

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Chitosan

Chitosan flake used in this work was kindly provided by Seafresh chitosan (lab) Co., Ltd. (Bangkok) without further purification. Degree of deacetylation and molecular weight of chitosan were reported to be 85% and 2×10^5 , respectively.

3.1.2 Other Chemicals

A water soluble dye and a heavy metal were used as textile waste species in the experiments. For water soluble dye, reactive dye RR180 was kindly supplied by DyStar Thai Ltd. and was used. Its chemical structure is shown in Figure 3.1 (Laszlo, 1997). Cu^{2+} , which was the most concentrated species in textile waste streams, was selected as a heavy metal model in this work; it was purchased in a form of $\text{Cu(II) SO}_4 \cdot 5\text{H}_2\text{O}$ from Labscan (Asia) Ltd.

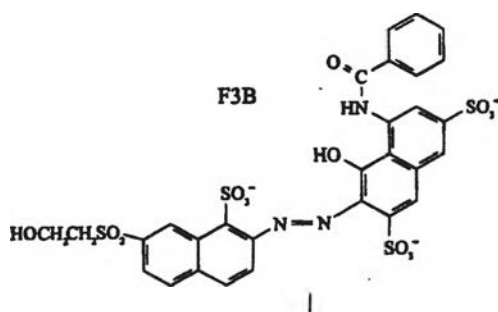


Figure 3.1 Structure of Reactive Red 180.

Acetic acid and sodium hydroxide used for chitosan beads preparation were purchased from Italma Co., Ltd. The crosslinking-agent in this work was glutaraldehyde, which was obtained from Fluka Chemika Ltd. All chemicals were used as analytical grade.

3.2 Methods

3.2.1 Bead Formation Procedure

Initially, the chitosan flake was dissolved in a 4 w/w% acetic acid solution. The final chitosan solution (2 w/v%) was well mixed, and then was pumped dropwise by passing through a hypodermic syringe into a precipitation bath containing a casting solution (2N of NaOH) where chitosan was solidified into a gel-bead form as shown in Figure 3.2. After the beads were formed, they were left in the casting solution for 16 hours, and were then washed with deionized water until the pH was constant.

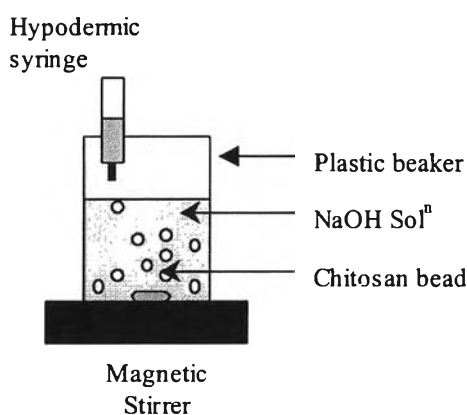


Figure 3.2 Chitosan bead formation by syringe injection technique.

3.2.2 Preparation of Cross-linked Chitosan Beads (CCB)

In order to enhance the acid tolerance and mechanical strength properties, the beads were cross-linked by 1.0 %wt glutaraldehyde aqueous solution at a ratio of 15 ml: 1 g. beads (touch-dried basis) for 10 hours. Before being used, the CCB was washed by deionized water until the pH was constant. All processes were done under atmospheric conditions and at room temperature. The CCB was dried and characterized by a scanning electron microscope (JEOL, JSM 5200) and a BET surface area analyzer (Quantachrome, Autosorb-1).

3.2.3 Batch Liquid Adsorption Experiments

Being major constituents in the waste streams from textile industry, water soluble dye (reactive red, RR180) and Cu^{2+} ions were used in batch adsorption studies by cross-linked chitosan beads.

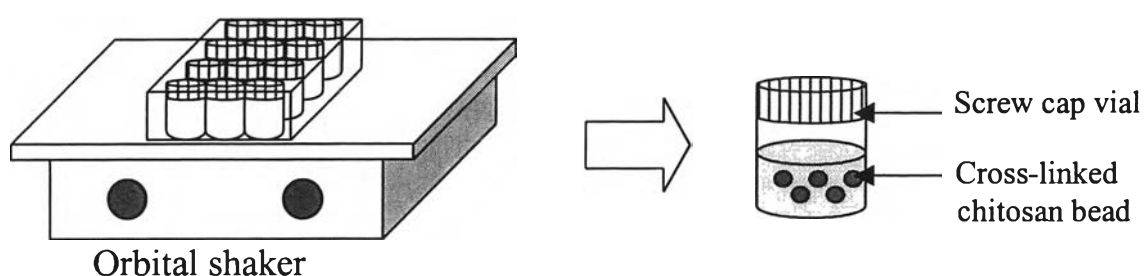


Figure 3.3 Schematic diagram of experimental apparatus for batch operation.

For the dye adsorption, the aqueous solution of reactive red 180 was prepared by dissolving the dye in deionized water to obtain the desired concentrations (200-2000 mg/L). The adsorption studies were carried out in the screw-cap vials shaken by the orbital shaker as shown in Figure 3.3. The ratio between CCB (touch-dried basis), and RR180 solution was fixed at 0.4 g: 25 ml. An adequate shaking speed was set to ensure that the beads were well mixed with the solution and that the effect of film diffusion was negligible. In addition, the variation of pH from 2.0-8.0 was investigated in order to observe the effect of pH during adsorption. A micro volume of hydrochloric acid and sodium hydroxide solution were used for pH adjustment. For the equilibrium study, the system was left for 24 to 48 hours until equilibrium was reached before any measurement was taken. For the kinetic study, samples, initially set as 200 ppm, were taken from the solution phase at predetermined time intervals. The dye concentration was measured by using a UV-VIS spectrophotometer (Perkin Elmer, Lambda 10) at 515 nm.

For Cu^{2+} adsorption, similar experiments as the dye adsorption were carried out. $\text{Cu(II)SO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved by deionized water to obtain the desired concentrations (30-1000 mg/L). The adsorption was performed in the screw-cap vial shaken by the orbital shaker. The ratio between the CCB and the solution was the

same as in the dye adsorption. The system was left on the shaker for 24-48 hours to attain equilibrium conditions. The effect of pH on adsorption was observed by varying the pH from 2.0-8.0. For the kinetic study, the initial concentration of Cu^{2+} ions used was 100 ppm. The concentration of Cu^{2+} ions was analyzed by using an Atomic Absorption Spectrometer (Varian, Spectro AA 300).

For the mixed system adsorption, the mixed solutions were prepared by fixing the molar ratio between RR180 and Cu^{2+} ions at 1:1, in which the concentration of dye and Cu^{2+} ions were in the range of 200-2000 ppm and 20-200 ppm, respectively. The adsorption conditions and wastes analysis were operated as the same as single ions system in both of kinetic and equilibrium adsorption.

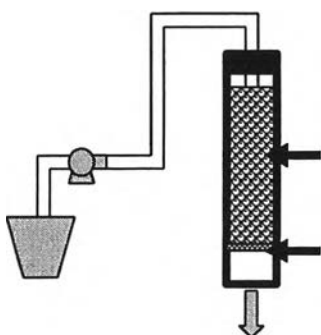


Figure 3.4 Schematic diagram of experimental set-up for continuous flow operation.

3.2.4 Column Adsorption Study

A new 1.6 cm. ID and 10 cm. (height) glass column was used in the continuous flow study. The column was equipped with a circular mesh at the bottom bearing the CCB inside this column, as shown in Figure 3.4. Approximately 13 g of the CCB was packed in the column, and after that the packed column was subjected to passing with deionized water in both upflow and downflow direction several times to ensure that the complete packing of the bed was obtained. The void fraction in the compacted bed (before fluidization) was found to be approximately 0.6. The height of the cross-linked chitosan beads was monitored by means of the scale mounted outside the glass column. The simulated textile wastes, RR180 or Cu^{2+} ions solution

at pH 4, which were initially set at 5 ppm and 10 ppm, respectively, was pumped through the column by a positive-displacement metering micro pump (Masterflex, 7518-12) in the downflow direction. The flow rate of these simulated wastes was predetermined at 1 ml/min. The effluent was pumped out at the bottom of the column and the concentration of the solute in the effluent was analyzed as a function of time by a UV-VIS spectrophotometer for RR180 and by an atomic absorption spectrometer for Cu^{2+} ions using the same method as in the batch adsorption system.