

# Preparation of Fructose-Mediated (Polyethylene glycol/Chitosan) Membrane and Adsorption of Heavy Metal Ions

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**ABSTRACT:** Chitosan is an efficient metal chelator, but its practical use is limited due to the stability in acid solutions, adsorption capacities. In this study, we attempt to find a new pH-dependent adsorbent based on fructose-mediated chitosan/PEG membrane and examines several experimental parameters relative to their formation and characteristics. The membrane was characterized in terms of their fourier transforms infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectra, X-ray diffraction (XRD) analysis, surface morphologies, tensile strength, mediating degree analysis, and swelling behavior at pH 3 and 6 medium. To estimate the potential of these membranes as a biosorbent, the capability and behavior for the adsorption of heavy metal ions were investigated using Lead ions as a model compound. FTIR-ATR result showed that the Schiff's base reaction was favor formed in high pH condition. Swelling study showed that the swelling degree of homogeneous

mediated membrane decreases as the pH of the final fructose-mediated chitosan/PEG gel increase, which was demonstrated by mediating degree analysis. Low crystallinity of fructose-mediated membranes is responsible for its sorption efficiency. With increasing the amount of fructose in the chitosan/PEG there is a proportionality of the adsorption capacity except that the high fructose content (10 wt %). The pH 6 treated 5 wt % fructose-mediated membrane has a maximum sorption capacity to about 185 mg/g. The adsorption isotherms could be well fitted by the Langmuir equation. The results showed the potential applicability of fructose-mediated chitosan/PEG membrane as a biosorbent for metal recovery. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1480–1489, 2007

**Key words:** adsorption; chitosan; fructose; swelling; stress

## INTRODUCTION

Heavy metal contamination of various water resources are of concern to the public because most of the heavy metals are toxic and are not biodegradable, accumulation and distribution of these metals to our environments. Traditional treatment methods such as ion exchange, reverse osmosis, adsorption, complexation, and precipitation have been applied. Adsorption is considered an effective and economical method for removal of pollutants from wastewater.<sup>1</sup>

Many materials of biological origins have been studied as adsorbents to remove various heavy metal ions from water and industrial effluents. Among biopolymers, chitosan has been one of the most promising adsorbents for the removal of metal ions from aqueous solution and is widely used in waste treatment applications. Chitosan is an amino polysaccharide derived from the *N*-deacetylation of chitin.

Chitosan and its derivatives have been extensively developed in many applications including paper production, textile finishes, heavy metal chelation, wastewater treatment, cosmetic, pharmaceutical production, and biomedical applications.<sup>2</sup> Chitosan molecules contain many of reactive hydroxyl and amino groups, and can adsorb metal ions in neutral solutions. However, in acidic solutions the protonation of amino groups lead to interesting properties for the electrostatic attraction of anionic complexed cations. It is possible to improve significantly adsorption properties by physical or chemical modification.

Physical modification increases the sorption properties, gel formation, and involves an expansion of the porous network. For example, through the formation of blends and interpenetrated or semi-interpenetrated polymer networks with highly hydrophilic polymers such as poly(vinyl-alcohol) (PVA)<sup>3</sup> and polyether,<sup>4</sup> membranes with varying degrees of hydrophilicity have been obtained and used as matrices for different applications. Polyethylene glycol (PEG) has been widely used because of their biocompatibility and minimal toxicity and good solubility in water or other common solvents. Chitosan/PEG hydrogel can swell extensively due to the positive charges on the network

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and in response to changes in the pH of the medium. It is possible significantly to improve adsorption properties of chitosan through the formation of blends with PEG.

Chemical modification, on the other hand, increases the sorption properties of chitosan while preventing the dissolution of chitosan in strong acids. Most commonly used chemical modifications are crosslinking, grafting, carboxymethylation, and acetylation.<sup>5</sup> A crosslinking step is required to reinforce the chemical stability of the biosorbents in acidic solutions. Crosslinking can change the crystalline nature of chitosan and enhance the resistance of chitosan against acid, alkali, and chemicals and also increase the sorption abilities of chitosan. Crosslinking with dialdehydes, such as glutaraldehyde, ethylene glycol diglycidyl ether, epoxides or epichlorohydrin are examples of chemical modifications on chitosan.<sup>6</sup> These reactions are usually carried out to prevent chitosan dissolution in acidic solutions or to increase metal adsorption capacity or to enhance selectivity. However, the chemical crosslinking agents may induce toxicity and another contamination.<sup>7</sup> Until now less of biocompatible reagent such as genipin have been used to crosslink chitosan.<sup>8</sup> Using reduced sugar such as glucose that have aldehyde group as a stabilizer has been developed in our group by homogeneous (modified membrane obtained by dissolution of chitosan/PEG gel in acetic acid and glucose) or heterogeneous (modified membrane obtained by mediating chitosan/PEG membrane in glucose solution) reaction process.<sup>9</sup> According to Koyama et al.'s study,<sup>10</sup> the adsorption capacity is reduced from the increase in heterogeneous crosslinking process but the homogeneous crosslinking process caused an increased adsorption capacity of metal ions. Therefore, a chitosan-based biosorbent prepared by a homogeneous process is preferred. Otherwise, the reaction between amino group and aldehyde groups involves the formation of a Schiff base is called maillard reaction. However, the reactivity and stability of maillard reaction end products are highly influenced by the pH of the reaction system. The open chain form of the glucose and the unprotonated form of the amino groups are favored at higher pH, but the stability of the end products is still a controversy. Fructose is the most important ketose sugar, a hexose, and is a reducing sugar. The keto group of fructose can react with free amino group of gelatin molecule resulting in formation of an aminoglycoside. The aminoglycoside can further react with another amine group (again from gelatin) originating a crosslinked structure.<sup>11</sup> Therefore, fructose was studied as a means to stabilize chitosan/PEG gel by a homogeneous reaction process.

In this article, we focused on the investigation of microstructure formation of fructose mediated-chitosan/PEG membrane by a pH-dependant homogene-

ous reaction. The effects of preparation conditions, such as the concentration of fructose and the reaction pH on the properties of fructose-mediated chitosan/PEG membrane were investigated by FTIR-ATR, X-ray diffraction (XRD) analysis, swelling studies, mediating degree analyses, tensile strength, and scanning electronic microscopy (SEM). Furthermore, the capability and behavior for the adsorption of heavy metal ions were investigated using lead ions as a model compound.

## EXPERIMENTAL

### Materials

Chitosan with low molecular weight (degree of deacetylation is 53%,  $M_W \sim 1.5 \times 10^5$ ) was obtained in the flake form from Fluka (Buchs, Switzerland). PEG ( $M_n = 6000$ ) was purchased from Riedel-de Haën (Seelze, Germany).  $\alpha$ -fructose was used as a mediating agent and was supplied by J. T. Baker (Phillipsburgh, USA). 2,4,6-trinitrobenzenesulfonic acid was used for determination of mediating degree of fructose-mediated chitosan/PEG membrane (Shanghai, China). Lead nitrate was supplied by Riedel-de Haën (Seelze, Germany). All other reagents were extra-pure grade and were used as received.

### Preparation of fructose-mediated chitosan/PEG membrane

Chitosan (3 g) was dissolved in 100 mL of 2% aqueous acetic solution. The mixture was stirred for 4 h to obtain a perfectly transparent solution. A chitosan/PEG blend solution was prepared by the mechanical stirring of the chitosan and PEG flakes in a 70:30 ratio at room temperature. The appropriate amount of fructose (0, 3, 5, and 10 wt %) was then added, with continued stirring until the solution was clear again. The final pH value of fructose-mediated chitosan/PEG gel was adjusted to 3 and  $4 \times 1M$  hydrochloride acid then to 5 and  $6 \times 1M$  sodium hydroxide, respectively. Then the fructose-mediated chitosan/PEG gel was thermally treated at 120°C in an oven for 1 h. The membranes of the resulting polymer blend were obtained by casting into polystyrene Petri dishes and incubating for 2 days in an oven at 68°C. The membrane was rinsing with deionized distilled water (DDW) and dried at ambient temperature overnight then cut into  $2 \times 2 \text{ mm}^2$  squares.

### FTIR-ATR spectrum analysis

FTIR-ATR spectra were recorded on Thermo Nicolet NEXUS 470 FTIR to observe the chemical structure of the fructose-mediated chitosan/PEG membrane. The pH treated fructose-mediated chitosan/PEG mem-

brane were dried in vacuum at 40°C for 24 h before the IR test.

### XRD analysis

The X-ray diffraction measurements of pH treated fructose-mediated membrane were carried out using Ni-filtered Cu K $\alpha$ -radiation on a Rigaku D/max3 Vx X-ray diffractometer (Tokyo, Japan) operating at 30 kv and 30 mA from 10 to 30° (2 $\theta$ ) at a scan rate of 4° (2 $\theta$ )/min.

### SEM observation

The surface morphology of pH treated fructose-mediated chitosan/PEG membranes were observed by using JEOL 3100 scanning electron microscope (Tokyo, Japan) at 25 kV. The platinum-coated membrane surface was prepared under an argon atmosphere.

### Equilibrium swelling study

The pH treated fructose-mediated chitosan/PEG membrane was predried in a vacuum oven at 30°C for 24 h before measurement. Then the membrane was suspended in a glass bottle containing 20 mL of swelling media and incubated in a water-bath at 30°C. After soaking for 24 h, the membrane was taken out, and the excess water was removed carefully with filter paper from membrane surface and then weighed immediately in a microbalance. The media for the swelling studies were pH 3 and pH 5 DDW, respectively. The degree of swelling for each sample at time  $t$  was calculated using the relation  $(W_t - W_0)/W_0$ , where  $W_t$  is the weight of the swollen membrane at time  $t$  and  $W_0$  is the initial weight of the membrane. The measurement was repeated several times to obtain an average value of swelling degree for each sample.

### Degree of mediating of the pH treated fructose-mediated chitosan/PEG membrane

Degree of mediating of the chitosan/PEG membrane was determined by 2,4,6-trinitrobenzenesulfonic acid (TNBS) assay.<sup>12</sup> Briefly, About 5 mg of membrane was treated with a mixture of 1 mL of 0.5% solution of TNBS and 1 mL of 4% sodium bicarbonate at 60°C for 4 h. The unreacted chitosan in the membrane reacts with TNBS and forms a soluble complex. One mL of this solution was further treated with 3 mL of 6N HCl at 40°C for 1.5 h and its absorbance was determined at  $\lambda_{\max} = 345$  nm after dilution spectrophotometrically. All the experiments were done in triplicate. The

degree of mediating was calculated as eq. (1):

$$\text{Degree of mediating(\%)} = \left\{ 1 - \frac{\frac{\text{Absorbance of mediated membrane/}}{\text{Mass of mediated membrane}}}{\frac{\text{Absorbance of nonmediated membrane/}}{\text{Mass of nonmediated membrane}}} \right\} \times 100(\%) \quad (10)$$

### Mechanical analysis

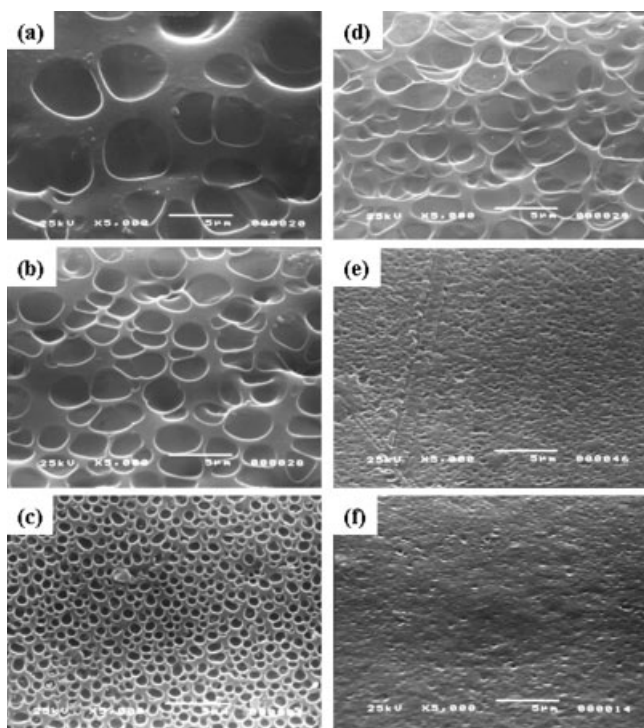
Tensile strength and elongation at break of the films were measured on a SANS CMT-6503 Test Machine versatile tester (Shenzhen, China) according to the ISO6239-1986 standard with a tensile rate of 5 mm min<sup>-1</sup>. The size of the films was 70 mm length, 10 mm width, with 50 mm distance between two clamps. Five parallel measurements were carried out for every sample.

### Lead adsorption experiments

Stock solution (1000 ppm) of Lead ion was prepared by using lead nitrate Riedel-de Haën (Seelze, Germany). The stock solution was then diluted to give standard solution of appropriate concentration. Batch experiments were conducted in 250 mL beakers and equilibrated using a magnetic stirrer. Then 100 mL aliquots of these standard solutions were placed in 250 mL beakers and chitosan/PEG or fructose-mediated chitosan/PEG membrane was added. After equilibration, the lead nitrate solutions were filtered through papers and quantified by GBC Scientific Equipment Sens AA Flame atomic absorption spectrophotometer (Melbourne, Australia). Lead-free and sorbent-free blanks were used as controls. Lead ions uptake experiments were conducted under constant pH value between 3 and 7 by adding 1M hydrochloride or 1M sodium hydroxide as required. Fructose-mediated chitosan/PEG membrane was equilibrated at the particular pH for about 24 h at 260 rpm and at an initial lead ion concentration of 100 ppm. Isotherm studies were conducted with a constant fructose-mediated chitosan/PEG membrane weight (0.10 g) and varying initial concentrations of lead ion in the range of 50–500 ppm. Amounts of lead ions taken up by the sorbent in each flask were determined by the following mass balance eq. (2):

$$Q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where  $Q$  is the sorption capacity (mg/g),  $C_0$  and  $C_e$  are, respectively, the initial and solution phase lead ions concentration at equilibrium (ppm),  $V$  the solution volume (L), and  $W$  the mass of sorbent (g).



**Figure 1** Surfaces morphology of (a) pH 3 treated 3 wt % fructose-mediated membrane (b) pH 3 treated 5 wt % fructose-mediated membrane (c) pH 3 treated 10 wt % fructose-mediated membrane (d) pH 4 treated 5 wt % fructose-mediated membrane (e) pH 5 treated 5 wt % fructose-mediated membrane (f) pH 6 treated 5 wt % fructose-mediated membrane.

For batch kinetic studies, 0.02 g chitosan/PEG and fructose-mediated chitosan/PEG membrane were equilibrated under optimum conditions as mentioned earlier. The membrane and 100 mL of lead ion solutions (100 ppm) were placed in 250 mL beakers and stirred by a magnetic stirrer. The sorption time was varied between 10 and 100 min. During the kinetic experiments, samples were withdrawn at fixed time intervals, filtered, and quantified by Flame atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

### Morphology of fructose mediated chitosan/PEG membranes

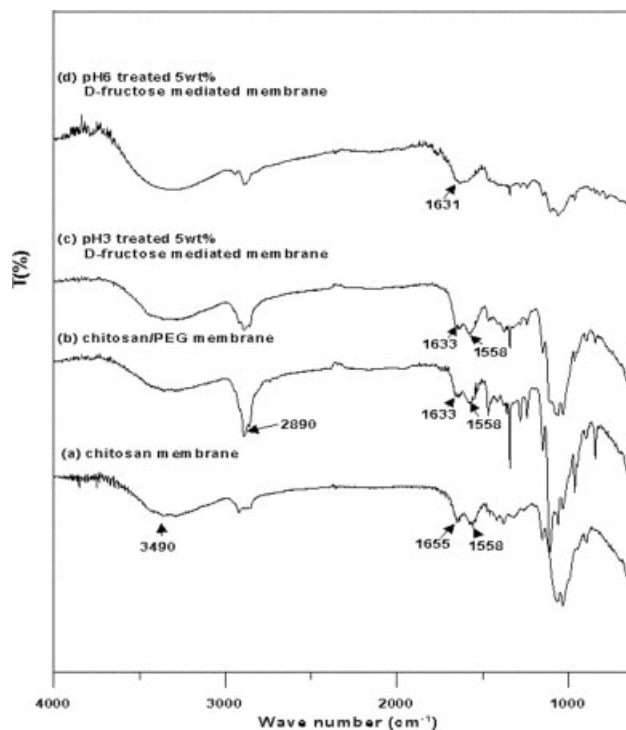
Figure 1(a–c) shows the morphologies of pH 3 treated fructose-mediated membrane with different fructose feeding weight. The 3 wt % fructose-mediated membrane display many round valley-like surfaces. It may be due to the low number of keto group reactive with free amino group of chitosan made the chitosan main chain rigid and restricted its engagement in gel solution. It will pull closer low number of the chitosan main chain displacement and the large valley-like structure will be formed. With increasing fructose feed in weight to 5, the surface morphologies changed

to more compact surface with small pores as shown in Figure 1(b). A homogeneous nature of the reaction mixture can be obtained. However, as fructose feed in weight increase to 10, larger micro pores presented on the surface that may decrease the physical property of membrane. It indicates that lot of unreactive form of fructose remain in membrane because of over feeding fructose in chitosan/PEG gel solution resulted in large micro voids formed.

The effects of reaction pH on the morphology of fructose-mediated membrane were distinct. The large pores vanish gradually on the pH 4 treated 5 wt % fructose-mediated membrane surface as shown in Figure 1(d). When the pH condition increase to 5, the mediated membrane has changed to a microporous surface pattern. Finally, the pH 6 treated 5 wt % fructose-mediated membrane shows a denser and compact surface pattern than the pH 5 treated 5 wt % fructose mediated one as shown in Figure 1(f). At high pH mediating environment, the membrane can change to uniform structure. It shows that the maillard reaction between chitosan/PEG and fructose are favored in high pH condition.

### Intermolecular interaction between the components

Figure 2 shows the FTIR-ATR spectra of chitosan, chitosan/PEG, pH 3, and pH 6 treated 5 wt % fructose-mediated membrane. Pure chitosan shows a distinct amide I band and amide II band at 1655 and 1558  $\text{cm}^{-1}$ ,



**Figure 2** FTIR-ATR spectra of (a) chitosan (b) chitosan/PEG (c) pH3 treated fructose-mediated membrane (d) pH 6 treated fructose-mediated membrane.

respectively. N—H stretching and O—H stretching vibrations can be characterized by the broad peak in the region of 3310–3450  $\text{cm}^{-1}$ . A relatively high intense peak seen at 2890  $\text{cm}^{-1}$  corresponded to an aliphatic C—H in the chitosan/PEG membrane. The 843, 1280, and 963  $\text{cm}^{-1}$  peaks can be clearly seen, which are the contributions from the crystalline region in PEG. Figure 2(c) shows that the pH 3 treated 5 wt % fructose-mediated chitosan/PEG membrane spectra except that the peak at 1655  $\text{cm}^{-1}$  moved to a lower wave number 1633  $\text{cm}^{-1}$  coupled with the decrease in the absorbance of the 1558  $\text{cm}^{-1}$  as shown in. In contrast with spectra Figure 2(c,d) (pH 6 treated fructose-mediated membrane), a significant peak at 1631  $\text{cm}^{-1}$  and coupled with the disappearance of peaks at 1558  $\text{cm}^{-1}$  in the spectra is due to the formation of C=N and this is because of the imines reaction between amino groups from chitosan and keto group in fructose. It also implied that the reaction between chitosan and fructose was favor in pH6 environment. This result was similar to chitosan/PEG mediating with glucose.<sup>13</sup>

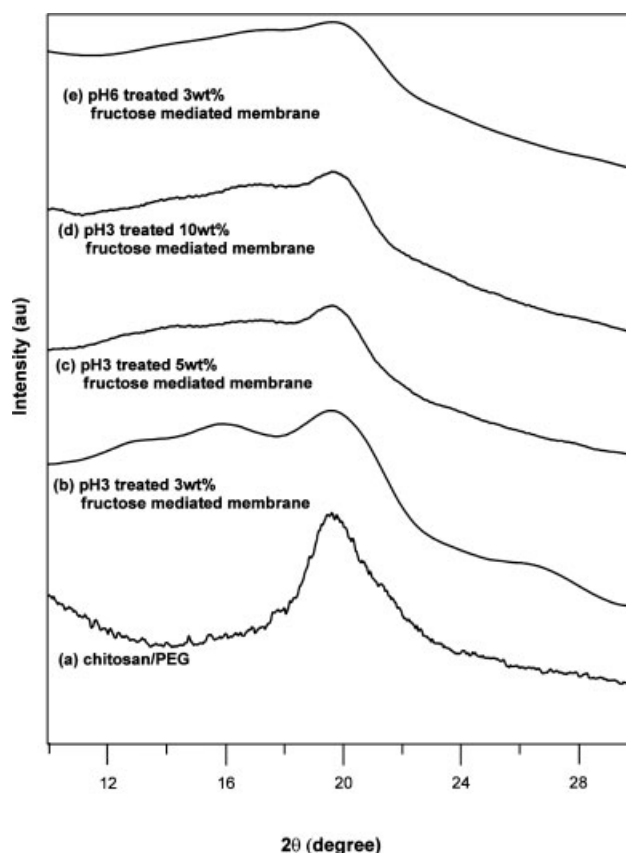
### XRD analysis

X-ray diffraction measurements were carried out to evaluate the crystalline state of chitosan and different pH treated fructose-mediated membrane. In Figure 3, the XRD pattern of chitosan sample exhibits the presence of major peak at  $2\theta = 20^\circ$ , which correspond to the (100) reflection. However, the major peak ( $2\theta = 20^\circ$ ) in pH 3 treated fructose mediated membrane lose their prominence as the fructose concentration increase. In addition, for pH 3 and pH 6 treated fructose-mediated membrane, the peak at  $2\theta = 20^\circ$  disappeared or decreased. The decrease in crystallinity of fructose-mediated membrane could be attributed to the deformation of strong hydrogen bond in the chitosan backbone as amino groups were reacted with the keto groups of fructose in linear form.<sup>14</sup> It suggests that the crystal structure of fructose-mediated membrane is more distorted due to more keto groups presented in high fructose concentration. In compared with the crystal structure of pH 6 and pH 3 treated 3 wt % fructose-mediated membrane, the broadening of the chitosan diffraction main peak is mainly because of to the more active fructose in linear form at high pH condition. In addition, for the pH 3 and pH 6 treated fructose mediated membrane, the diffractograms did not show any other peak, which is illustrated in Figure 3. This indicates that the crystal structure of chitosan/PEG have been destroyed after mediated with fructose. Many studies have shown that decreasing the crystallinity results in an improvement in metal ion sorption properties.<sup>15</sup> Fructose-mediated chitosan/PEG membrane exhibits lower crystallinity

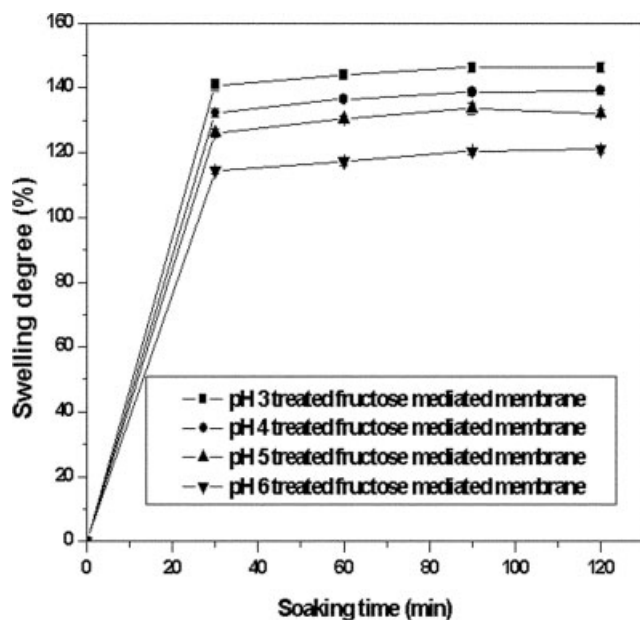
due to the malliard reaction, as a result, the lead sorption rate would improve significantly.

### Swelling studies

The swelling behavior of pH treated fructose mediated chitosan/PEG membrane in pH 3 medium is shown in Figure 4. As can be seen in Figure 4, swelling degree of the fructose-mediated membrane decreases gradually from 145.32% to 116.03% with an increasing pH treated condition in pH 3 mediums. As we know, most of the fructose molecule is a stable chair ring form at low pH environment. However, the fructose is much easier to transform into a reactive linear open chain molecules from stable chair ring structure due to open ring reaction at high temperature and high pH condition. Therefore, more fructose is expected to reduce the numbers of  $-\text{NH}_2$  groups of chitosan at high pH condition. Hence, the low swelling degree of the pH 6 treated fructose-mediated membrane may be due to more fructose molecule presented in a linear form at pH 6 condition and resulted in more Schiff base products formed. Therefore, the polymer precipitates contain more Schiff base product and less free amino groups. This can be demonstrated by media-

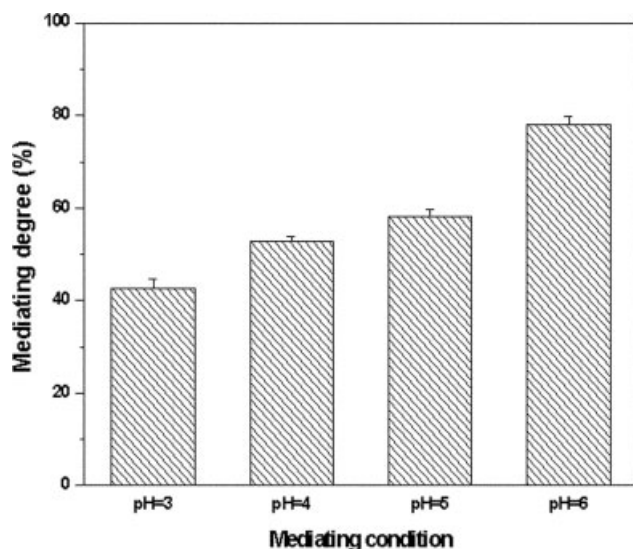


**Figure 3** XRD patterns of chitosan/PEG and pH treated fructose-mediated membrane. XRD patterns of chitosan/PEG and pH treated fructose-mediated membrane.

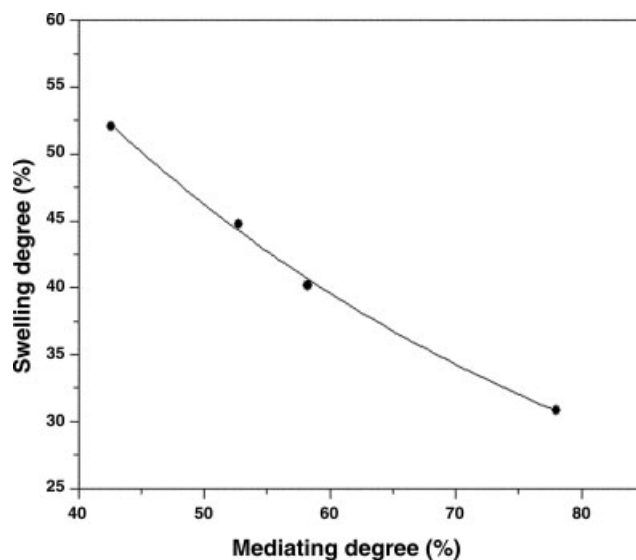


**Figure 4** Swelling behavior of fructose-mediated chitosan/PEG membrane as prepared by different pH condition (pH = 3, 4, 5, and 6) in pH 3 medium.

ting degree measurement. The increase of mediating degree indicates that the decrease of the free amine groups can easily explain the swelling behavior.<sup>12</sup> Figure 5 shows that an increase of the mediating degree with the increase of the pH value of the mixture, which demonstrates that the Schiff's reaction occurs. Figure 6 also shows the swelling degrees with the variations of the mediating degree between the chitosan/PEG membranes in pH 6 mediums. It can be found that as the mediating degree increase, the swelling degree decrease in pH 6 medium, which demon-

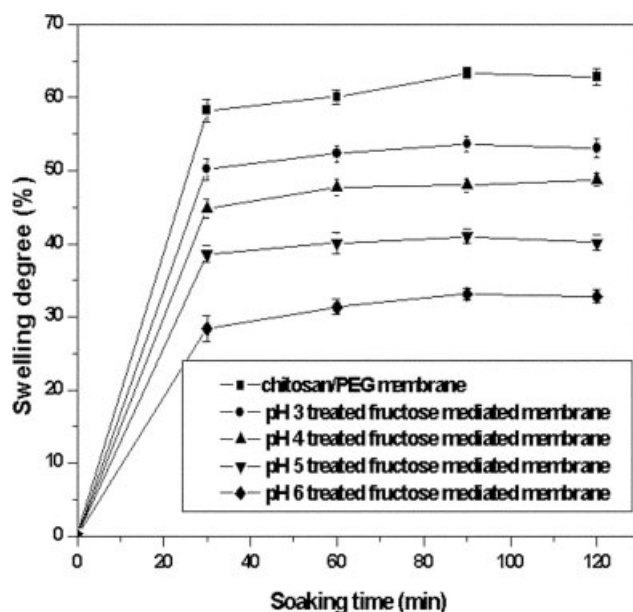


**Figure 5** Degree of mediating of fructose-mediated chitosan/PEG membrane with different mediating condition.

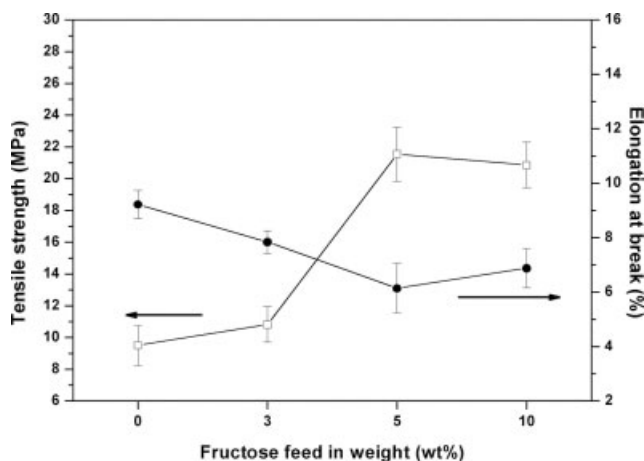


**Figure 6** Effect of mediating degree on the swelling degree of fructose-mediated membranes in pH 6 medium.

strated that the reaction between the keto and the NH<sub>2</sub> group lead to the decrease in the amino group number of chitosan. As we expected, the swelling degrees of the pH 3, 4, and 5 treated fructose-mediated membranes also are higher than the pH 6 treated one at pH 6 mediums as shown in Figure 7. It may also be because of the more stability of Schiff base formation product in neutral medium. In general, fructose can improve the stability of chitosan/PEG membrane especially prepared by high pH condition and a pH-dependent membrane can be obtained.



**Figure 7** Swelling behavior of fructose-mediated chitosan/PEG membrane as prepared by different pH condition (pH = 3, 4, 5 and 6) in pH 6 medium.



**Figure 8** The fructose feed in weight dependence of the tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) for the pH 6 treated fructose-mediated membrane.

### Mechanical properties of fructose-mediated membrane

The fructose feed in weight dependence of the tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) for the pH 6 treated fructose-mediated membrane is shown in Figure 8. The elongation at break of the fructose-mediated membrane increases to maximum values 6.14%, with a decrease of the fructose feed in weight to 5 wt %, and then slightly increase to 6.88% with the fructose feed in weight to 10 wt %. The tensile strength of pH 6 treated fructose-mediated membrane increases to maximum values 21.54 MPa with the fructose feed in weight increases to 5 wt %, and then slightly decreases to 20.86 MPa with the increase of fructose feed in weight to 10 wt %. The results indicate that the fructose could be a stabilizer with the chitosan/PEG network and contribute to their ultimate strength. Meanwhile, as the fructose feed in weight increases, the improvement in the tensile strength could be resulted from an enhancement in maillard reaction between chitosan/PEG and fructose. According to Wan et al.'s study,<sup>16</sup> when chitosan membranes were prepared with glutaraldehyde as crosslinking agent, the crystalline domains in the crosslinked chitosan membrane are partially destroyed, and the crystallinity of the membranes decreases gradually with an increasing concentration of the glutaraldehyde. The decrease in crystallinity of fructose-mediated membrane was similar to Wan et al.'s study. The crystal structure of fructose-mediated membrane is more distorted because of more keto groups presented in high fructose concentration. As we know, for chitosan membranes, the mechanical properties are simultaneous controlled by both the crystallinity and crosslinking degree. Normally, larger crystalline regions and higher crystallinity in a membrane can enhance the mechanical strength of the membrane if only one factor, the crys-

talline of the membrane, have been considered. However, the membrane is also enhanced by crosslinking between chitosan molecules, although the crosslinking degree is low. When the concentration of the fructose is increased to a certain point, after which a higher crosslinking degree is achieved, enough bridges and even a crosslinked network may be set up between the chitosan molecules so that the tensile strength of the membrane is enhanced further.

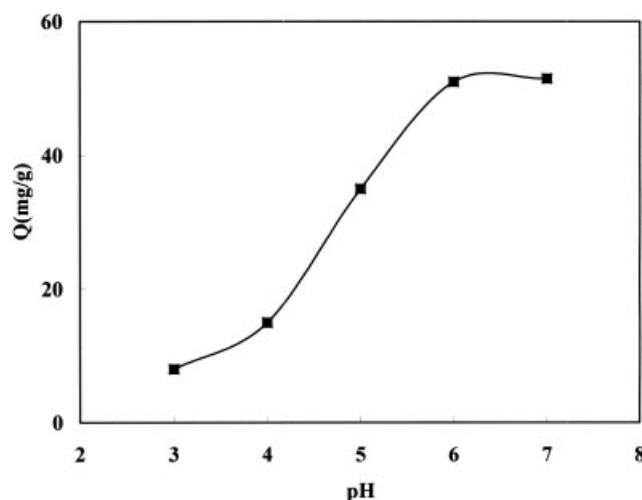
### Sorption kinetics for lead ions

#### Influence of pH value on sorption

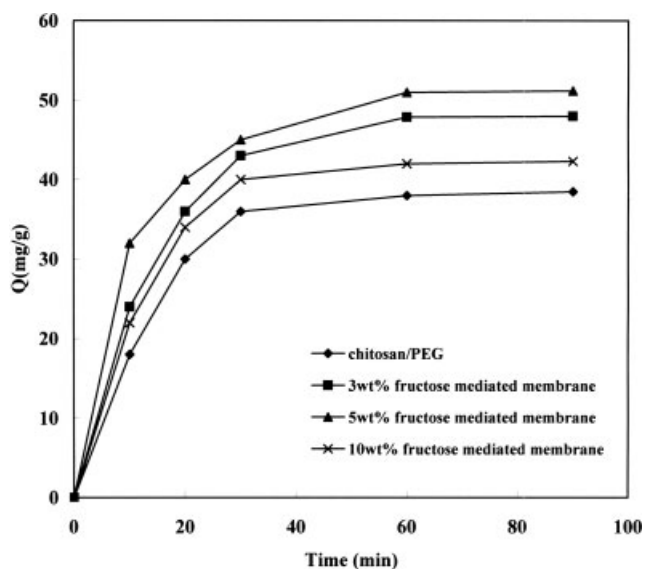
Figure 9 shows the effect of the pH on the sorption of  $\text{Pb}^{2+}$  by pH 6 treated 5 wt % fructose-mediated membranes. It is found that the adsorption of lead increased with increasing pH of the solution. In acidic solutions, more protons will be available to protonate amine groups to form groups  $-\text{NH}_3^+$ , reducing the number of binding sites for the adsorption of lead. While, higher pH adsorption of lead increases due to the decrease of  $\text{H}^+$ . The maximum adsorptions of lead ions on fructose-mediated membrane were found at pH 6. It is reported that the pKa value of chitosan is about 6.5, at higher pH beyond 6.5, precipitation of lead hydroxide occurs simultaneously with the sorption of lead ions, which will affect the sorption of the membrane.<sup>17</sup> Hence, the capacity of the membrane is limited up to certain value above pH 6.

#### Influence of mediating degree on sorption

Figure 10 shows the sorption kinetics at different mediating degree with pH 6 treated fructose-mediated membrane. The adsorption capacities of all the fructose-mediated membranes are distributed between 5 and 10 wt % fructose-mediated membrane.

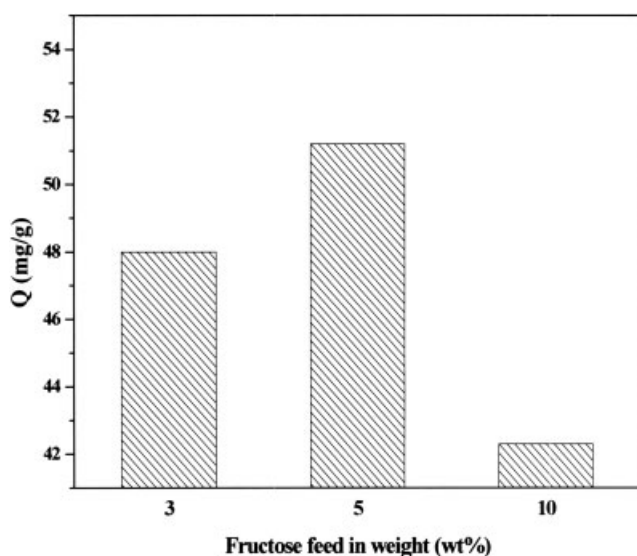


**Figure 9** Effect of the pH on the sorption of  $\text{Pb}^{2+}$  by pH 6 treated 5 wt % fructose-mediated membranes.



**Figure 10** Sorption kinetics at fructose feed in weight with pH 6 treated chitosan/PEG membrane.

Fructose-mediated membrane (5 wt %) have a high sorption capacity to 52 mg/g when contacting with 100 ppm lead ion solution. However, all fructose-mediated membranes show very similar adsorption kinetics with 100 min of batching at 30°C. Comparing chitosan and fructose-mediated membrane, an increase in the maximum adsorption amount is observed in the latter. This result is similar to Oyrton et al.<sup>14</sup> studied the adsorption of  $\text{Cu}^{2+}$  ions on natural and crosslinked chitosan. The studied shows that the adsorption capacity is reduced from the increase in heterogeneous crosslinking process. However, the homogeneous crosslinking process obtained by the dissolution of chitosan in acetic acid and glutaraldehyde



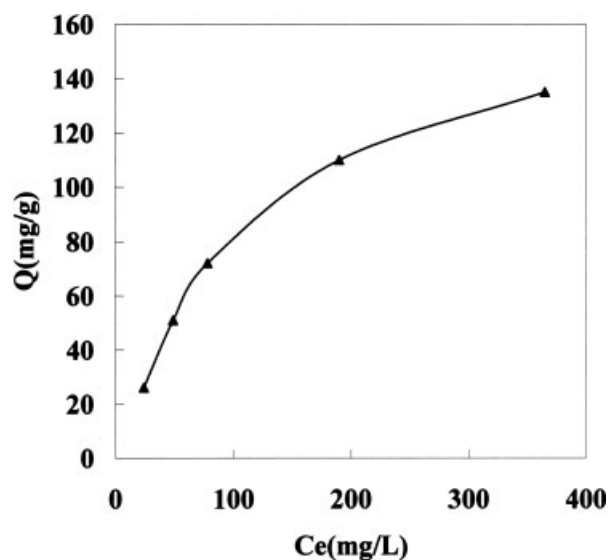
**Figure 11** The fructose feed in weight dependence of the adsorption capacities of lead ions.

solution caused an increased adsorption capacity to metal ions. The fructose-mediated membrane obtained also was by a homogeneous solution process, which resulted in increased adsorption of lead ions.

Figure 11 shows that the adsorption capacities of lead ions increase slowly as the fructose feed in weight was raised from 3 wt % to 5 wt %. However, beyond the point of 5 wt %, increasing the fructose feed in weight leads to the significant decrease of the adsorption capacity. The results were similar to Suna and Wang who studied the adsorption properties of  $\text{Cu}^{2+}$  on glutaraldehyde crosslinked carboxymethyl-chitosan.<sup>18</sup> The initial increase in lead ions adsorption was attributed to the lower levels of mediating in the precipitates prohibiting the formation of closely packed chain arrangements without any great reduction in the swelling capacity. At higher levels of mediating, the precipitates had lower swelling capacities, which resulted in lower accessibilities, because of the more extensive network and also its amino groups blocked with increased fructose content. Otherwise, the impact of the mediating treatment is observed on the availability of adsorption sites. Since fructose mediated with amino groups are involved in Schiff's base reaction with keto groups of the fructose, and the amino groups involved in the chemical reaction is unable to chelate lead ions, then the adsorption capacity obviously decreases. As a result they are not available for adsorption.

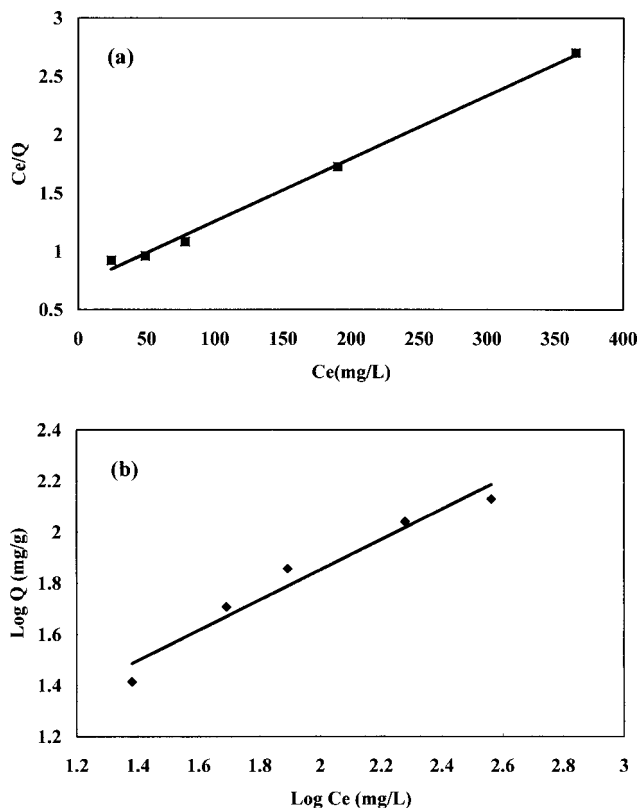
### Isotherm of adsorption of lead ions

Figure 12 shows the experimental equilibrium isotherms for sorption of lead ions on pH 6 treated 5 wt % fructose-mediated membrane. The result showed that



**Figure 12**  $\text{Pb}^{2+}$  sorption isotherms by pH 6 treated 5 wt % fructose-mediated membrane.





**Figure 13** (a) Langmuir and (b) Freundlich plots for  $\text{Pb}^{2+}$  uptake by pH 6 treated 5 wt % fructose-mediated membrane.

the concentration of lead ions remaining in solution and the sorption capacity increased with the initial concentration of lead ions increasing. When the concentration of lead ions at equilibrium was 365 ppm, the sorption capacity reached 136 mg/g, which had been improved than that of chitosan.<sup>19</sup> The Langmuir model<sup>20</sup> [Eq. (3)] was used to describe the data obtained for the equilibrium of Pb adsorbed onto fructose-mediated membranes.

$$\frac{C_e}{Q} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max}b} \quad (3)$$

where  $C_e$  is the equilibrium concentration of lead ions ppm,  $Q$  the amount of lead ions sorbed per unit weight of fructose-mediated membrane/chitosan at equilibrium (mg/g),  $Q_{\max}$  the maximum amount

adsorbed on a monolayer (mg/g), and  $b$  the Langmuir sorption equilibrium constant (mL/mg) and it is a measure of the energy of sorption. A linearized plot of  $C_e/Q_e$  against  $C_e$  gives  $Q_{\max}$  and  $b$  [Fig. 13(a)]. The widely used empirical Freundlich equation [Equation (4)] based on sorption on a heterogeneous surface is given by<sup>21</sup>:

$$\log Q_e = \left(\frac{1}{n}\right) \log C_e + \log k \quad (4)$$

where  $k$  and  $n$  are Freundlich constants indicating sorption capacity and intensity, respectively.  $k$  and  $n$  can be determined from a linear plot of  $\log Q_e$  against  $\log C_e$  [Fig. 13(b)]. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table I. It is found that the adsorption of  $\text{Pb}^{2+}$  on the fructose mediated membrane correlated well ( $R > 0 : 99$ ) with the Langmuir equation as compared to the Freundlich equation under the concentration range. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,  $R_L$  which is used to predict if an adsorption system is "favorable" or "unfavorable". The separation factor,  $R_L$  is defined by eq. (5)<sup>22</sup>:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where  $C_0$  is the initial  $\text{Pb}^{2+}$  concentration (ppm) and  $b$  is the Langmuir adsorption equilibrium constant (mL/mg). Table II lists the calculated results. Based on the effect of separation factor on isotherm shape, the  $R_L$  values are in the range of  $0 < R_L < 1$ , which indicates that the adsorption of  $\text{Pb}^{2+}$  on fructose-mediated membrane are favorable. Thus fructose-mediated membrane is favorable adsorber.

## CONCLUSIONS

A pH-responsive fructose-mediated chitosan/PEG membrane was successfully prepared by homogeneous mediating process at different pH condition. Swelling measurements showed that fructose can improve the stability of chitosan/PEG membrane especially

**TABLE I**  
Langmuir and Freundlich Isotherm Constants and Correlation Coefficients

Metals	Langmuir			Freundlich		
	$Q_{\max}$ (mg/g)	$B$ (mL/mg)	Correlation coefficient	$k$	$n$	Correlation coefficient
$\text{Pb}^{2+}$	185.185	0.0075	0.9957	4.6644	1.6880	0.9542

**TABLE II**  
 **$R_L$  Value Based on the Langmuir Equation**

$C_0$ (mg/L) <sup>a</sup>	$R_L$ values
50	0.727273
100	0.571429
150	0.470588
200	0.307692
500	0.210526

<sup>a</sup> Where  $C_0$  stands for the initial concentration of lead ions in solution.

prepared by high pH condition (pH = 6) and a pH-dependent membrane can be obtained. The result of tensile strength of pH 6 treated fructose-mediated membrane, which is coincidence with the result of swelling study and mediating degree measurement, indicate that the fructose could be a stabilizer with the chitosan/PEG network and contribute to their ultimate strength. Fructose-mediated membranes possess lower crystallinity than chitosan illustrated by XRD patterns. The low crystallinity of fructose-mediated membranes is responsible for its sorption efficiency. The concentration of fructose strongly affects the physical and chemical properties of the chitosan/PEG membrane formed. With increasing the amount of fructose in the chitosan/PEG, there is a proportionality of the adsorption capacity. Therefore, the adsorption capacity of all fructose-mediated membrane are distributed between the 5 and 10 wt % fructose-mediated membrane. The pH 6 treated 5 wt % fructose-mediated membrane has a maximum sorption capacity to about 185 mg/g. The adsorption isotherms could be well fitted by the Langmuir equation. The results showed the potential applicability of fructose-

mediated chitosan/PEG membrane as a biosorbent for metal recovery.

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