PA 9 - Removal of Copper(II) from Aqueous Solution with Cross-linked Chitosan Beads: a Thermodynamic and Kinetic Study

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Chitosan flakes that were prepared from chitin material extracted from the exoskeleton of lobsters collected from the surroundings of Cape Town, were used to prepare beads. The beads were characterized on pka, degree of deacetylation, degree of cross-linking and water contents relevant to thermodynamic and kinetic studies.
In the adsorption of heavy metals, it is known that the pH influences the adsorption parameters. The pH has two distinct effects: i) it influences the speciation of the metals in solution and ii) it affects the adsorbent, in the specific case of chitosan, this can be quantified in the degree of protonation. In most studies, therefore, different adsorption characteristics are determined at different pH.
In this study, the influence of pH on the mechanism of copper uptake was investigated and a novel equilibrium model was developed in which the adsorption characteristics of the chitosan were described by two equilibrium reactions and a mass balance for the available amine groups.
Adsorption and desorption experiments were performed in batch systems with copper solutions, equilibrium data were collected at different pH values and the proposed equilibrium model was fitted to the data. The model was able to successfully describe the adsorption of copper on cross-linked chitosan beads, and the calculated equilibrium constant (pK_{ads}), which was found to be independent of pH, was determined in the range 2.12-2.83 for beads having different values of DCL. This constant was found to decrease with an increase in the DCL. The adsorbent capacity was a fitted parameter and the maximum capacity (qmax) was determined to be 4.0 (± 2.0) mmol/g. It was found that particle size, DCL and salt concentrations have no significant influence on the maximum adsorbent capacity.
To verify the kinetics of adsorption, a shrinking core model was used, and the model was able to describe the experimental data accurately. Effective diffusion coefficients for copper were obtained by best fit and the calculated average value was in the range $(2\text{-}12)\times10^{-11}$ m^2s^{-1}. The initial uptake rate for beads with higher DCL was found to be lower due to their smaller water contents. Column applications were shown to be adequate for copper regeneration and a regeneration of 3 cycles was achieved in this study.