5 Sorbents Used in this Work

5.1 Crosslinked Chitosan

Chitosan was supplied by ABER-Technologie (France) as a flaked material, with a deacetylation percentage ca. 87%. Once crushed, four particle sizes are obtained: G1 < 125 μm < G2 < 250 μm < G3 < 500 μm < G4 < 710 μm.

Chemical crosslinking of chitosan was performed by reacting chitosan flakes with glutaraldehyde aqueous solutions with differing concentrations. The glutaraldehyde crosslinking bath contained concentrations between 0.145 and 1.45 M. The ratio of glutaraldehyde to chitosan (crosslinking ratio CR: mol GA/mol -NH_2) varied between 0.42 and 4.15. Crosslinking lasted for 16 hours. The crosslinking chitosan particles were extensively rinsed with demineralized water. This general procedure was applied to manufacture crosslinked chitosan flakes at the four sizes mentioned above.

5.2 Thiourea Derivative of Chitosan

The thiourea grafting was performed in a two steps procedure: (a) thiourea was reacted with glutaraldehyde for 16 hours, and then, (b) the mixture was contacted with chitosan for 72 hours. After filtration the sorbent was rinsed several times with water and dried at about 50ºC overnight.

Thiourea amounts were chosen among four values: 0 (reference), 1, 2 and 3 g. A glutaraldehyde solution (50% w/w in water) was added at the following levels: 1, 3 and 5 mL. After the reaction between the thiourea and glutaraldehyde, 1 g of chitosan was added to the solution.

The nomenclature, a:b:c was used for the description of the sorbents, were "a" is the mL of glutaraldehyde (50% w/w in water); "b", g of thiourea and "c" g of chitosan (in 20 "c" mL of water).

For the exhaustive investigation of optimized chitosan derivatives (Guibal et al. 2000), the contact time increased for both the preparation time (between thiourea and glutaraldehyde) from 3 to 16 hours and the contact time of the intermediary product with chitosan which was increased from 16 to 72 hours: It is noticeable that the sorbent particle size does not significantly change after chemical modification.

5.3 Chitosan Gel Beads

Chitosan is dissolved in acetic solution (4 w/w %), with a final weight percentage of approximately 4 w/w % chitosan concentration. The viscous solutions is filtered onto 0.5 mm sieve, to remove non-dissolved particles and allowed to stand overnight. The solution is then pumped dropwise into a casting solution of sodium hydroxide (2.5 M), using the apparatus shown in Figure 5.1. The internal diameter of the nozzle is 0.6 mm. To reduce the diameter of the beads, air flows through the apparatus with an increasing flow rate. The air flow made the chitosan drops fall down sooner than they would have fallen by their own weight. Three different sizes of beads were prepared, referred to as small (S), middle (M) and large (L). The chitosan drops coagulated in the alkaline solution and gave perfect spherical beads, whose diameter was measured. After 24 hours of contact with the alkaline solution, beads were removed and rinsed several times with de-mineralized water till the pH did not vary. The same process was applied to the fabrication of gel bead 6 w/w % chitosan concentration.

The crosslinking was performed by mixing for 16 hours the appropriate amount of chitosan beads (calculated using the dry weight) with an aqueous solution of glutaraldehyde at an equimolar concentration (compared to the number of free amine groups in chitosan). The beads were then rinsed several times with water to remove unreacted glutaraldehyde. At each stage of the fabrication, samples (100 or 250 beads, depending on the size of the beads) were collected and dried at 105ºC overnight, to compare water content and measure the weight of the bead for each fabrication procedure. The mean diameter of the beads was also determined for the final products. These measurements were performed in triplicate.

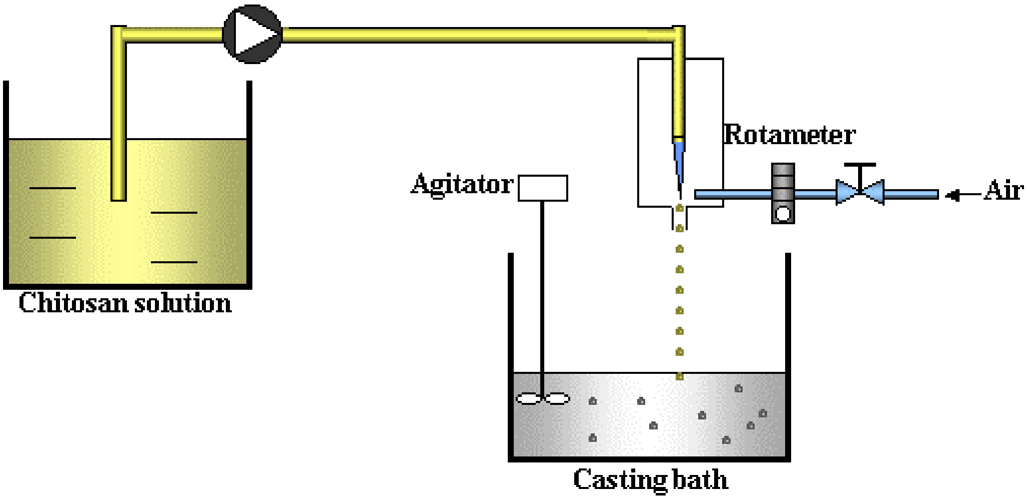

Figure 5.1: Fabrication of chitosan beads.

5.4 Dried and Re-hydrated Beads

After crosslinking, appropriate number of chitosan gel beads of the size M and 4 w/w % chitosan concentration was dried at 60ºC in a oven till their weight became constant. These samples were referred to as dried samples (DB). Dried samples were also re-hydrated in water for 2 days. This sample was referred as re-hydrated chitosan beads (RB).

5.5 Saccharose Beads

Crosslinked beads was brought into contact with a concentrated saccharose solution (145 $g \cdot L^{-1}$) for 30 minutes. The beads were then removed from the solution and dried in an oven at 60ºC till weight was constant. Finally the beads were re-hydrated in water for 2 days and the saccharose was released. The beads were then used for sorption experiments, and referred to as saccharose samples (Sa).

5.6 Hydrogenated Chitosan Gel Beads

The imine functions may be reduced by hydrogenation using sodium cyanohydride or sodium borohydride: the double linkage >C=N- is replaced by a single linkage >C-N< in order to increase the reactivity of the nitrogen site (Wan Ngah and Liang 1999; Muzzarelli 1985; Baba et al. 1998).

The hydrogenation of imine function in the crosslinked material was performed by dissolving 1 g of sodium borohydride in 100 mL of demineralised water, 10 g of wet crosslinked beads were then added to the solution and the slurry was agitated for 6 hours.

The beads were then removed from the solution and rinsed several times with demineralised water. The beads were used as produced, (BH) and after drying/rehydration.

5.7 PEI-grafted Beads

Polyethyleneimine-grafted beads (PEI GA) were prepared according to the following procedure: 5 g of PEI (M_W: 600.000-1000.000) were dissolved in 100 mL dimethylacetamide, 5 g (dry weight) of wet chitosan beads were then added under agitation for 16 hours. The impregnated beads were then separated from the solution and rinsed with 30 ml of dimethylacetamide and the mixed with impregnated beads for 6 hours. Finally, the beads were rinsed several times with water.

5.8 Thiourea-grafted Beads

Two different thiourea derivatives were produced with increasing amounts of thiourea, using a procedure similar to the method previously used for the synthesis of thiourea derivatives of chitosan flakes (section: 5.2). The 3:2:1 thiourea derivative was prepared by mixing 14.4 mL of glutaraldehyde (50% w/w; 8.5 mmol) with 9.6 g of thiourea (12 mmol) and 96 mL of demineralized water for 3 hours. Wet chitosan beads were added (4.8 g, dry weight, 29 mmol -NH_2) and agitated for 16 hours. The modified beads were removed from the solution, rinsed several times and stored in water. For the 1:1:1 thiourea derivative 4.8 mL of glutaraldehyde (3 mmol) was used and 4.8 g of thiourea (6 mmol) for 4.8 g, dry weight (29 mmol -NH_2) of wet chitosan beads (all other experimental conditions were the same). Samples preparations were submitted to the hydrogenation procedure to preparate 3:2:1 BH and 1:1:1 BH samples.