Equilibrium Studies on Complexation Reactions between Chitosan and Heavy Metal Ions by Membrane Ultrafiltration

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Abstract

Chitosan is a natural polycationic polymer including the amine and carboxyl groups, so it is apt to form complexes with heavy metal ions and possesses an excellent adsorption capability for heavy metal ions in wastewater treatment. In this paper, batch ultrafiltration (UF) experiments were conducted to obtain the rejection data of chitosan and metal ions including Cu(II), Ni(II), Zn(II) in aqueous solutions, into which chitosan was dissolved. The feasibility for removing metal ions from dilute solutions with the help of chitosan was also checked. The equilibrium constants of the reactions between chitosan and H^+ (K'_a) as well as between chitosan and metal ions (K'_M), and the average stoichiometric number (n) were evaluated based on the pH trends of UF rejections of metal ions according to a proposed chemical equilibrium model.

Keywords: complexation reactions; chitosan; heavy metals; ultrafiltration; equilibrium constants

1. Introduction

Chitosan is derived from chitin, a polysaccharide found in the exoskeleton of shellfish such as shrimp, lobster, and crabs. It is a natural polycationic polymer (polyelectrolyte) including the amine and carboxyl groups, so it is apt to form complexes with heavy metal ions and possesses an excellent adsorption capability for heavy metal ions in wastewater treatment. In the case of metal anions, the sorption proceeds by electrostatic attraction on protonated amine groups in acidic solutions. However, the presence of ligands and the pH strongly control sorption performance and the uptake mechanism [1]. The sorption of heavy metals including Cu(II), Co(II), Ni(II), Zn(II), Hg(II), Cr(III), Pb(II), and Cd(II) by raw and chemically modified chitosans has been extensively studied [2-8].

Membrane filtration processes can be successfully used for the separation of inorganic species and for their enrichment from dilute solution with the aid of a water-soluble polymer [9]. Nowadays, ultrafiltration (UF) has been shown a promising process for trace metals removal from industrial wastewater, if the metal ions were primarily bound to water-soluble polymers [9-13]

This study focuses on the batch ultrafiltration experiments were conducted to obtain the rejection data of chitosan and metal ions including Cu(II), (II), Zn(II) in aqueous solutions, into which chitosan was dissolved. The feasibility for removing metal ions from dilute solutions with the help of chitosan was also checked. The equilibrium constants of the reactions between chitosan and H^+ (K'_a) as well as between chitosan and metal ions (K'_M), and the average stoichiometric number (n) were evaluated based on the pH trends of UF rejections of metal ions according to a proposed chemical equilibrium model.

2. Materials and Methods

2.1. Materials

Samples of chitosan flakes with average molecular weight 4.1×10^5 by the Mark-Houwink equation from viscosity data of solutions containing chitosan in 0.4 vol% acetic acid and with the deacetylation of approximately 87 mol% following the method of Tan et al. [14], prepared from lobster shell wastes was offered from Ying Huah Co., Kaohsiung, Taiwan. Heavy metals and inorganic chemicals were purchased from Merck Co., as analytical-reagent grade. The deionized water (Millipore Milli-Q) used to prepare all the solution. Commercial cellulose acetate membranes YM10 (MWCO 10,000) and YM30 (MWCO 30,000), manufactured by Amicon Co. were used throughout the experiments.

2.2. Experimental set-up

Membrane filtration experiments were carried out using a dead-end stirred cell (Advantec Model UHP 62, Japan) holding a flat-sheet membrane with an effective area of 28.7 cm^2 (Fig. 1). The cell was stirred at 300 rpm by a magnetic motor, which was high enough but could prevent formation of a serious vortex in the cell.
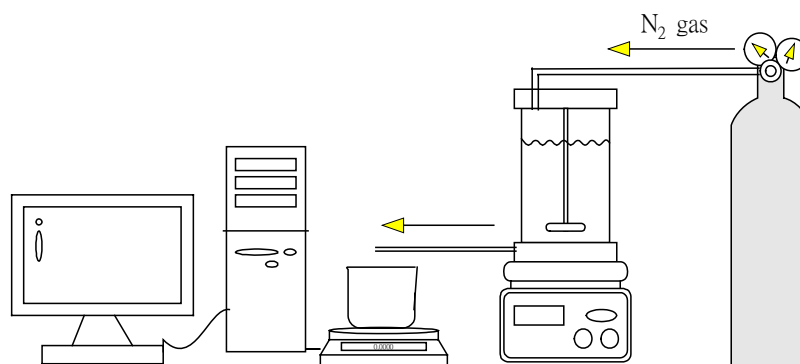

Figure 1. Laboratory installation for dead-end ultrafiltration with computer module

2.3. Experimental procedures

In UF stirred cell experimental, the cell pressure was monitored with N$_2$ gas by means of a transducer and the temperature was fixed at 25°C by air conditioner. The feed volume was 200 cm^3 and the first 10 cm^3 permeate was discarded. A pH meter (Horiba F-23, Japan) can measure the values of solution pH. The concentration of metals in aqueous solutions was measured with an atomic absorption spectrophotometer (GBC Model 9321).

3. Results and Discussion

3.1. UF fluxes and rejection of pure solvent (HAc)

Figure 2 illustrates the effect of applied pressure on the normalized UF flux (J_v/J_w) and solvent rejection for pure acetic acid. Here, the removal efficiency of acetic acid is in terms of the rejection R_{HAc}. It is observed that J_v nearly equals J_w and maintains as well in the applied pressures range tested. However, pure solvent can mostly pass through YM10 and YM30 at pH 2.3.
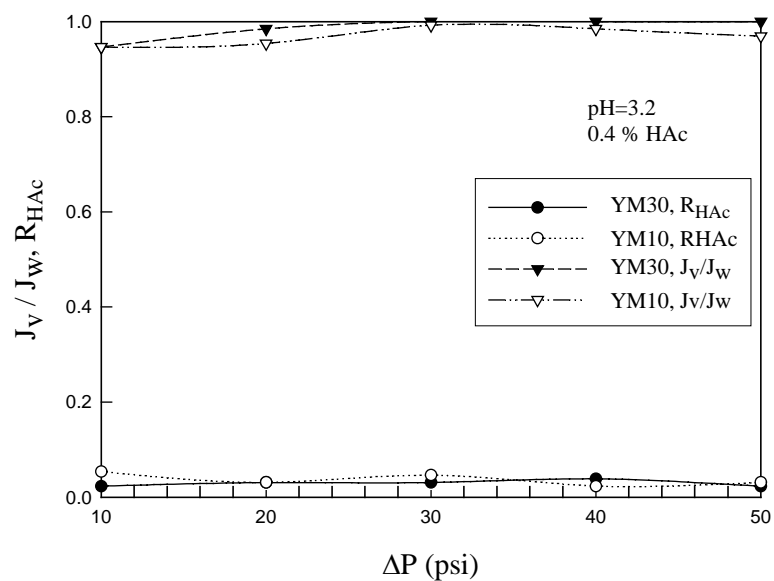
Figure 2. UF flux and HAc rejection at different applied pressures

3.2. Influence of pH on UF fluxes and rejection of pure chitosan solution
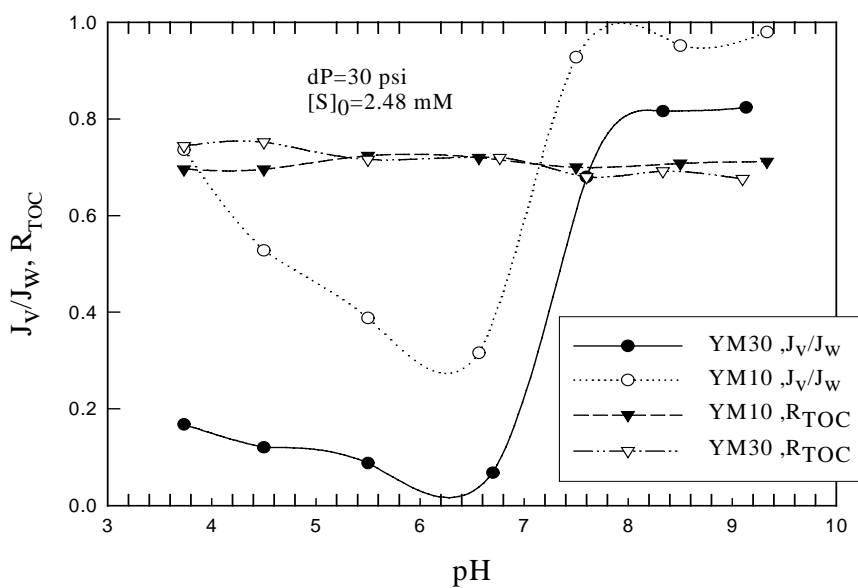

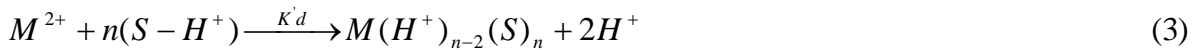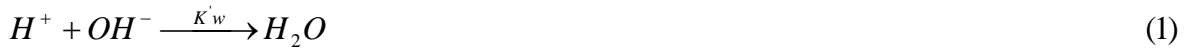Figure 3. UF flux and TOC rejection at different pH values

It is seen that the rejection of chitosan, R_{TOC}, with YM10 and YM30 is about 0.7 (Fig. 3). This is

because the chitosan has a wider molecular weight was measured to be 4.1 x 10^5 or the degradation of chitosan chains are under alkali conditions. On the other hand, (J_v/J_w) drops by raising pH up to 7. A continued increase in pH up to 7 may cause the "more flexible" chitosan aggregates, due to hard protonation of the amino groups in chitosan [15], to enter the pores or make the deposited cake more compressible, resulting in lower flux.
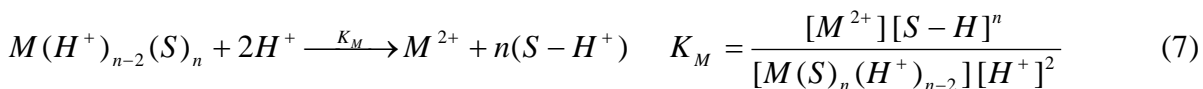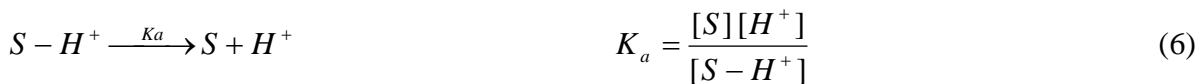
3.3. Equilibrium constants of the reactions between metal and chitosan

Some authors [12,16-17] propose the complexation model applied to the ultrafiltration. The number of chitosan ligands participating in the complex formation with divalent metal ions was found to be one, two, or more than two amino groups, depending on the conditions.

To simplify the calculations, the following assumptions were made: (a) there is no interaction between free metal ions or soluble hydroxyl complexes with the membrane, that is, free metal ions and hydroxyl complexes are not retained by the membrane; (b) the equilibrium constants do not depend on the pH or the concentration of species involved in the reactions; and (c) a rejection coefficient of the unbounded chitosan, R_{TOC}, is the same as that of the metal-chitosan (M^{2+}-S) complex of the unbound [18]. However, these models are not valid to explain the observed phenomenon in the case of chitosan. Taking in account the decrease of retain efficiency when the pH is upper as optimal value, we have considered the competition between hydroxide and polymer to complex the metal [17]. We obtain 4 equations:

$$H^+ + OH^- \xrightarrow{K'w} H_2O \tag{1}$$

$$S + H^+ \xrightarrow{K'a} S - H^+ \tag{2}$$

$$M^{2+} + n(S - H^+) \xrightarrow{K'd} M(H^+)_{n-2}(S)_n + 2H^+ \tag{3}$$

$$M^{2+} + OH^- \xrightarrow{K'b} M(OH)^+ \tag{4}$$

Eqs. (1)–(4) are rearranged, and we have

$$H_2O \xrightarrow{Kw} H^+ + OH^- \qquad\qquad k_W = [H^+][OH^-] \tag{5}$$

$$S - H^+ \xrightarrow{Ka} S + H^+ \qquad\qquad K_a = \frac{[S][H^+]}{[S-H^+]} \tag{6}$$

$$M(H^+)_{n-2}(S)_n + 2H^+ \xrightarrow{K_M} M^{2+} + n(S - H^+) \qquad K_M = \frac{[M^{2+}][S-H]^n}{[M(S)_n(H^+)_{n-2}][H^+]^2} \tag{7}$$

$$M(OH)^+ \xrightarrow{Kb} M^{2+} + OH^- \qquad\qquad K_b = \frac{[M^{2+}][OH^-]}{[M(OH)^+]} \tag{8}$$

The total concentrations of divalent metal ions in the initial feed solution and the permeate can be expressed by the following mass balance relations.

$$[M^{2+}]_0 = [M^{2+}] + [M(S)_n(H^+)_{n-2}] + [M(OH)^+] \tag{9}$$

$$[M^{2+}]_P = [M^{2+}] + [M(OH)^+] \tag{10}$$

Some papers [16,19-20] define the most important features in membrane filtration, which is the rejection coefficient for divalent metal ions.

$$R_{M^{2+}} = 1 - \frac{[M^{2+}]_P}{[M^{2+}]_0} \tag{11}$$

where $[M^{2+}]_p$ and $[M^{2+}]_0$ are the concentrations of divalent metal ions in the permeate and initial feed solution, respectively.

Combing Eqs. (9)-(11), we obtain an expression for the rejection coefficient of metal ions.

$$R_{M^{2+}} = \frac{[M(S)_n(H^+]_{n-2}}{[M^{2+}]_0} \tag{12}$$

Substituting Eqs. (7) and (8) into the Eq. (12), we have

$$R_{M^{2+}} = \frac{\dfrac{[S-H^+]^n}{K_d[H^+]^2}}{1 + \dfrac{[S-H^+]^n}{K_M[H^+]^2} + \dfrac{[OH^-]}{K_b}} \tag{13}$$

Furthermore, only the retention data in the pH 2.3~4.0, were adopted in the present study for the investigation of binding equilibrium. In this case, the effect of the formation of soluble metal hydroxyl complexes can be ignored [21]. Consequently, Eq. (13) become

$$R_{M^{2+}} = \frac{\dfrac{[S-H^+]^n}{K_M[H^+]^2}}{1 + \dfrac{[S-H^+]^n}{K_M[H^+]^2}} = \frac{[S-H^+]^n}{K_M[H^+]^2 + [S-H^+]^2} \tag{14}$$

The total concentration of chitosan, $[S]_0$, can be determined from the following mass balance.

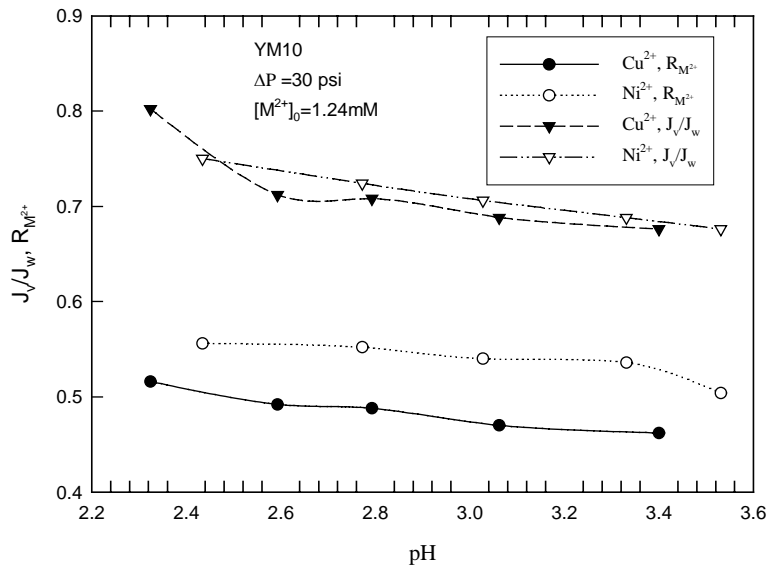$$[S]_0 = [S] + [S-H^+] + n\,[M(S)_n(H^+)_{n-2}] \tag{15}$$

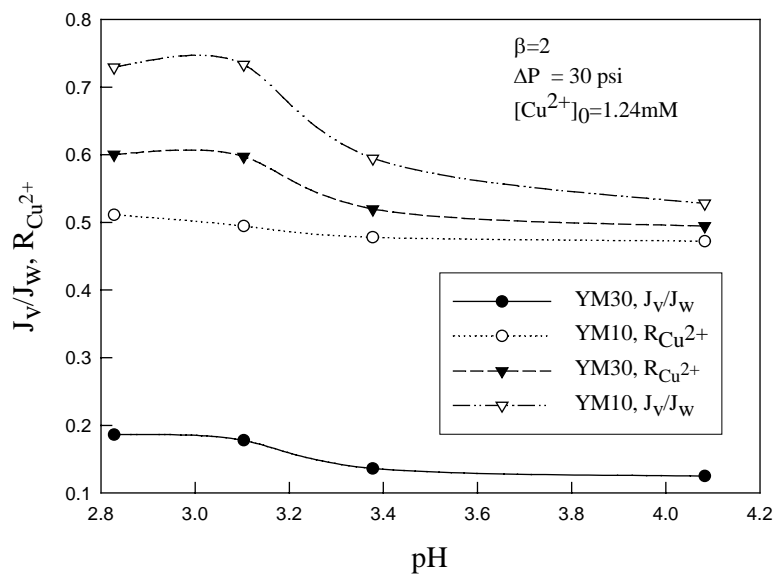Figure 4. UF flux and metal rejection with different pH values atYM10

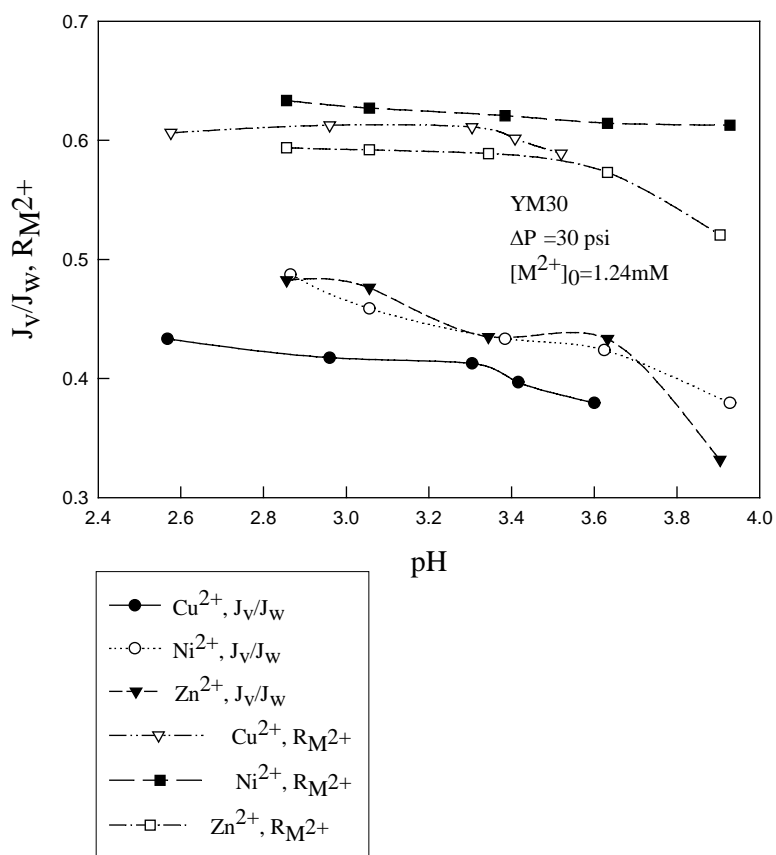Figure 5. UF flux and Cu^{2+} rejection with different pH values at YM10 and YM30

Figure 6. UF flux and metal rejection with different pH values at YM30

We will find out the equilibrium constants of the reactions between chitosan and metal ions (K_M), as the following Eq. (16) from Eqs. (14) and (15) by Masse model [18,21-22].

$$K_M = \frac{1 - R_{M^{2+}}}{R_M^{2+}} \left[\frac{[M^{2+}](\beta - nR)}{K_a + [H^+]} \right]^n [H^+]^{n-2} \tag{16}$$

where β is the initial concentration ratio of chitosan to metal ions, $[S]_0/[M^{2+}]_0$.

The value of n, K_a, K_M can be determined by a trial and error method from Eq. (16), if the values of R_M^{2+}, $[M^{2+}]_0$, β, $[H^+]$ are known by the experiment data of Figs. 4-6. The equilibrium constants of the reactions between chitosan and H^+ ($K'_a = 1/K_a$) as well as between chitosan and metal ions ($K'_M = 1/K_M$) were obtained, and the calculated results are listed in Table 1.

Table 1. Equilibrium constants of chitosan and H^+ (K_a) as well as chitosan and metal ions

		K'_a	K'_M	n
$\beta = 1$	Cu(II)	0.45	7.9×10^7	3.4
	Ni(II)	0.46	5.76×10^6	3.3
$\beta = 2$	Cu(II)	0.53	1.23×10^7	2.9
$\beta = 5$	Cu(II)	0.32	6.1×10^2	0.59
	Ni(II)	0.29	3.9×10^3	0.7
	Zn(II)	0.4	7.89	0.52

4. Conclusions

Equilibrium studies for the binding of chitosan with metals in aqueous sulfates have been carried out at 25^oC by batch UF. The equilibrium constants of the reactions between chitosan and H^+ (K'_a) as well as chitosan and metal ions (K'_M) and the average stoichiometric number (n) between the derived formulae and experimental results were obtained as follows.

$$K_M = \frac{1 - R}{R} \left[\frac{[M^{2+}](\beta - nR)}{Ka + [H^+]} \right]^n [H^+]^{n-2}$$

At pH 2.3~4.0, the value of n increased with increasing concentration ratio (β), and K'_a and K'_M increased with decreasing β on complexations reaction of chitosan-Ni(II). But the values of n and K'_M increased with decreasing β for Cu(II).

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