

The Study of Heavy Metal Treatment through Chitosan Matrix

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INTRODUCTION

Chitosan is polysaccharide and can be obtained by alkaline deacetylation of chitin, which is wide-spread naturally-occurring, structural material. It occurs as principal constituent of the protective cuticles of crustacea and insects, and also in the cell wall of some fungi and microorganism¹⁾. Although chitin is insoluble to water and usual organic solvent, chitosan is soluble in dilute acidic solution and a chitosan membrane can easily be prepared²⁾.

Recently, chitosan has been used in biomedical fields because of its favorable characteristics, such as good biocompatibility, and was reported useful for pharmaceutical preparations³⁻⁶⁾.

Few studies of chitosan have been done on the permeation sodium, copper⁷⁾, and halogen ion through chitosan membrane⁸⁾, chelating film-forming and coagulating ability of the chitosan-glucan complex from *Aspergillus niger* industrial waste⁹⁾.

It is worthwhile to evaluate chitosan membrane with a view to finding a possible utility for treatment of heavy metal. Mercury, cadmium and chrome were used as model metal in this study.

Therefore, the permeation of several metal through chitosan membrane was investigated influence by the pH value.

EXPERIMENTAL METHODS

Materials

Chitosan was purchased from Sigma Co.(Saint Louis, Mo, U.S.A). The other reagents were obtained from various commercial sources and the highest grade available.

Preparation chitosan membrane

Chitosan membrane was prepared according to the method reported by Hirano¹⁰. Chitosan (300mg) was dissolved in 2% acetic acid at room temperature to give a viscous solution. The solution was diluted with 95% methanol and poured into a glass Petri dish to give a thin liquid layer. To the liquid layer was added two mol equivalent of a carboxylic anhydride, which had been dissolved in 95% methanol. The solution was decanted. The treatment was repeated several times. The membrane was washed with ether and air-dried to give the corresponding membrane. Finally, the membrane was soaked in 10% NaOH solution for 24 hours and washed with water.

Measurement

Permeability of heavy metal in the chitosan membrane was determined in a glass diffusion cell (Fig 1) with two compartment of equal volume (176ml), the membrane (14.2cm²) was clamped between the compartment. Each compartment was stirred continuously at 1600 r.p.m. by externally mounted constant-speed synchronous motors. Initially, one chamber was filled with pH solution. The second chamber was filled with a desired pH solution containing 1 mM/l of mercuric chloride, cadmium chloride and chromic chloride, respectively.

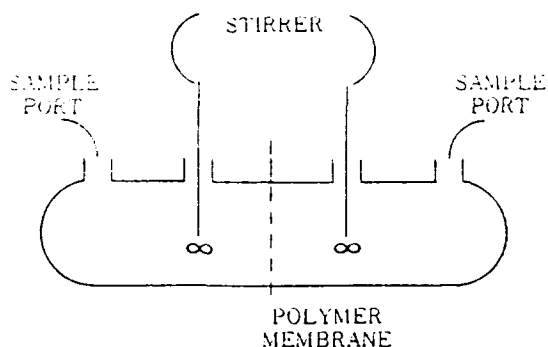


Fig. 1 Schematic diagram of the diffusion cell.

The thickness of the membrane was measured at several points by micrometer, and the mean value was 0.05 cm for the chitosan membrane.

The water content of the membrane was measured by the usual method shown as follows:

$$\text{water content (\%)} = (W_w - W_d) \times 100/W_w$$

where W_w (g) and W_d (g) are the weight at wet membrane and dry membrane, respectively. The degree of swelling of the membrane was determined by the following equation.

$$\text{swelling degree} = S_m / S_o$$

where S_o (cm³) is the volume of the membrane swollen with the mixed aqueous solution of 0.1M NaCl and 0.1M NaOH and S_m (cm³) is the volume of the membrane swollen with a desired pH solution adjusted by adding 0.1M HCl to the above-mixed aqueous solution.

The concentration of metals was determined by the ultraviolet absorption method, using a shizazu 210 A set spectro photometer ; Hg⁺² at 490 nm ; Cd⁺² at 520 nm ; Cr⁺³ at 540 nm. All experiments were carried out in triplicate.

pH variation

The effect of pH on the permeation properties of chitosan membrane was measured concentration of released 1 mM metals from pH 4 to pH 14, obtained by addition of HCl or NaOH to the sink solution only.

RESULT AND DISCUSSION

A schematic representation of the permeation through a membrane is given Fig 2, where it has been assumed that the equilibrium partition coefficient, K_d , defined ;

$$K_d = \frac{V_s (C_o - C_s) d}{V_m \cdot C_s}$$

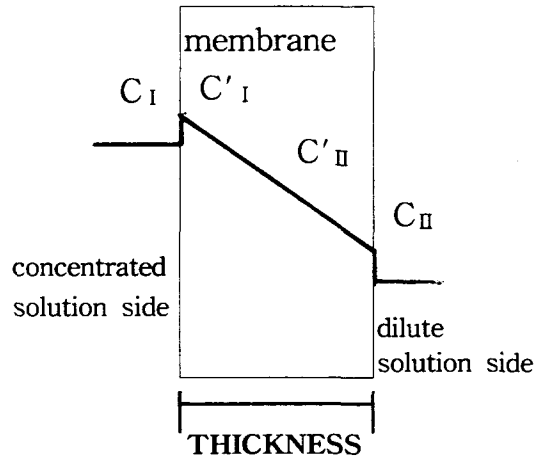


Fig.2 Diagrammatic representation of solute permeation through a polymer membrane.

where V_s , V_m , C_o , and C_s are the volume of solution, volume of chitosan membrane, initial metal concentration in solution at equilibrium, respectively. Transport through a polymer membrane is governed by Fick's first law

$$J = - D \left(\frac{d m}{d \ell} \right) \quad - 1$$

When a linear concentration gradient exists within a barrier membrane, the instantaneous concentration gradient within the membrane may be expressed

$$\frac{- d C_m}{d \ell} = \frac{C_I - C_{II}}{\ell} \quad - 2$$

where C_I and C_{II} represent the surface concentration of solute at the donor (I) and receptor (II) sides of the membrane.

ℓ represents the membrane thickness. Provided the partition coefficient, K_d , is independent of the solute concentration, this equation may be rewritten as

$$\frac{-d C_m}{d \ell} = \frac{K_d(C_I - C_{II})}{\ell} \quad - 3$$

where C_I and C_{II} are the donor and receptor phase concentration. Substituting equation 3 into equation 1 gives

$$J = \frac{DK_d (C_I - C_{II})}{\ell} = \frac{U (C_I - C_{II})}{\ell} \quad - 4$$

where the permeability $U = D \times K_d$

During the steady state, the flux out of compartment I equals the flux into compartment II which equals the flux within the polymer membrane.

This is expressed as

$$-J = \frac{V}{A} \times \frac{dC_I}{dt} \quad - 5$$

$$J = \frac{V}{A} \times \frac{dC_{II}}{dt} \quad - 6$$

where V is the compartment volume and A is the membrane area. Subtracting equation 6 from equation 5 and equating to equation 4, gives

$$\frac{d(C_I - C_{II})}{d t} = \frac{-2UA(C_I - C_{II})}{V \ell} \quad - 7$$

assuming equal compartment volumes. Equation 7 is valid only during steady state flux. Using these restrictions as limits of integration for equation 7, gives

$$\ln \left(\frac{C_3 - C_4}{C_1 - C_2} \right) = \frac{-2UA}{V \ell} (t_{ss} - t_{oss}) \quad - 8$$

Steady state mass balancing gives

$$C_0V = C_1V + C_2V + C_mV_m \quad - 9$$

$$C_0V = C_3V + C_4V + C_mV_m \quad - 10$$

where C_0 is the initial concentration of solute in the donor phase, C_m is the solute concentration within the membrane and V_m is the membrane volume.

The equation within the membrane may be defined as

$$C_m = \frac{Kd(C_1 + C_2)}{2} = \frac{Kd(C_3 + C_4)}{2} \quad - 11$$

substitution of equation 11 into equation 9 and 10 and rearranging, gives

$$C_1 = \frac{2}{2V + KdV_m} \left(C_0V - C_2V - \frac{Kd C_2 V_m}{2} \right) \quad - 12$$

and

$$C_3 = \frac{2}{2V + KdV_m} \left(C_0V - C_4V - \frac{Kd C_4 V_m}{2} \right) \quad - 13$$

Substituting equation 12 and 13 into equation 8 and rearranging, gives

$$\ln \left(\frac{C_0V - (2V + Kd V_m) C_4}{C_0V - (2V + Kd V_m) C_2} \right) = \frac{-2UA}{V \ell} (t_{ss} - t_{oss}) \quad - 14$$

In the limit where Kd is small and t_{oss} approaches zero, C_2 will also approach zero and equation 14 may be written as

$$-\ln \left(1 - \frac{2C_4}{C_0} \right) = \frac{-2UA}{V \ell} t \quad - 15$$

Equation 15 was developed for the case of quasi-steady state diffusion in a membrane assuming that the amount of solute within the membrane was negligible.

The permeation coefficient for the metals in membrane was calculated from equation 14. A plot of

$$\ln \left(\frac{C_0V - (2V + Kd Vm) C_4}{C_0V - (2V + Kd Vm) C_2} \right) = \text{versus } (t_{ss} - t_{oss}) \quad - 16$$

will yield a line with a slope of $\frac{-2UA}{V \ell}$

From known values of A,V and ℓ , the permeability, U, is calculated¹¹⁾.

The diffusion coefficient is obtained from equation $D = \frac{U}{Kd}$

The values of U, Kd, and D for the various metal through chitosan membrane are shown in table I. Figures 4 is plots of the fraction of metal permeation versus pH value for chitosan membrane.

Table I. Permeability coefficient (U), diffusion coefficient (D) and partition coefficient (Kd) of metal through chitosan membrane at room temperature

Metal	pH	$U \times 10^{-7} \text{ cm}^2/\text{s}$	$D \times 10^{-9} \text{ cm}^2/\text{s}$	Kd
Hg ⁺⁺	7.0	3.479	2.806	124
Cd ⁺⁺	8.0	1.369	1.181	116
Cr ⁺⁺⁺	8.0	1.399	1.166	120

membrane thickness 0.05cm. surface area 14.2 cm²

Table I was calculated from the data up to 6 hrs.

The permeation of metal through the chitosan membrane followed equation 16 and was thought to proceed mainly by the charge state, it also depended upon the metal ion chelation¹²⁾ on chitosan membrane.

The effect of pH of the solution on the swelling degree of membrane is shown in Fig 3.

The membrane swelled in the acidic solution, but not in alkaline solution.

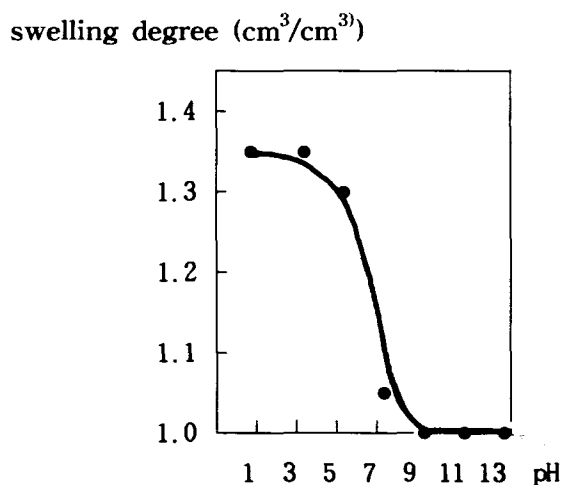


Fig. 3 Effect of H⁺ ion concentration in the solution immersed the membrane on the swelling degree of the chitosan membrane.

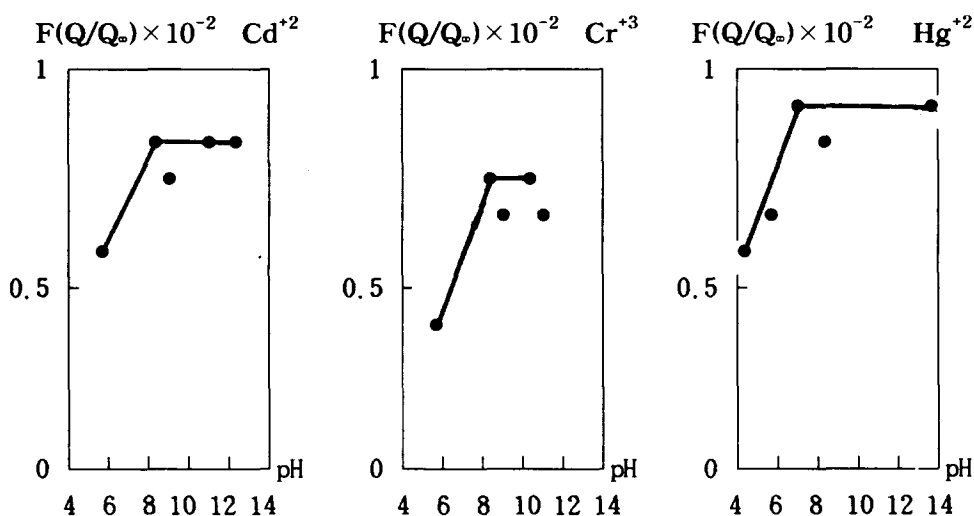


Fig. 4 Fraction permeability for metal ions on chitosan membrane vs pH value. $F(Q/Q_0)$; Fraction permeability

In Fig 4, with Hg^{+2} maxima is observed from pH 7, whereas Cd^{+2} and Cr^{+3} show maxima from pH 8, respectively.

The result behaved as expected, showing on increased treatment for metal ions through chitosan membrane as the pH increased.

Therefore, if a state of alkali in sink solution both sides could be kept for longer times, that is, the diffuse transport of metal ion from chitosan membrane should be prevented.

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The Study of Heavy Metal Treatment through Chitosan Matrix

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> Abstract <

Chitosan (β -D-glucosaminan) is chemically prepared from chitin (N-acetyl- β -glucosaminan), which is on natural resources.

We now report on the suistability of the chitosan matrix for use as vehicles for the treatment heavy metal in waste water.

Mercury, cadmium, and chromium were used as model metals in this study.

The permeation of mercury, cadmium and chromium on chitosan membrane was determined in a glass diffusion cell with two compartment of equal volume, and was investigated influence versus pH value, respectively.

The permeability of mercury, cadmium, and chromium were $3,479 \times 10^{-7} \text{cm}^2/\text{s}$, $1,369 \times 10^{-7} \text{cm}^2/\text{s}$, and $1,399 \times 10^{-7} \text{cm}^2/\text{s}$, respectively.

With mercury maxima is observed from pH 7, whereas cadmium and chromium show maxima from pH 8, respectively.

The effect of pH of the solution on the swelling degree of membrane is shown swelling in the acidic solution, but not in the alkaline solution. Therefore, if a state of alkali in sink solution both sides could be kept for longer times, that is, the diffuse transport of metal ion from chitosan membrane should be prevented.