CHAPTER THREE

ADSORPTION KINETICS FOR COPPER BIOSORPTION

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Kinetic models are very useful for the understanding of the biosorption process. The design of pilot plant studies and full-scale operations are normally based on preliminary data derived from kinetic models.

For biosorptive metal uptake, biosorption equilibrium isotherms can be quantitatively evaluated using methods similar to the performance evaluation of activated carbon (Volesky, 1990). Hence, the analysis of biosorption is quite similar to that of carbon adsorption processes.

According to Volesky (1990), the analysis of biosorption process involves three steps: macrotransport, followed by microtransport and finally sorption. Macrotransport is the movement of the metallic species through the water to the liquid-solid interface by advection and diffusion. Microtransport initially involves the diffusion of the metallic species through the macropore system and then to the adsorption sites in the micropores and submicropores of the immobilized biomass. Sorption is the term used to describe the attachment of the metallic species to the immobilised biomass. The term sorption is

used because it is difficult to differentiate between chemical adsorption and physical adsorption. When the rate of sorption equals that of desorption, equilibrium is achieved and the capacity of the immobilised biomass is saturated. The theoretical biosorption capacity of the immobilised biomass for a particular metallic species can be determined from its adsorption isotherm.

The quantity of adsorbate (metallic species) that can be taken up by an adsorbent (immobilised biomass) is a function of both the characteristics and concentration of the adsorbate and solution temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature and the resulting function is called an adsorption isotherm. Equations that are often used to describe the experimental isotherm data were developed by a number of researchers such as Freundlich, Langmuir and Brunauer, Emmet and Teller (Shaw, 1966; USEPA, 1973). The adsorption isotherm developed by Brunauer, Emmet and Teller is also commonly recognized as the BET adsorption isotherm.

3.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm describes the equilibrium between a surface and solution as a reversible chemical equilibrium between species (Langmuir, 1918). The adsorbent or biosorbent surface is considered to be made up of fixed individual sites where molecules of adsorbate maybe chemically bound. Denoting an unoccupied surface site as -S and the adsorbate in dilute solutions as species A with concentration C, the reaction between the two will form occupied sites (-SA):

$$- \quad S + A \Leftrightarrow - SA$$

Assuming that this reaction has a fixed free energy of adsorption equal to ΔG_a° that is not dependent on the extent of adsorption and not affected by interactions among sites, each site is then assumed to be capable of binding at most one molecule of adsorbate, therefore the Langmuir model allows accumulation only up to a monolayer.

In practice, the actual number of sites per surface area and the energy of adsorption are usually unknown. Instead, the variable of interest is q, the number of moles of adsorbate at equilibrium. Hence, the Langmuir equation becomes:

$$q_{eq} = \frac{q_{\max} k C_{eq}}{1 + k C_{eq}} \tag{3.1}$$

q_{eq} = Solid phase equilibrium metal concentration (mg/g biomass),

C_{eq} = Liquid phase equilibrium metal concentration (mg/L),

q_{max} = Maximum metal adsorption capacity (mg/g biomass),

k = Langmuir equilibrium constant (L/mg)

The Langmuir model can be used to estimate the maximum metal adsorption capacity (q_{max}) of a biosorbent. The constant k is related to the energy of adsorption. 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:

$$q_{eq} = \frac{V(C_i - C_f)}{M} \tag{3.2}$$

where

V = Volume of the metal bearing solution (L),

M = Amount of the biomass (g),

C_i = Known initial metal concentration (mg/L),

C_f = Final or equilibrium metal concentration (mg/L)

The maximum sorption uptake value is an important feature of the sorbent characterizing its performance at high residual metal concentrations. The shape of the biosorption isotherm is also important. An isotherm which is steep from the origin at low residual concentrations of the sorbate is highly desirable because it indicates high affinity of the sorbent for the given sorbed species.

The Langmuir adsorption isotherm has found wide applicability to adsorption of compounds in water and wastewater treatment. Its advantages include its simplicity, its foundation in a model with some physical basis and its ability to fit a broad range of experimental data.

3.2 Freundlich Adsorption Isotherm

This isotherm assumes that the frequency of sites associated with a free energy of adsorption decreases exponentially with increasing free energy (Ozer *et al.*, 1994; Zhou and Kiff, 1991). Thus, the isotherm will have the form:

$$q_{eq} = KC_{eq}^{1/n} \tag{3.3}$$

where

q_{eq} = Solid phase equilibrium metal concentration (mg/g biomass),

K = Constant,

C_{eq} = Liquid phase equilibrium metal concentration (mg/L),

n = Exponential number

The log-log plot of q_{eq} against C_{eq} for this equation is linear. Here, the surface concentration of adsorbate does not approach a saturating value as C_{eq} increases, since there are always surface sites with higher free energies of adsorption to fill. The Freundlich adsorption isotherm is very widely used to fit observed data empirically even when there is no basis for its underlying assumptions.

Both models describe many available biosorption isotherm data equally well. Nevertheless, they are not models whose terms or parameters would have a convenient and appropriate physical interpretation attached to them. Therefore, the use and significance of these models are highly limited. As such, fitting the model to the process behaviour does not necessarily imply that a "pure" adsorption phenomenon has taken place. Figure 3.1 describes common adsorption isotherms typically encountered in the treatment of heavy metal wastewater.

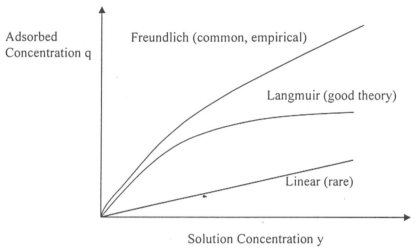

Figure 3.1: Common adsorption isotherms. Most useful isotherms are nonlinear and curve downward; these are termed "favourable". Note all can be approximated as linear in highly dilute solution
Source: Metcalf and Eddy (1992)

3.3 Materials and Methods

3.3.1 Materials

Fresh samples of brown marine alga *S. baccularia* were harvested from the sea off the coast of Port Dickson, a beach located on the West Coast of Peninsula Malaysia. The biomass was extensively washed with distilled water to remove residual seawater and adhering sand. It was then dried in an oven at 60^0C overnight.

The dried biomass was then disintegrated in a laboratory blender (Janke and Kunkel GMBH). The biomass particles were sorted by sieving using a Laboratory Test Sieve (Endecotts Ltd., England) to a size range of 106 μm and stored in capped plastic containers at room temperature.

All glassware and plasticware were washed thoroughly with detergent and rinsed with distilled water. To eliminate possible metal contamination, all containers and test flasks were soaked overnight in 10% nitric acid solution. They were then rinsed with distilled water.

Solution pH was measured by using a calibrated pH meter (Metrohm, Switzerland). Adjustments to the pH were made by the addition of either 1 M of nitric acid (HNO_3) or 1 M of sodium hydroxide (NaOH) solutions. Analytical grade solutions from Fluka, Switzerland were used in all experiments. Polyvinyl alcohol (PVA) with a molecular weight of 72 000 was used as the immobilising agent to immobilised *S. baccularia*. Stock solution of copper at concentration of 1000 mg/L was prepared by dissolving 3.8

grams of $Cu(NO_3).3H_2O$ in 1.0 L of distilled deionized water according to the following equation:

$$\text{Salt (g)} = \frac{Volume(L)xConcentration(g/L)xMolecularWeightx10^{-4}}{AtomicWeight(g/mol)xPurity(\%)xNormality(N)} \quad (3.4)$$

All working copper solutions were prepared by diluting the stock solution with concentration of 1000 mg/L in distilled deionized water.

Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) using a Baird ICP 2000 (Baird, Switzerland) instrument was used to determine and analyzed copper concentration in aqueous solutions. The ICP copper standard solution from Fluka, Switzerland was used.

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

As mentioned in Chapter One, the immobilisation procedure to entrap the biomass of *S. baccularia* using polyvinyl alcohol (PVA) will be based on techniques developed by Tan (1999). It was reported that the use of PVA offers several advantages over other commonly used polymeric substances such as acrylamide, alginate and agar in that they are economical, elastic, strong and chemically stable (Ting and Sun, 2000; Hashimoto and Furukawa, 1987).

According to Tan (1999), approximately 15% weight to volume (w/v) of PVA were added into distilled water and the resulting mixture was magnetically stirred with heat applied until a gel like substance is formed. Then about 15% w/v biomass of *S. baccularia* in the size range of 106 μm were added into that PVA aqueous solution and the mixture was thoroughly stirred to form a completely mixed heterogeneous compound. The mixture was then transferred into a syringe and gently extruded into saturated boric acid to form spherical beads. Saturated boric acid was prepared by dissolving about 87.2 g/L of boric acid into 1 liter of distilled water at 40^0C (Perry and Green, 1984) and the solution was cooled to room temperature. Cross-linking between PVA and undissolved boric acid crystals progresses according to the following reaction:

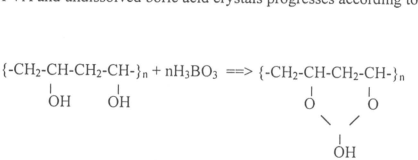

Figure 3.2: The entrapment of *S. baccularia* biomass in a monodiol-type PVA-boric acid gel lattice
Source: Tan (1999)

Upon contact with boric acid, cross-linking occurred immediately at the surface of the beads. In the immobilisation of *S. baccularia*, this process was completed after the beads were suspended in saturated boric acid for almost 20 hours to allow diffusion of boric acid into the pores of the PVA matrix.

The formed beads were then transferred into 1M of sodium phosphate solution for solidification which was accomplished by esterification of PVA with phosphate (Chen and Lin, 1994). This is necessary because the beads have a tendency to agglomerate into a mass of polymer that would make its utilisation in fixed bed configuration difficult. The esterification of PVA with phosphate was pH sensitive. Studies by Tan (1999) revealed that pH 5.5 and a contact time of 5 hours was most suitable for bead formation. Any other pH range was to be unsuitable and would incur instability to the beads (Chen and Lin, 1994) and contact time less than 5 hours would make the beads soft and easily broken (Tan, 1999).

For batch adsorption isotherm studies, copper solutions in the range of 20 - 80 mg/L were prepared from the stock solution. About 0.11 g of immobilised biomass were suspended in 250 mL Erlenmeyer flasks with varying copper concentrations and pH values of 3 and 6 were studied by the addition of 1M nitric acid or 1M sodium hydroxide solution. The flasks were agitated in a rotary shaker (ISF-1-V, Kuhner, Switzerland) at 200 rpm and 25^{0}C for 24 hours. For the mass transfer studies, approximately 0.11 g of immobilised biomass were suspended in 100 mL of copper solution with an initial concentration of 50 mg/L of copper ions. The test flask was shaken at 200 rpm and 25^{0}C. Solution samples were drawn from the flask at a fixed

time interval. For both experiments, samples were filtered using cellulose acetate membrane filters with pore size of 0.45 μm (Sartorius, Germany). The filtrate was diluted appropriately with distilled water and analysed for its copper content.

3.4 Results and Discussion

3.4.1 Properties of Porous Beads

Immobilised bead size was determined by averaging the diameter of 50 beads. The average diameter of the beads was 3.5 mm with a standard deviation of 0.4 mm. Using a Micromeretics ASAP 2010 surface analysis instrument, the pore size of the spherical beads and the surface area were determined. Prior to analysis, the beads were freeze dried to remove water from the beads. This method is able to preserve the structure and the porosity of the beads, thus preventing it from collapsing (Tan, 1999). Using the BET method, the internal surface area of the beads were determined to be 24.1 m^2/g, indicating a porous internal structure. The average pore diameter calculated by this method is 181.6A. Table 3.1 summarizes the properties of the beads.

Table 3.1: Biosorbent physical properties

Parameters	
Diameter	= 0.35 ± 0.04 cm*
Density	= 1.15 g/cm^3
Bead Porosity	= 0.481
Internal surface area	= 24.1 m^2/g
Average pore diameter	= 181.6 Å

* Standard Deviation

3.4.2 Mass Transfer Studies

Experiments were carried out over a period of 48 hours to allow the diffusion of copper ions onto the immobilised biomass to attain equilibrium. At regular intervals of time, samples were pipette out, filtered and diluted for analysis of copper concentration. Figure 3.3 shows the difference between pure PVA beads and immobilised biomass beads of *S. baccularia*.

For the immobilised biomass beads, about 20 hours was needed to attain equilibrium. Copper uptake for the pure PVA beads as control is negligible, indicating that PVA is not responsible for any metal uptake. In earlier studies by Tan (1999) using native biomass of *S. baccularia*, equilibrium was achieved in as little as 1 hour of contact. Such rapid equilibrium results were also obtained by Roy *et al.* (1993) in the biosorption of cobalt and nickel and Ozer *et al.* (1994) in removing lead and chromium using a green microalgae of *Chlorella minutissima*.

Leusch *et al.* (1995) observed that the biosorption of metal by granulated biomass of marine algae depended on chemical modification. This explains why the steady state condition achieved by the immobilised biomass of *S. baccularia* is slower than its native counterpart. This is because of mass transfer limitations. Copper ions have to first diffuse into the film surrounding the immobilised bead. This is then followed by diffusion into the macro and micropores of the PVA matrix and eventual binding of the ions onto the active sites. Unlike the native biomass, mass transfer is limited only to surface film transfer. According to Tan (1999), the kinetic profile of the immobilised biomass of *S. baccularia* is also dependent upon the particle and bead size.

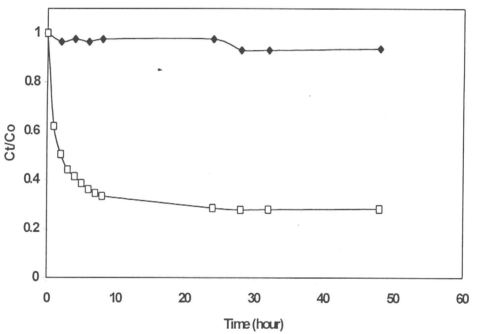

Figure 3.3: **Copper biosorption by immobilised biomass of *S. baccularia* and pure PVA beads (♦, PVA beads; □, PVA immobilised biomass beads)**

Dried biomass in the range of 106 μm immobilised onto PVA with bead size of 0.35 cm exhibited optimum metal uptake of copper. This is in agreement with the results obtained by Tsezos and Deutchmann (1990) and Tsezos *et al.* (1988) when immobilised biomass of *Rhizopus arrhizus* with bead size of 0.5 mm took 40 hours to achieve steady state whereas bead size at 1.0 mm required 200 hours.

The data presented in Figure 3.3 also depicts that copper biosorption with immobilised *S. baccularia* occurs in two phases: initial fast phase which lasted for 2 hours followed by a slower second phase which continued till the end of the experimental period. This type of biosorption trend relates the two different mechanisms of copper biosorption by the immobilised biomass of *S. baccularia*. The faster first phase of copper biosorption is attributed to the surface adsorption through ion exchange with the participation of the carboxyl groups present in cell structure which are known metal sequestering sites (Prakasham *et al.*, 1999). The slower phase maybe represented by the diffusion of metal ions into the cell debris over a period. These results are similar to other two-phase biosorption of heavy metals observed by other researchers in algal biomass (Yang and Volesky, 1999; Kuyucak and Volesky, 1990; Crist *et al.*, 1988).

3.4.3 Kinetics of Copper Biosorption

The Langmuir and Freundlich adsorption isotherms were employed to evaluate the equilibrium kinetics of copper biosorption. Experiments were carried out in pH 3 and pH 6 as described in Section 3.3.2. Higher pH values were not examined for biosorption studies due to precipitation of copper ions. Equations 3.1, 3.2 and 3.3 that describe Langmuir and Freundlich adsorption isotherms were solved using a non linear least square method to determine their constants. Table 3.2 summarizes the constants of the respective isotherms at pH 3 and pH 6 where R^2 is the correlation coefficient. The non linear regression model for both isotherm models are depicted in Figure 3.4.

Table 3.2: Langmuir and Freundlich constants at pH 3 and pH 6 for the immobilised biomass of *S. baccularia*

	pH = 3	pH = 6
Langmuir model		
q_{max} (mg/g)	31.15	40.31
k (l/mg)	0.28	1.14
R^2	0.97	0.94
Freundlich model		
K ([mg/g][l/mg]$^{1/n}$)	13.39	21.10
n	5.19	5.75
R^2	0.96	0.99

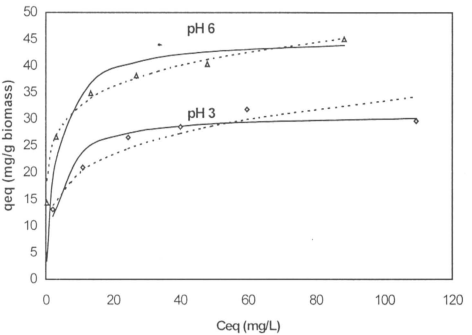

Figure 3.4: Cu (II) biosorption isotherms: Experimental data with Langmuir regression model (solid line) and Freundlich regression model (dotted line)

From Figure 3.4, both Langmuir and Freundlich adsorption models were able to predict the experimental data reasonably well. The agreement of the experimental data with both these models implied that both monolayer adsorption and constant adsorption energy existed for the experimental conditions used (Zhou and Kiff 1991). At low pH, the Langmuir regression model resulted in higher correlation coefficient than those obtained from the Freundlich model. However, at pH 6, the Freundlich model could represent the isotherm better. Valdman and Leite (2000) as well as Yang and Volesky (1999) noted similar observations. For the former, biosorption of cadmium, zinc and copper were well correlated by Freundlich model in comparison to Langmuir at pH 6 using *Sargassum* sp. biomass. In the work by Yang and Volesky (1999), in which *S. fluitans* were used in the uptake of uranium, the Langmuir model predicted the curves better at pH values of 2.6 and 3.2. Nevertheless, at pH 4, the Freundlich model provided a better representation.

The value of q_{max} represents the adsorption capacity when the surface of the immobilised biomass is fully saturated with metal ions. The highest value for q_{max} was obtained at pH 6 at 45.44 mg/g of biomass. However, at both pH values, q_{eq} was found to be smaller than q_{max}. According to Ozer *et al.*, (1994), this indicate that the biosorption of copper is by a monolayer type of adsorption in which the surface of the immobilised biomass of *S. baccularia* is not fully covered. Similarly, K and n values obtained by evaluating the Freundlich isotherm revealed that the constants are higher at pH 6. K and n values can be considered as indicators of adsorption capacity and adsorption intensity according to Ozer *et al.*, (1994). Since the n values are higher than 1.0, copper biosorption by the immobilised biomass of *S. baccularia* is quite

intense. The magnitude of k and n also shows easy uptake of copper ions and high adsorptive capacity of the biomass. Both Langmuir and Freundlich isotherms have steep initial slopes as indicated in Figure 3.6, indicating high adsorption affinities for the copper ion.

It is well known that both the cell surface metal binding sites and the availability of metal in solution are affected by pH (Ahuja *et al.*, 1999; Holan *et al.*, 1993; Volesky, 1990). At pH 3, the copper uptake was lower. Kuyucak and Volesky (1989) also reported that lower uptake of cobalt by *Sargassum natans*, *A. nodosum*, *Porphyra tenera*, *Palmaria palmata*, *Chondrus crispus*, *M. pyrifera* and *Laminaria* sp. at pH 2. The reduction in metal binding at low pH has also been reported in fungi (Kiff and Little, 1986) and in gram positive and gram negative bacteria (Gourdon *et al.*, 1990). However, different cell composition will exhibit different biosorption characteristics at a given pH (Gardea, 1988; Greene *et al.*, 1987). For biomass of *S. baccularia*, the predominant functional groups responsible for metal binding are -COOH-, -OH and -NH_2. These functional groups would acquire a positive charge at low pH that would not promote the biosorption of positively charged metallic ions because the isoelectric point for most microalgae is in the region of pH 3 (Stumm and Morgan, 1970). Hence only at pH values higher than 3 would the overall surface charge of the algal biomass promotes biosorption of copper (Tan, 1999).

In addition to the functional groups, the presence of competing ions especially protons, are also affected by solution pH. Bedell and Darnall (1990) suggested that protons compete for the same binding sites on the biomass because metallic ions such as Cu(II),

Ni(II), Zn(II), Co(II), Pb(II), Cr(III), Cd(II), U(IV), Co(II), Be(II) and Al(III) were found to bind more strongly to the dried *Chlorella vulgaris* as the pH was increased from 2 to 5. The reverse was equally true for oxoanions such as MoO_4^{2-}, SeO_4^{2-}, CrO_4^{2-} and other anionic complexes such as $Au(CN)_2^-$ and $PtCl_4^{2-}$ that bound *Chlorella vulgaris* strongly at pH 2 instead of pH 5. According to Bedell and Darnall (1990), the increased binding of these metal ions was consistent with electrostatic binding to positively charged groups, such as amines or imidazoles. Anions would be expected to interact more strongly with the cells as the concentration of positive charges increases due to protonation of groups at low pH values.

At low pH, although there is an increase in metal availability and mobility, protons tend to compete with the cations to bind to the active sites (Crist *et al.*, 1990; Greene *et al.*, 1987), thus lowering the extent of biosorption (Ahuja *et al.*, 1999). According to Zhou and Kiff (1991), at low pH values, the cell wall ligands would be closely associated with the hydronium ions (H_3O^+) that restrict access to ligands by metallic ions as a result of repulsive forces. As pH is increased, more ligands would be exposed. The exposed ligands would carry negative charges that would promote the subsequent attraction of metallic ions with positive charge and adsorption onto the immobilised cell surface of *S. baccularia*.

Conclusion

Equilibrium studies revealed that the biosorption of copper by the biomass of *S. baccularia* is pH dependent with higher pH values promoting better biosorption characteristics. Both Langmuir and Freundlich adsorption isotherms fitted the experimental data well, denoting their suitability in predicting the equilibrium conditions of this biosorption process. Nevertheless, Freundlich model was found to fit the experimental data better at pH 6 whereas the Langmuir model predicted the experimental data better at pH 3. Maximum adsorption capacities, q_{max} for the uptake of copper ions by the Langmuir model were estimated to be 9.46 and 45.44 mg/g at pH 3 and 6 respectively. For Freundlich model, K values estimated are 11.96 and 22.87 for pH 3 and 6 respectively. It is possible that the major mechanism governing the biosorption of copper onto the surface of immobilised biomass of *S. baccularia* to be electrostatic interaction that is pH dependent.

Mass transfer studies revealed that the biosorption of copper is a bi-phasic process. The first phase was a rapid biosorption of copper that occurred within 2 hours of solution contact with the beads of immobilised biomass of *S. baccularia*. The slower phase approached saturation after 20 hours of contact time. The former rapid phase is probably due to physical sequestering of the copper ions onto the surface of the beads of *S. baccularia* while the slower phase was attributed to diffusion of copper ions into the macro and micropores of the PVA matrix. The results therefore suggest that a combination of sorption mechanisms were involved in the biosorption of copper ions by the immobilised biomass of *S. baccularia*.