KINETICS INVOLVING DIVALENT ZINC IONS COMPLEXATION WITH CHITOSAN: APPLICATION TO METAL ION EXTRACTION

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Abstract
A batch process equilibrium study of a snail shell based chitosan-divalent zinc metal complexation in aqueous solution was studied. Zn (II) complexation behaviour could be described using the Langmuir isotherm over the whole concentration range of 10 to1000 mg.L^{-1} Zn at pH 4.5. The results indicate that as the concentration of the Zn (II) is increased, so does the time taken before equilibrium is reached. However that with this method, end concentrations of below 1 mg·L^{-1} can hardly be obtained.

Keywords: Chitosan ligand, complexation, divalent metal, Langmuir

Introduction

The capacity of the chitosan to complex metallic ions is one of its most important potentialities [1]. Depending on the considered cation, this polymer shows selectivity which seems to be independent of the size and the hardness of the ions. Complexing abilities of polymers are used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection [2].

Chelation ion exchange using biopolymers takes advantage of the three dimensional structure of the molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions [3]. This approach is inherently attractive since only the toxic metal ions are removed while the harmless ions can be released into the environment. From the literature it is clear that chitosan can be used to remove numerous trace metals like Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V) and V(IV) from wastewater. In these studies, chitosan has been used in a variety of forms, which include chitosan beads, flakes and membranes [2-5].

Recently, the chitosan from snail shell has been shown to demonstrate an efficient chelating capacity with Zn metal ions and high stability [4]. This strong chelating power serves as technical and economic advantage for chitosan over other biosorbent materials. Generally, the complexing ability which leads to the formation of chelates is attributed to the free amino groups exposed in chitosan and the free OH groups in the ring skeleton [6-8]. A kinetic study is herein carried out using concentration and complexation time as parameters to establish the ligand-metal complexation dependency and the results are hereby reported.

Materials and Methods

The chitosan sample preparation involving sample procurement, deproteinization, demineralization and N-deacetylation of the chitin were carried out using literature methods of Adewuyi *et al.*, [4] and Taboada et al., [9].

The equilibrium complexation reaction was performed by agitating 100 mg of prepared chitosan and 20 ml of different concentrations of zinc metal ion (10-1000 mg.L^{-1} $ZnSO_4.7H_2O$) in a glass-stoppered flask at 300 rpm for the range time of 0 - 2h 30min at room temperature. The mixtures were filtered at desired equilibrium time and the concentration of zinc ion in the filtrate determined by atomic absorption spectrophotometric method.

Results and Discussion

Removal of Zn (II) by chitosan as a function of time at pH 4.5 and at various initial Zn (II) concentrations is shown in Fig. 1. The results indicate that the concentration of the complexed divalent zinc metal increased with increasing agitation time before the attainment of equilibrium. At lower concentrations, less amount of Zn (II) complexed with the chitosan than at higher concentrations. The amount of zinc removed were 195, 130, 85, 45, 25 and 3.1 $mg.L^{-1}$ from initial concentrations of 1000, 800, 400, 100, 50 and 10 $mg.L^{-1}$ respectively.

In a two-component system (sorbent and solution) a graph of the solute concentration in the solid phase Cads ($mg.g^{-1}$) can be plotted as a function of the solute concentration in the liquid phase Ceq ($mg.L^{-1}$) at equilibrium [7] hence, an isotherm can thus be represented. Fig. 2 shows the isotherm of the complexation of the zinc ions by this polymeric chitosan ligand.

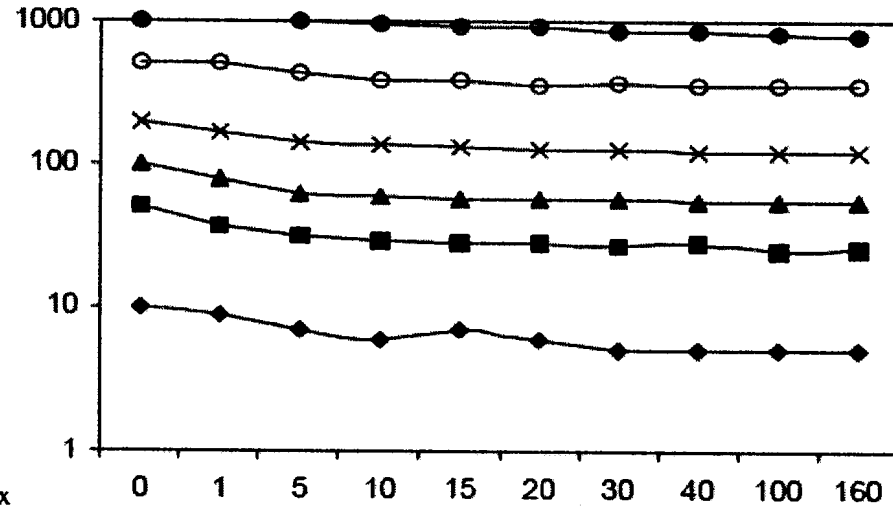

Figure 1: Complex ·), 50(■), 100(▲), 400(x), 800(○) and 1000(●) $mg.l^{-1}$ Chitosan 100 mg; pH = 4.5; Agitation speed = 300 rpm; T = 25 °C

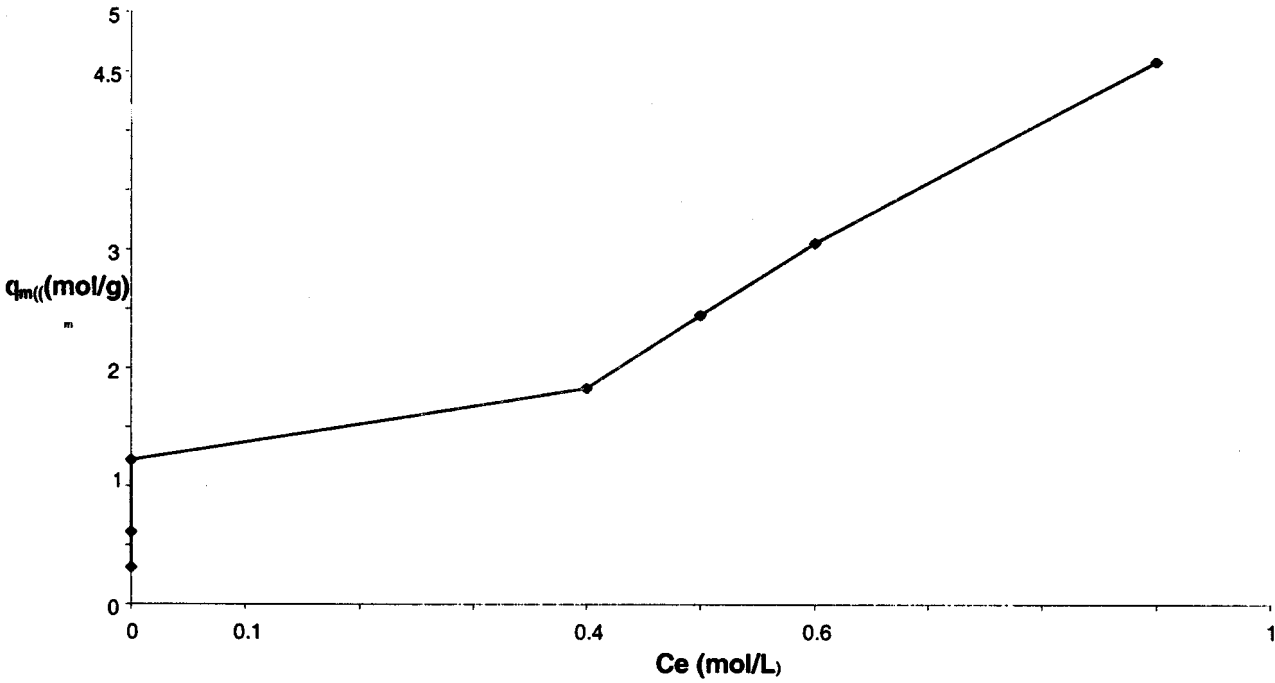

Figure 2 Complexation isotherm of Zn (II) at pH 4.5

The isotherm is characterised by the initial region, which is represented as being parallel to the complexed quantity axis. However, increase in the curve depicts the relevance of its description using the Langmuir isotherm. Hence, the results of the Zn (II) concentration dependence phenomenon were subjected to analyses by means of Langmuir adsorption isotherm (Fig. 3). Langmuir model describes the adsorption taking place in a monolayer i.e. the complexation can only occur at a fixed number of definite localized sites at the surface, and each of these sites can adsorb only one molecule (monolayer). Linearise form of the Langmuir isotherm was employed

$Ce/q = bCe/KL + 1/K_L$

Where:

q= amount of Zn (II) adsorbed (mol.g^{-1})

Ceq = equilibrium concentration of Zn (II) in solution (mg.L^{-1})

K_L = Langmuir constant (Lg^{-1})

b = Langmuir constant (Lmg)

The constant b in the Langmuir equation is related to the energy of the net enthalpy of the complexation process. The constant K_L can be used to determine the enthalpy of the process [1,9]. A plot of the Ce/q vs Ce yielded a straight line (Fig. 3) confirming the applicability of the Langmuir adsorption isotherm.

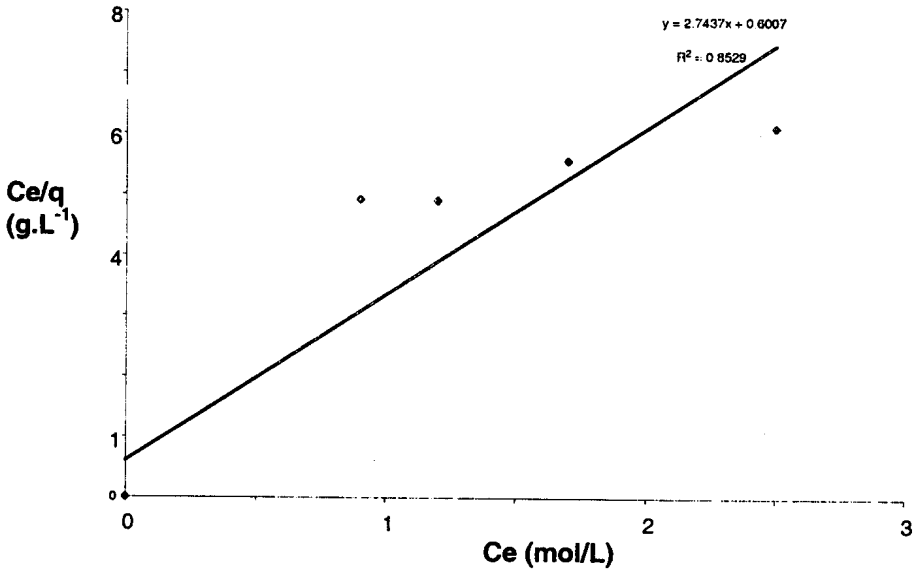

Figure 3: Langmuir isotherm for Zn (II) complexation on chitosan

Conclusion

This study showed that the complexation of Zn (II) ions with chitosan of snail shell origin seems to be concentration driven. The Langmuir isotherm was found as the best isotherm model which explains the ligand- metal interaction in heterogenous mixture. From the experimental data, it is observed that the metal concentration of zinc metal ions can be lowered by means of batch process from 10 $mg.L^{-1}$ (initial lowest concentration) to 3.1 $mg.L^{-1}$.

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