easily precipitated. On the other hand, pH variation of the metal solution also determines the chemical state of the functional groups responsible for metal binding on the biosorbent surface. Each metal has its own individual optimal pH value, depending on its solution chemistry.
In this work, the effect of pH on the equilibria of copper biosorption by the native as well as immobilised biomass of *S. baccularia* was investigated using the batch technique. Equilibrium isotherms of copper biosorption by the native biomass of *S. baccularia* at two pH values are shown in Figure 3.3. The results indicate that biosorption of copper was affected by the solution pH. The Langmuir isotherm parameters were derived from the experimental data by performing nonlinear regression on each set of the data. Estimated values of $q_{\text{max}}$ and $k$ are tabulated in Table 3.1. $r^2$ is the correlation coefficient. Table 3.1 indicates that the maximum adsorption capacity, $q_{\text{max}}$, increases with increasing initial solution pH.

Table 3.1: Langmuir isotherm parameters at pH 3.0 and 6.0 for the native biomass of *S. baccularia*.

<table>
<thead>
<tr>
<th>pH</th>
<th>$q_{\text{max}}$ (mmol/g)</th>
<th>$k$ (mM$^{-1}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.06</td>
<td>5.43</td>
<td>0.984</td>
</tr>
<tr>
<td>6</td>
<td>1.66</td>
<td>7.12</td>
<td>0.948</td>
</tr>
</tbody>
</table>

From Figure 3.3, it is apparent that the uptake of copper increase with increasing pH values. Based on these results, it may be concluded that the biosorption of copper on the algal biomass is pH dependent. Stumm and Morgan (1970) showed that the isoelectric point, or zero-point charge, of most microalgae is in the region of pH ~3. This implies that at pH values greater than
Figure 3.3: Effect of initial solution pH on the equilibria of copper biosorption on the native biomass of *Sargassum baccularia*. The solid lines are fitted curves using the Langmuir model.
3.0, the surface of the algal biomass possesses a net negative charge which promotes adsorption of positively charged species. As the pH is lowered, however, the overall surface charge on the biomass becomes positive. It was reported that the adsorption edge for \textit{S. baccularia} lies between the pH range of 2.0 to 3.0 where a sharp rise of metal adsorption was observed (Samuel, 1996).

Generally, the isoelectric state of the biomass surface is determined by the solution pH. At pH values above the isoelectric point, ligands responsible for metal binding such as $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$ on the surface of the biosorbent acquire a net negative charge due to deprotonation or the loss of protons (Crist \textit{et al.}, 1981). This would lead to electrostatic attractions between positively charged cations and negatively charged binding sites, thus promoting adsorption via electrostatic interaction. As the solution pH is lowered, the overall surface charge on the biomass becomes positive. This phenomenon will inhibit the approach of positively charged cations by electrostatic repulsion between the biomass surface and the metal ions, resulting in decreased adsorption.

Therefore, at pH values above 3.0, the surface charge on the algal biomass promotes copper adsorption, thus increasing the adsorption capacity of the biomass. Zhou \textit{et al.} (1998) found that the optimum pH for copper and cadmium uptake by two brown algae, \textit{Sargassum kjellmanianum} and \textit{Laminaria
*japonica*, lay between pH 4.0 and 5.0. On the other hand, at pH values below 3.0, the surface charge was not conducive for metal binding.

These results suggest that one of the possible mechanisms of copper binding on the surface of *S. baccularia* is electrostatic interaction. In a study by Crist *et al.* (1991), it was concluded that adsorption occurred between positively charged metal ions and the unprotonated carboxyl oxygen and sulphate groups present on the algal surface via electrostatic binding.

The Langmuir equilibrium isotherms for copper biosorption by the native biomass of *S. baccularia* at pH 3.0 and 6.0 are shown in Figure 3.3. The values of the Langmuir parameters are tabulated in Table 3.1. The capacity of the native biomass of *S. baccularia* for copper increased with metal concentration and reached a maximum capacity of 1.66 mmol/g (105.41 mg/g) at pH 6.0.

From Table 3.1, it can be seen that the correlation coefficients ($r^2$) were well above 0.94. This indicates that there was a strong relationship between the experimental results and the Langmuir isotherm model. The agreement between the experimental data and the Langmuir model implies that the isotherm model can be satisfactorily applied to copper biosorption by the algal biomass.

The copper adsorption capacity obtained in this study is comparable to those obtained by previous studies employing marine macroalgae, banana pith and
also rice-milling by-products as adsorbent. The brown algae *Laminaria japonica* and *Sargassum kjellmanianum* were shown to adsorb copper at high levels, giving a maximum capacity of 1.23 mmol/g (78 mg/g) and 1.45 mmol/g (92 mg/g), respectively (Zhou *et al.*, 1998). In another study by Low *et al.* (1995) using banana pith as the biosorbent, maximum adsorption capacity was estimated to be 0.21 mmol/g (13.46 mg/g). However, Marshall and co-workers (1993) reported a substantially lower value of 0.02 mmol/g (1.21 mg/g) for copper adsorption where the adsorbent used was rice-milling by-products. The difference is likely to be due to different binding groups present on the various types of biosorbent.

As such, it may be concluded that brown macroalgae contain a significant percentage of binding sites that could bind copper to a greater extent. The brown algae have demonstrated impressive metal-binding properties for copper. The species used in this study, *S. baccularia*, obtained from the coastal areas of Port Dickson, is also found abundantly in Cape Rachado off the west coast of Peninsular Malaysia (Phang, 1995). A large quantity of the biomass can therefore be easily collected and processed for laboratory-scale or pilot-scale studies.

Similar equilibrium experiments were conducted to investigate the effect of pH on copper biosorption on the biomass of *S. baccularia* immobilised on PVA gel beads. Equilibrium isotherms of copper biosorption by the immobilised biomass
at pH 3.0 and 6.0 are shown in Figure 3.4. The Langmuir isotherm parameters estimated by nonlinear regression analysis are tabulated in Table 3.2.

Table 3.2: Langmuir isotherm parameters at pH 3.0 and 6.0 for the immobilised biomass of *S. baccularia*.

<table>
<thead>
<tr>
<th>pH</th>
<th>$q_{\text{max}}$ (mmol/g)</th>
<th>k (mM$^{-1}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.49</td>
<td>17.81</td>
<td>0.933</td>
</tr>
<tr>
<td>6</td>
<td>0.63</td>
<td>72.45</td>
<td>0.859</td>
</tr>
</tbody>
</table>

It can be noted from Tables 3.1 and 3.2 that the values of $q_{\text{max}}$ for the immobilised biomass were lower than those of the native biomass. This could be due to the fact that part of the biomass surface might be covered or shielded by the PVA gel matrix and thus was not available for copper binding.

In addition, as metal ions penetrate the porous beads and adsorb onto the binding sites near the outer surface, the formation of adsorbed metal clusters may constrict or completely block the pores. This phenomenon would render the biomass deep within the interior of the beads inaccessible for adsorption with metal ions. This pore blockage effect would be more pronounced near the outer surface of the beads where the metal ion concentration is the highest. This effect might have also contributed to the lower levels of copper uptake by the immobilised algal biomass compared to the native biomass.
Figure 3.4: Effect of initial solution pH on the equilibria of copper biosorption on the immobilised biomass of *Sargassum baccularia*. The solid lines are fitted curve using the Langmuir model.
Generally, chemical treatment of biomass often results in decreased metal uptake. A study by Wong et al. (1993) showed that copper uptake by the immobilised bacterial cells of *Pseudomonas putida II-11* was only 54% of the free cells. Comparison of lead uptake by the native biomass of *Stichococcus bacillaris*, a microalga, with that immobilised in silica gel revealed a 40% loss of adsorption efficiency due to the loss of binding sites as a result of the immobilisation procedure (Mahan and Holcombe, 1992). Reduced cadmium uptake by the chemically cross-linked biomass of *Sargassum fluitans*, a macroalga, was observed when compared with the performance of the native biomass (Leusch et al., 1995).

However, Garnham et al. (1992) showed that immobilised cells of *Chlorella salina*, a microalga, accumulated greater amounts of cobalt, zinc and manganese than free cells under similar experimental conditions. Similar observations were reported by Rai and Mallick (1992) who studied metal uptake by the immobilised microalgal biomass of *Anabaena dolioolum* and *Chlorella vulgaris*. In a recent communication, Brady et al. (1999) reported that the immobilisation procedures had no discernible effect on the biosorption capacity of the fungal biomass of *Rhizopus arrhizus* for copper ions.
Figure 3.5 shows the accumulation ratio of copper at initial solution pH values of 3.0 and 6.0. The accumulation ratio was estimated according to the following equation:

\[
\text{Accumulation ratio (\%) = \frac{\text{Total amount of copper adsorbed by biomass (mmol)}}{\text{Initial amount of copper in the solution (mmol)}} \times 100}
\]  

(3.4)

From Figure 3.5, it can be seen that with increasing external copper concentration, the accumulation ratio of copper by the immobilised biomass decreased. When the external copper concentration was low (< 0.016 mM or 1 mg/L), the extremely high accumulation ratio was found at both pH values. However, the accumulation ratio was higher when the initial pH of the copper solution was at pH 6.0. Almost 100 % removal was observed when the equilibrium copper concentration was less than 0.016 mM (< 1 mg/L) at pH 6.0. The accumulation ratio was higher than 90 % for an external copper concentration of 0.079 mM (5 mg/L). The results imply that the immobilised biomass is suitable for the removal of copper ions from low concentration solutions.
Figure 3.5: Copper accumulation ratios in solution containing different amounts of copper at pH 3.0 and 6.0.
3.5 Conclusions

The kinetic and equilibrium behaviour of copper biosorption on the native as well as immobilised biomass of the brown alga *S. baccularia* was characterised in this chapter. Kinetic studies using the native biomass of *S. baccularia* indicate that copper biosorption was relatively fast, reaching equilibrium within 1 hour of contact. The native biomass particles demonstrated high equilibrium uptake of copper from aqueous solutions. Adsorption equilibrium data obtained using the batch techniques was found to correspond well to the Langmuir isotherm although the mechanism of metal adsorption may not truly obey the ideal assumptions of the Langmuir model. Solution pH was a critical factor in the biosorption process as it was found to influence the equilibria of copper biosorption on the native biomass. The maximum capacities for native biomass were found to be 1.06 and 1.66 mmol/g at pH 3.0 and 6.0, respectively. The major mechanism involved in biosorption is most probably electrostatic interaction where metal ions bind to pH-dependent sites.

The immobilised biomass beads developed in this study were mechanically strong and suitable for use even in low pH solutions. Kinetic studies on copper biosorption by the immobilised biomass required a much longer time (about 20 hours) to attain equilibrium compared to the native biomass. The maximum adsorption capacities of the immobilised biomass for copper were approximately 40 % of the native biomass under identical experimental conditions. The decrease in copper adsorption capacity suggests that the metal
ions might not have completely penetrated the porous beads and the metal preferentially adsorbed onto the biomass near the outer surface of the beads.

The kinetic and equilibrium studies in this chapter represent an important step in the characterisation of metal biosorption by the native as well as immobilised biomass of *S. baccularia* and can be used as a basis for process design and scale-up.