

Chapter 3: Materials and Methods

3.1 ADSORPTION

The wood-ash which was used as an adsorbent in these experiments was treated using 0.5M HNO₃. Nickel(II) sulphate hexahydrate, NiSO₄.6H₂O (Fluka Chemika; Analar) was used as an adsorbate. The salts of sodium chloride, calcium chloride, potassium chloride, sodium nitrate and ethylenediamine tetraacetic acid (EDTA), (Fluka, Switzerland) were used as complexing and chelating agent respectively in these experiments. Nitric acid (69-71.0%)(Fluka, Switzerland) was of analytical or reagent grade quality and cellulose nitrate membrane filters (0.45µm) obtained from Sartorius (Germany) were used in these experiments.

3.1.1 Preparation of Wood-ash

The wood ash samples were prepared by grinding wood-charcoal in a laboratory hammer mill (Ika, Germany). The samples were then incinerated in the furnace (Carbolite, UK) at 600⁰C for 4 hours. The average value of combustible carbon in the sample was about 0.38%. The particles were sieved through 53µ seive. The sieved particles(10g) were soaked in 400ml of 0.5M HNO₃ for 4 hours. It was then filtered and rinsed with distilled water until the filtrate was near neutral. After washing, the particles were dried overnight at 60⁰C. The average size of the particles was found to be 6µm measured by Laser defraction particle size analyzer (Coulter, USA).

3.1.2 Preparation of Metal Solution

All glassware were washed throughly by detergent solution, followed by ultrapure water. The glassware were then soaked overnight in 50% nitric acid solution and

rinsed thoroughly with ultrapure water. Metal stock solution was prepared by dissolving $\text{Ni}_2(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$ in ultrapure water using the formula below:

$$\text{Salt (g)} = \frac{\text{Volume(ml)} \times \text{Concentration (mg/l)} \times \text{Molecular Weight} \times 10^{-4}}{\text{Atomic Weight} \times \text{Purity} \times \text{Normality}}$$

3.1.3 Kinetics of Metal Adsorption

Batch adsorption experiments were carried out by agitating 1.0 g of ash with 50 ml aqueous solutions of nickel sulphate in concentrations of 2.07, 1.98, 1.72, 1.55, 1.21, 0.86, 0.603, 0.345 & 0.17 mMol.respectively. All the solutions were prepared in ultrapure water. The initial pH of the solution was adjusted with 0.1 M NaOH and HCL using a pH meter. The flasks were incubated and agitated in a shaker (New Brunswick Scientific,U.S.A.) at 30 °C and at 120 r.p.m. The contents of the flasks were filtered through cellulose nitrate membrane filters. The filtrates were analysed for nickel ions by Inductively Coupled Plasma spectrometry method (Baird ICP 2000 Spectrometer,USA). The amount of metal adsorbed by the wood-ash, i.e., the solid phase equilibrium concentration q^* is the difference between the metal quantity added to solution (C_i) and the measured liquid phase equilibrium concentration (C_{eq}). This is in accordance with the following material balance equation:

$$q^* = \frac{V}{m} (C_i - C_{eq}) \quad (3-1)$$

Where,

V= Solution volume (L)

m = dry weight of the biomass (g)

The two important aspects of the adsorption study are the kinetics and the equilibria of adsorption. The sorption of nickel from liquid phase to solid phase can be considered to be a reversible reaction (Bhattacharya and Venkobachar, 1984). A simple first order kinetic model was used to establish the rate of reaction which can be expressed as follows:



If the first order reversible kinetic model holds true, the rate of equation for the reaction may be expressed (Bhattacharya and Venkobachar, 1984) as :

$$\begin{aligned} \frac{dC_B}{dt} = - \frac{dC_A}{dt} = C_{Ai} \frac{dq}{dt} &= k_1 C_A - k_2 C_B \\ &= k_1 (C_{Ai} - C_{Ai} q) - k_2 (C_{Bi} + C_{Ai} q) \end{aligned} \quad (3-3)$$

Here, C_B is the concentration of nickel in the sorbent and C_A is the concentration of nickel in solution at any time. C_{Bi} and C_{Ai} are the initial concentrations of nickel on sorbent and solution, respectively. The fractional conversion of nickel is defined as q , and k_1 and k_2 are the first order rate constants. At equilibrium,

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0 \quad (3-4)$$

$$q_e = \frac{k_c - C_{Bi}/C_{Ai}}{k_c + 1} \quad (3-5)$$

Here, q_e is the fractional conversion of nickel at equilibrium, and k_c is the equilibrium constant as given by Eqn. (3-6)

$$k_c = \frac{C_{Be} C_{Bi} - C_{Ai} q_e}{C_{Ae} C_{Ai} - C_{Ai} q_e} = \frac{k_1}{k_2} \quad (3-6)$$

In Eqn. (3-6) C_{Be} and C_{Ae} are defined as the equilibrium concentrations for nickel in the sorbent and in solution, respectively. The rate equation in terms of equilibrium conversion can be obtained from Eqn. 3-4, 3-5 and 3-6 as follows.

$$\frac{dq_e}{dt} = (k_1 + k_2) (q_e - q) \quad (3-7)$$

Integration of Eq. 3-7 and substituting for k_2 from Eq. 3-6 gives

$$-\ln(1 - q/q_e) = k_1 (1 + 1/k_c) t \quad (3-8)$$

Eq. 3-8 can be rewritten in the following form.

$$-\ln [(q_e - q) / q_e] = (k')t \quad (3-9)$$

$$\text{or, } [k' = k_1 (1 + 1/k_c)]$$

$$-[\ln (q_e - q) - \ln q_e] = (k')t \quad (3-10)$$

$$-\ln (q_e - q) + \ln q_e = (k')t \quad (3-11)$$

$$\ln (q_e - q) = -(k')t + \ln q_e \quad (3-12)$$

$$\log 2.303(q_e - q) = -(k')t + \log 2.303q_e \quad (3-13)$$

in which k' is the overall rate constant.

3.1.4 Equilibria of Adsorption

Isotherm measurements were carried out using batch techniques. In these experiments 1.0 g of wood-ash was suspended in 50ml of metal solution with initial metal ion concentration ranging from 0.17mMol (10mg/l) to 2.07mMol (120mg/l).

The pH of the metal solution was adjusted to 5 by the addition of 0.1M NaOH or 0.1M HNO₃. Two types of control flask, i.e., ash free control and metal free control were prepared. The flasks were incubated in a shaker (New Brunswick Scientific, U.S.A.) at 30 °C and agitated at a speed of 120 rpm for 4 hours. The mixtures were then centrifuged (Sigma 2-15, Germany) at 4500 rpm for 15 minutes to separate the supernatant from the biomass. The controls were treated in the same way. The supernatant was then filtered and analyzed for nickel concentrations by I.C.P.

3.1.5 Effect of Biomass Concentration

The effect of biomass concentration on adsorption process was investigated by using different concentrations of biomass. The concentration of nickel ranged from 0.17 mMol to 2.07 mMol (120mg/l) and the biomass concentrations were 0.1, 0.25, 0.5, 1.0, 1.5, and 2.0 g/50 ml respectively.

3.1.6 Effect of Initial pH

In this experiment, the initial pH values of metal ions solutions were adjusted to 2.0, 4.5, 5.0, 5.5, 6.5 and 8.0 with 0.1 M NaOH or 0.1M HNO₃ prior to the addition of biomass. The experiments were then carried out to determine the adsorption isotherms.

3.1.7 Zeta Potential Measurement

The biomass was suspended in 0.17 mMol (10mg/l) and 2.07 mMol (120mg/l) of nickel solutions. The pH values of these solutions were adjusted to 2.0, 4.5, 5.5, 6.5 and 8 using 0.1M NaOH and 0.1M HNO₃. The mixtures were then stirred in an orbital shaker (New Brunswick, USA) at 30⁰C and at 120 rpm. Upon equilibration, 5

ml of sample was injected into the zeta analyzer (Zetasizer 4, Malvern, UK). The zeta potential of the sample was recorded. In another set of experiments, sodium sulfate at 1 and 10 mMol were used instead of metal solutions to determine the effect of ionic strength on the zeta potential of biomass. All of the above experiments were carried out in duplicate.

3.1.8 Effect of coincidental anions and complexing agents

In this study, the initial metal concentration was 0.17 mMol (10mg/L). EDTA and NaCl and Na₂SO₄ were employed as complexing agent and coincidental anions respectively. Stock solutions of 5mMol of each salt were prepared. A known volume of stock solution and metal ion solution were added to flasks containing 1g/L of adsorbent. For the present study, each anion was maintained at concentration of 0.0172, 0.0343, and 0.172 mM. The reaction mixtures were then incubated for 4 hours, agitated at 120 rpm and the temperature was maintained at 30 °C. The initial pH of the reaction medium was adjusted to 5 and the experiments were performed in duplicates.

3.1.9 Effect of coincidental cations

Two salts namely NaCl and KCl were employed in this study. The metal concentration was maintained 0.17mM (10mg/L) and each cation concentration was kept at 0.0172, 0.0343, and 0.172 mmol respectively. The reaction mixtures were then treated as described above. The initial pH of the solution was adjusted to 5 and each experiment was replicated.

3.1.10 Metal Ion Concentration Analysis

Batch kinetic studies were carried out taking the above mentioned amount of metal-ligands solution and adsorbent. After equilibration, the whole reaction mixture was centrifuged at 4500 rpm for 15 minute to separate the supernatant from the biomass. The supernatant was then analyzed by I.C.P. after filtering it through a membrane filter. The amount of metal adsorbed by the biomass was calculated from the difference between metal quantity added to the biomass and the metal content of the supernatant.

3.2 MEMBRANE SEPARATION

3.2.1 Chemicals

Nickel (II) sulphate hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Fluka Chemika; Analar), was used to study the effect of operating parameters on the separation characteristics.

3.2.2 Preparation of metal solutions

Three different feed concentrations of Nickel sulphate was prepared for the experiments. The feed solutions were prepared in concentrations of 50 mg/L, 30 mg/L and 10 mg/L. The solutions were prepared by weighing requisite amounts of the chemicals, according to the formula below:

$$\text{Salt (g)} = \frac{\text{Volume (ml)} \times \text{Concentration (mg/L)} \times \text{Molecular Weight} \times 10^{-4}}{\text{Atomic Weight} \times \text{Purity} \times \text{Normality}}$$

3.2.3 Membrane unit

The membrane unit used in this experiment was of a B-14A-PT model from Applied Membranes Inc. San Marcos, CA92069. The schematic of this unit given in Figure 3.1 below.

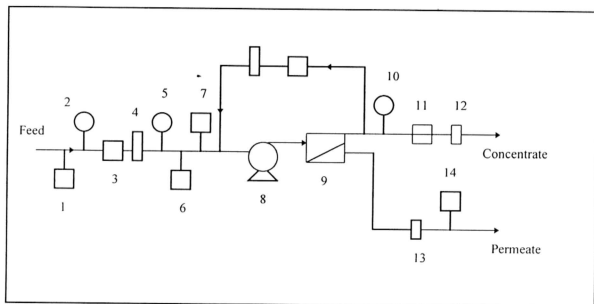


Figure 3.1: Schematic diagram of reverse osmosis system

Component identification:

- | | |
|-----------------------------|--|
| 1. Sample Valve | - For sample of feed solution |
| 2. Temperature Indicator | - Monitors feed solution temperature |
| 3. Solenoid Valve | - Opens during operation for feed solution |
| 4. Cartridge Filter | - 5 micron sediment filter |
| 5. Inlet Pressure Gauge | - Measures pressure of incoming solution |
| 6. pH Sensor | - Probe to monitor feed pH |
| 7. Low Pressure Switch | - Shuts the system down if the inlet pressure is lower than 40 psi |
| 8. High Pressure Pump | - To pressurize the incoming water to the design pressure |
| 9. Membrane Module | - Membrane elements housed in fibreglass epoxy pressure tubes |
| 10. System Pressure Gauge | - Measures the pressure at the exit end of the membrane module |
| 11. Control Valve System | - To adjust concentrate flow |
| 12. Concentrate Flowmeter | - Measures the amount of concentrate water going to drain |
| 13. Permeate Flowmeter | - Measures the amount of permeate |
| 14. Permeate Quality Sensor | - Measures the quality of the permeate |
| 15. Recycle Valve | - Flow control for recycle of concentrate |
| 16. Recycle Flowmeter | - Measures the amount of recycle concentrate |

The capacity of this unit is 5677.5 L/day at 25°C. The system pressure of the unit is 225 psi and the pump feed pressure must be maintained above 40 psi. The membrane used for the spiral-wound module was a thin-film composite reverse osmosis membrane. A schematic of the cross-section of the thin-film composite membrane is shown in Figure 3.2.

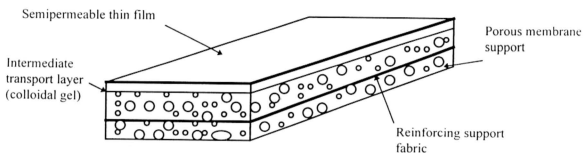


Figure 3.2: Schematic of the cross-section of the thin-film composite membrane used.

3.2.4 Metal Analysis

Nickel in the sample were analysed by an Inductively Coupled Plasma Atomic Emission Spectrometer model 2000 (Baird).