

## **Preparation, Characterization and Application of Chitosan/ Polyethylene Glycol Blend Film for Removal of Iron from Water**

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### **Abstract**

Cross-linked chitosan (CS) with sub-micrometer porous structure were prepared by extraction of poly(ethylene glycol) (PEG) from CS/PEG blend film according to wet phase inversion method and were examined for iron removal from aqueous solutions. The developed films were characterized using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and differential scanning calorimeter (DSC) analysis to understand their physico-chemical properties. The adsorption parameters, such as contact time, pH, and metal ion concentration were studied. By increasing CS:PEG ratio in the blend film the adsorption capacity of iron ions increase, and the equilibrium achieved after 60 minutes. The experimental data were better fitted to Freundlich equation than Langmuir equation. The regenerated blend films could be used up to four cycles of adsorption/desorption without losing efficiency.

**Keywords:** *Chitosan, Blend Film, Adsorption, Iron Ions*

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### **1. Introduction**

Heavy metals are well known for their toxicity for human beings. They are soluble in water as ions or chemical complexes and they could be ingested if water is not correctly treated [1-3]. Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries [4]. Membrane processes are increasingly used in the environment protection, drinking-water production, and medical applications [5,6,7]. Adsorptive microfiltration and ultrafiltration membranes have been used to remove heavy metal ions from aqueous solutions effectively due to the presence of relative functional groups on their surfaces, including  $-NH_2$ ,  $-SO_3H$ , and  $-COOH$  that can interact with heavy metal ions [8].

Chitosan (CS) is an N-deacetylated product of chitin that is one of the most abundant polysaccharides in nature and has good physical, biological, and biodegradable properties. It is readily processable into membranes from aqueous acid solutions. The membranes obtained by chitosan and its blend has been

reported to be suitable for various applications such as wound dressing [9,10], chromatographic media [11,12]. The high adsorption potential of chitosan for heavy metals can be attributed to high hydrophilicity due to large number of hydroxyl groups of glucose units, presence of large functional groups, high chemical reactivity of these functional groups, and flexible structure of the polymer chain [13]. Polymer blending is an effective way to obtain new polymeric materials with optimized properties. The advantages of this technology include versatility, simplicity and inexpensiveness [14,15].

In this study, cross-linked chitosan (CS) film with sub micrometer porous structure was prepared by extraction of poly(ethylene glycol) (PEG) from CS/PEG blend film for the synthesis of micro porous films with high adsorption potentials, chemical stability, and reusability. Characterization of the films was done using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and differential scanning calorimeter (DSC). The influence of metal-ion concentration and pH of the feed solution on the iron retention has been analyzed by atomic absorption spectroscopy (AAS), and the desorption/regeneration of the used CS/PEG blends were studied.

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## 2. Materials and Methods

### 2.1. Materials

Chitosan powder (CS) (high MW, > 75% deacetylated) was purchased from Sigma Aldrich. Acetic acid (glacial, 99%-100%), Poly (ethylene glycol) (PEG 6000), and glutaraldehyde were obtained from Merck (Mumbai, India). Mineral salt, ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were obtained from SD fine Chemistry Ltd. (Mumbai, India). The water used for experiments was obtained by double distillation of de-ionized water.

### 2.2 Preparation of chitosan-PEG blend (CSB) films

Chitosan dissolved in 2% acetic acid (75 mL) and the counterpart polymer (PEG 6000) dissolved in water (25 mL) with different mass ratios (CS:PEG = 1:1, 2:1 and 4:1) were mixed thoroughly and stirred for 1 hr. To this solution, 1 mL of 2% glutaraldehyde solution (cross-linking agent) was added under stirring at room temperature (27°C). The solution was transferred immediately into a Teflon covered glass plate (100 mm × 100 mm × 3 mm) and dried at 80°C in an electric oven (TK 3108, EHRET, Germany) for 4 hr. The formed cross-linked chitosan-PEG blend films were neutralized with 2% aqueous NaOH solution for 30 min. after drying. Afterwards, the film was washed with water to remove the remaining NaOH. Finally, the film was kept in water with bath temperature 80-90°C for more than 10 hr to dissolve the PEG component and to generate porous structure. The wet film was wiped with a filter paper to remove the excess water present on the surface of the film, then framed on a glass to prevent shrinkage along the surface and allowed to dry. The thickness of the films was 250 μm. The photos of chitosan-PEG blend membranes with different composition of chitosan are shown in Fig. 1.

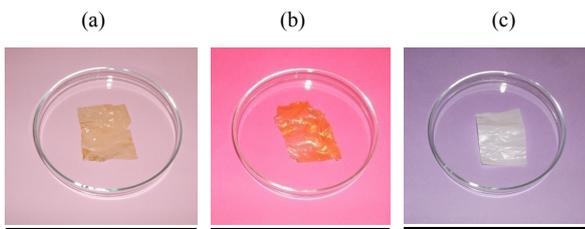


Fig. 1. Photos of CSB films with different composition of CS:PEG (a) 1:1, (b) 2:1 and (c) 4:1

### 2.3 Swelling study

Pre-weighed film samples (2 cm X 2 cm) were cut from the CSB films. The thickness of the films was found to be in the range 200-250 μm as measured by a digital micrometer. The swelling behavior was tested by immersing the pre-weighed film samples in 250 mL of phosphate buffer (pH 7.4) at 27°C for predetermined intervals. The sample weights were then determined as function of time by an analytical balance (AP250D, OHAUS Company, Switzerland) after blotting the film with a tissue paper to remove surface water. The swelling ratio (SR) of the films was calculated using Eq. (1)

$$SR = \frac{W_s}{W_d} \quad (1)$$

where,  $W_s$  (g) is the weight of the swollen film, and  $W_d$  (g) is the weight of the dry film.

### 2.4 Characterization of chitosan-PEG blend (CSB) films

The structures and morphologies of the blend films were examined through scanning electron microscopy (Inspect S, FEI Ltd., Holland) after gold coating. The fractured cross-sections of the films were achieved by breaking the samples deeply cooled in liquid nitrogen.

The crystallinity of the blend films was measured by X-ray diffraction (X Pert Bro, Panalytical, Holland). XRD measurements were carried out at room temperature, using Nickel-filtered Cu K radiation generated at 45 kV, and 50 mA. The diffraction patterns were determined over a diffraction angle range of  $2\theta = 5-80^\circ$ .

Thermal studies of the blend films were measured using a differential scanning calorimeter (DSC-H50, Shimadzu, Japan). Heating and cooling rates were 10°C/min. All experiments were done with dry  $\text{N}_2$  at flow rate 10 mL/min from room temperature to 400°C.

### 2.5 Adsorption and desorption experiments

The films were cut into pieces at about 1 cm length then dried in a vacuum oven at 80°C for 2 hr. Then it was removed quickly and stored in desiccators over a fresh silica gel at ambient temperature. The adsorption and desorption experiments were performed in flasks containing 250 mL of Fe(II) solutions. The mixture in flask was stirred at 300 rpm and  $27 \pm 2^\circ\text{C}$ , and solution pH was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH solution. The Fe(II) concentration in the solutions were determined using an atomic absorption spectrophotometer (AAS) (ICE 3300, Thermo Scientific Ltd., UK). Each experiment was conducted in triplicates and the mean values were reported.

To examine the adsorption capacities of the CSB films, dried film samples were added into solutions with initial Fe(II) concentration varying from 2-10 mg/L. The pH of Fe(II) solution was adjusted at 5. Then, the mixture in flasks was stirred for 90 min. (more than the adsorption equilibrium time). Afterwards, the amount of metal ions adsorbed per unit mass of the film ( $q_e$ , mg metal ions/g film) and the percentage of metal ions adsorbed (R) were obtained using Eqs. (2) and (3), respectively.

$$q_e = \frac{(C_0 - C) \times V}{m \times 1000} \quad (2)$$

$$R = \frac{(C_0 - C)}{C} \times 100\% \quad (3)$$

where,  $C_0$  (mg/L) and  $C$  (mg/L) are the concentrations of the metal ions in the sorption medium before and after equilibrium, respectively;  $V$  (mL) is the volume of the sorption medium; and  $m$  (g) is the weight of the dry film.

Adsorption kinetic studies were conducted for the CSB films with CS:PEG ratio of 1:1 and 2:1. Certain amounts of the dried CSB film pieces was added into Fe(II) ion solutions adjusted at pH 5. Initial Fe(II) ion concentrations were 2 mg/L. The samples were taken at desired time intervals for the analysis of metal ion concentrations.

The mixture of Fe(II) solution and CSB films was agitated during the period of 0-90 min. to determine the time required to reach equilibrium at ambient temperature. The adsorption capacity is referring to the maximum amount of metal ions removed from the solution when the ionic sites of the films are saturated.

pH dependent metal adsorption was performed by agitating the mixture of CSB film samples, Fe(II) solution for 1 hr and varying pH in the range 2-9.

A fixed amount of dried CSB film samples with different CS:PEG ratios (1:1 and 2:1) were stirred in metal ion solutions with concentrations varying in the range 2-10 mg/L for 1 hr to determine the effect of initial metal ions concentration on adsorption. The pH was adjusted to 5 for Fe(II) solution.

Desorption of heavy metal ions was achieved using 0.1 mol/L HCl as desorbing agent. The metal loaded CSB film samples were placed in desorption medium and left for 6 hr, then the film samples were washed with deionized water several times and were subjected again to adsorption/desorption process for four cycles.

### 3. Results and Discussion

#### 3.1. Swelling Capacity

Figure 2 illustrates the swelling capacity of CSB films with time. As shown in Fig. 2, decreasing chitosan content from (4:1) to (1:1) result in slightly improved swelling capacity of CSB films, because of the increase in porosity of the network structures that allow more water to enter inside the films by decreasing the chitosan content.

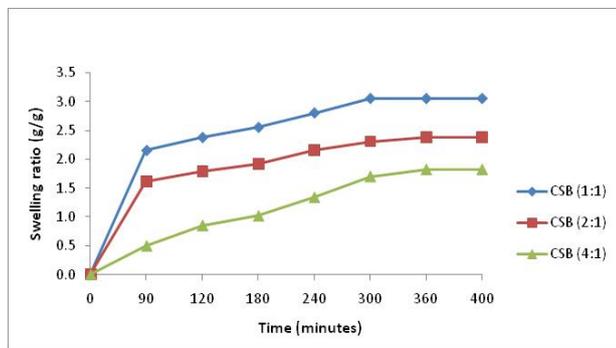


Fig. 2. Swelling rate of CSB films prepared at different compositions of CS:PEG

#### 3.2. Membrane Characterization

The scanning electron microscopy was used to collect information regarding morphology and cross-sectional structures of chitosan powder and CSB films which prepared by selective dissolution of counterpart polymer from the CS/PEG blend films with CS:PEG ratio of 1:1 and 2:1 (Fig. 3). In general, CSB films exhibited a dense and uniform plain micro structure, and it is observed that, bigger pore structure and pore size openings occurred for its higher PEG content. This phenomenon is in agreements with the results obtained by researchers studied the preparation of sub-micrometer porous film from chitosan/polyethylene glycol semi-IPN [16].

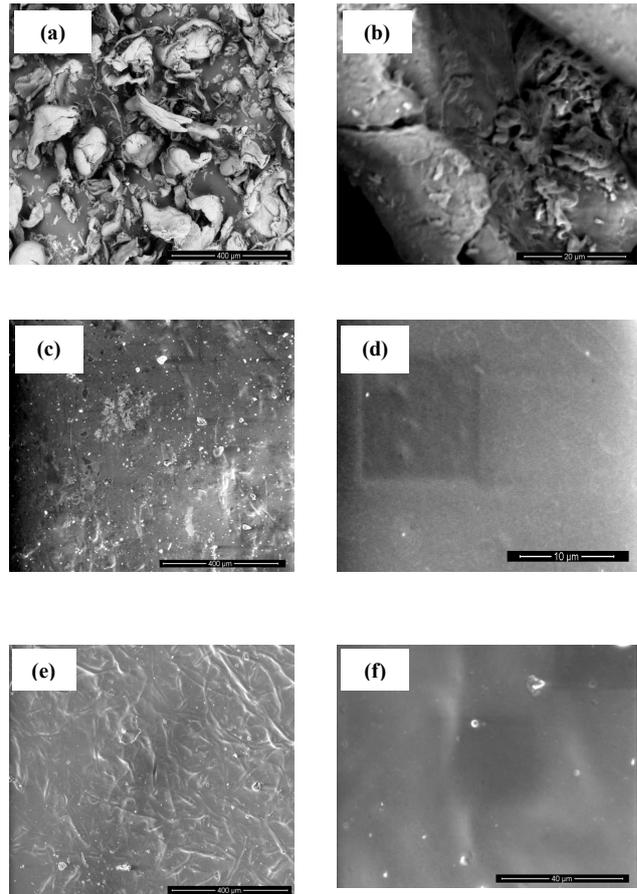


Fig. 3. SEM observation of: chitosan powder (a) surface; (b) cross-section, CSB film with CS/PEG ratio (1:1) (c) surface; (d) cross-section, and CSB film with CS/PEG ratio (2:1) (e) surface; (f) cross-section

Differential scanning calorimeter (DSC) analysis was carried out to determine the thermal properties of the films. Special care must be taken during DSC measurements since chitosan and the counterpart polymer are apt to adsorb moisture, which strongly affect the DSC measurements. To eliminate the effect of moisture, two cycles of heating and cooling runs were adopted. DSC curves of CS, and CSB films are described in Fig. 4. In the CS curve, the main feature is a broad endothermic peak at 250°C. Similar remarkable endothermic peak has been reported by researchers who attributed this peak to the dissociation process of inter chain hydrogen-bonding of chitosan [17]. As for CS/PEG blend system, the melting peak of PEG is affected remarkably by blending with CS (Fig. 6), and it is observed that the thermal stability of CSB is higher than that of CS, but the thermal stability decreases by increasing CS/PEG ratio in the blend film. The current work is in agreements with the results obtained by Lee et al. (2000) [18] as they found that  $T_m$  of CS/PEG blend tended to decrease by increasing CS content over the complete composition range. This could be attributed to crystallization disturbance of CS in the blend state.

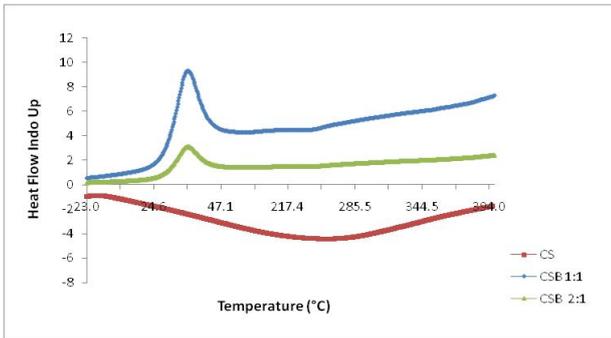


Fig. 4. DSC curves of CS, CS:PEG blend (1:1), and CS:PEG blend (2:1)

The XRD patterns of CS powder and CSB films are shown in Fig. 5. Crystalline peaks for CS appears at  $2\theta = 20.1^\circ$ ,  $12.5^\circ$ , and  $8.9^\circ$ . While for CSB films with CS:PEG ratio (1:1), its reflection pattern at  $2\theta = 12.5^\circ$ ,  $8.9^\circ$  are almost the same as those of CS but its reflection pattern at  $2\theta = 20.1^\circ$  becomes broader and stronger which reveals that the crystalline structure of each component of CSB film increased upon blending, thus, the stability of the blend films is higher than that of chitosan powder.

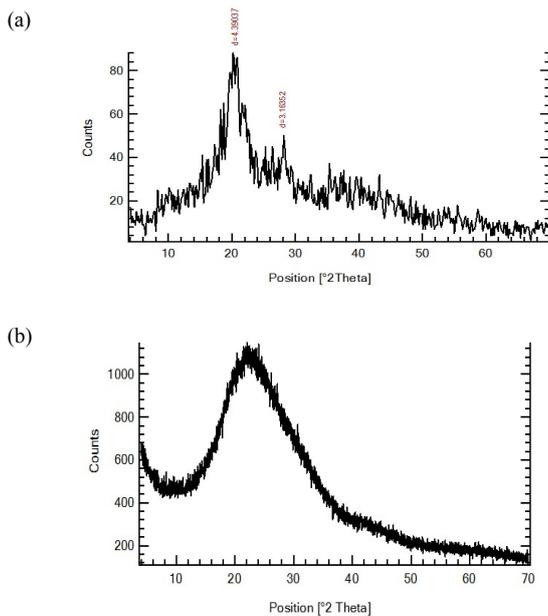


Fig. 5. XRD curves of (a) CS powder and (b) CSB films with CS:PEG ratio (1:1)

### 3.3. Adsorption Studies

Time courses of Fe(II) ions adsorption onto CSB films are illustrated in Fig. 6. Rapid adsorption kinetics can be seen within the first 20 min, while equilibrium was attained after 60 min. The maximum value of iron adsorption capacity in CSB films were found to be 38 mg/g. Kinetics in a chelating polymer are not only relying on the availability of chelating functional groups, but also on their accessibility by counter ions without a steric hindrance, which is greatly determined by the polymeric matrices characteristics [19]. The rapid metal adsorption kinetics in the CSB films can be attributed to the

strongly acidic and hydrophilic nature of the film caused by the presence of amine and hydroxyl groups which are responsible of interaction with the metal ions by electrostatic attraction. However, time required to attain equilibrium in this study for the adsorption of Fe(II) ions onto CSB films seems to be suitable from kinetic considerations when compared with the results stated in the literature [20] where time required to attain equilibrium ranged from 30 min to 7 hr.

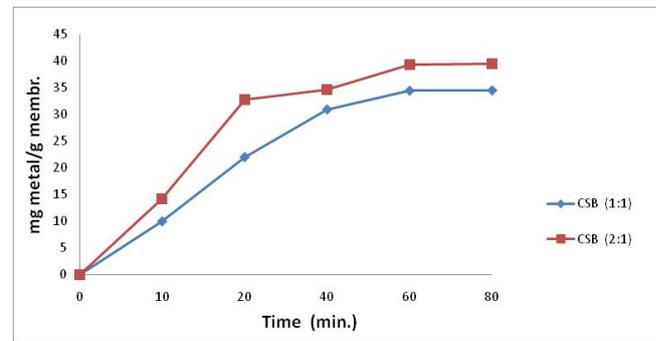


Fig. 6. Effect of contact time on iron removal using CSB films with different CS:PEG ratios. Adsorption conditions: initial concentration  $2.0 \text{ mg l}^{-1}$ ; sorption medium volume 250 ml; agitation rate 300 rpm; temperature  $27^\circ\text{C}$  and pH 5

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [21]. Since CSB film is anionic sorbent with its molecular structure having pendant amine and hydroxyl functional groups, the effect of pH on the adsorption capacities of heavy metal ions was examined in the pH range 2-9. As shown in Fig. 7, the metal adsorption increases with increasing pH in the range of 2-5, beyond which it tends to level off. Therefore, the optimum pH of sorption experiments was set at 5. The low adsorption of metal ions at low pH can be ascribed to competitive adsorption of hydronium ( $\text{H}^+\text{H}_2\text{O}$ ) ions and therefore, electrostatic attraction between the metal ions and the functional groups in the film surface is likely to be increase with the increase in the solution pH. In addition, other parameters taking part in metal uptake process i.e. ion exchange capacity together with the nature of the active sites in the film are pH dependent [22]. From Fig. 7, it can be noticed that by increasing CS:PEG ratio in the CSB film, the adsorption capacity of  $\text{Fe}^{+2}$  ions increase.

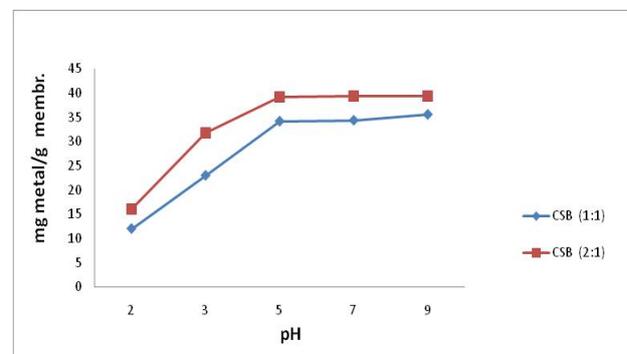
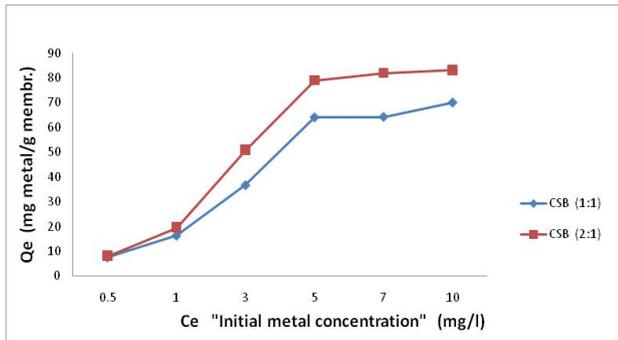


Fig. 7. Effect of pH on iron removal using CSB films with different CS:PEG ratios. Adsorption conditions: initial concentration  $2.0 \text{ mg l}^{-1}$ ; sorption medium volume 250 ml; agitation rate 300 rpm; temperature  $27^\circ\text{C}$ ; and contact time 60 minutes

The adsorption capacity of metal ions was investigated in correlation with the variation in the initial metal ion concentrations in the range of 2 to 10 mg/L (Fig. 8). The adsorption of metals increased by increasing initial metal ion concentrations and level off at 4.8 mg/L. This behavior can be attributed to the fact that cation affinity of CSB film is mainly due to the electrostatic interaction between the hydrophilic negatively charged hydroxyl groups and the counter metal ions in the solution [22]. By increasing CS:PEG ratio, the metal uptake by CSB films increases. This is due to the increase of hydroxyl groups, accordingly, increasing the electrostatic interaction between the hydrophilic negatively charged hydroxyl groups and the counter metal ions in solution. After reaching the maximum value, the decreasing trend in the metal uptake with the increase in initial metal ion concentrations is most likely to be caused by the decrease in the affinity of hydroxyl functional groups with rising degree of site occupation, which followed the early and easy access of the binding sites at low metal concentration. Such trend also suggests an increase in the equilibrium constant with the decrease in the metal affinity. These results suggest that CSB films is most effective for removal of Fe(II) at initial feed concentrations in the range of 1 to 8 mg/L.



**Fig. 8. Effect of initial metal concentration on iron removal using CSB films with different CS:PEG ratios. Adsorption conditions: sorption medium volume 250 ml; agitation rate 300 rpm; temperature 27°C; pH 5 and contact time 60 minutes**

### 3.4. Desorption of metal ions and reusability

To qualify the films for practical use, the utilized films have to be chemically stable and reusable. Saturated CSB films could be regenerated by treatment with 0.1 mol/L HCl for 6 hr. The desorbed blend films can be able to adsorb almost the same amount of metal ions even after four cycles as listed in Table 1. This clearly shows that, CSB films can be effectively and economically used for the removal of iron ions from aqueous solutions.

**Table 1 Reusability of CSB films for removal of iron**

Cycles	Amount of adsorbed metal ions (mg/g)
1	80.0
2	78.8
3	76.1
4	76.0

Fe(II)	
1	80.0
2	78.8
3	76.1
4	76.0

Adsorption conditions: initial concentration of metal ions 5 mg/L; volume of adsorption medium 250 mL; agitation rate 300 rpm; pH 5.9; temperature 27°C; adsorption time 60 min.

Desorption conditions: desorption medium 0.1 mol/L HCl; volume of desorption medium 250 mL; desorption time 6 hr, temperature 27°C.

### 3.5. Adsorption Isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase. As the adsorption isotherms are important to describe how adsorbates interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation [23]. Freundlich and Langmuir sorption isotherm equations were adopted in this study.

Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm is defined as:

$$q_e = k C_e^{\frac{1}{n}} \quad (4)$$

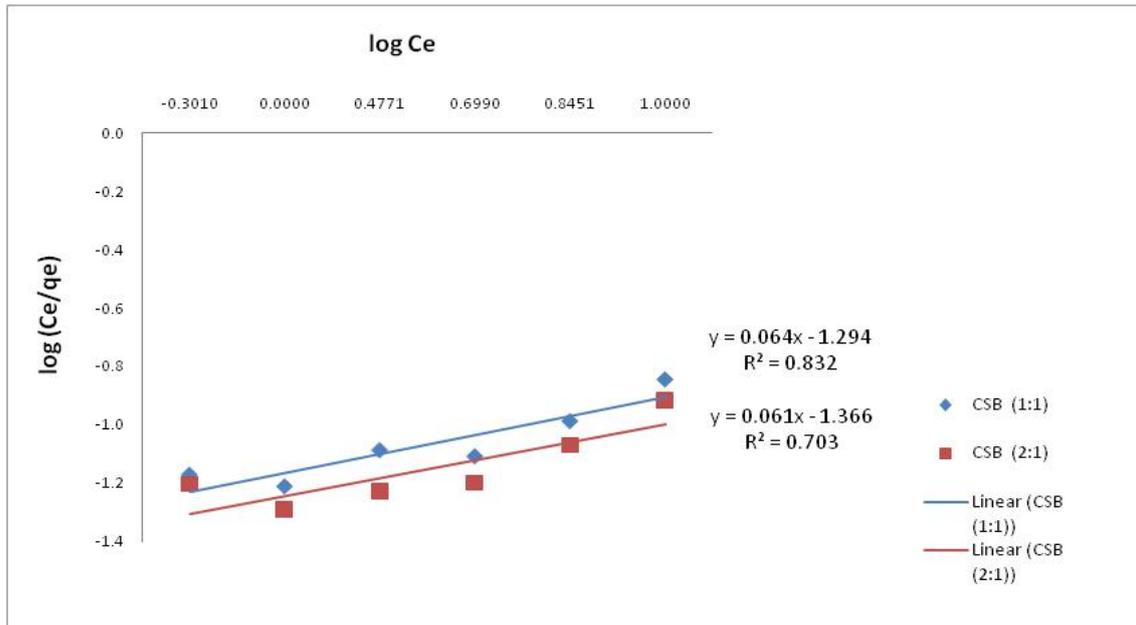
where,  $C_e$  (mg/L) is the equilibrium concentration,  $q_e$  (mg/g) is the adsorbate amount adsorbed per unit weight of adsorbent, “k” is a parameter related to the temperature, and “n” is a characteristic constant for the adsorption system. The plots of  $\log q_e$  against  $\log C_e$  are shown in Fig. 9a.

Langmuir equation is based on the assumptions that maximum adsorption corresponds to saturated mono-layer of adsorbate molecules on the adsorbent surface. Therefore, the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface [24]. The Langmuir isotherm is defined as:

$$q_e = \frac{(b q_m C_e)}{(1 + b C_e)} \quad (5)$$

where,  $q_m$  and  $b$  are Langmuir constants related to the sorption capacity, and sorption energy, respectively. The plots of  $C_e/q_e$  against  $C_e$  are shown in Fig. 9b.

The constants and correlation coefficients ( $R^2$ ) of Freundlich and Langmuir isotherm are listed in Table 2. As can be observed, experimental data were better fitted to Freundlich equation than to Langmuir equation, and therefore it is more suitable for the analysis of kinetics.



(a).

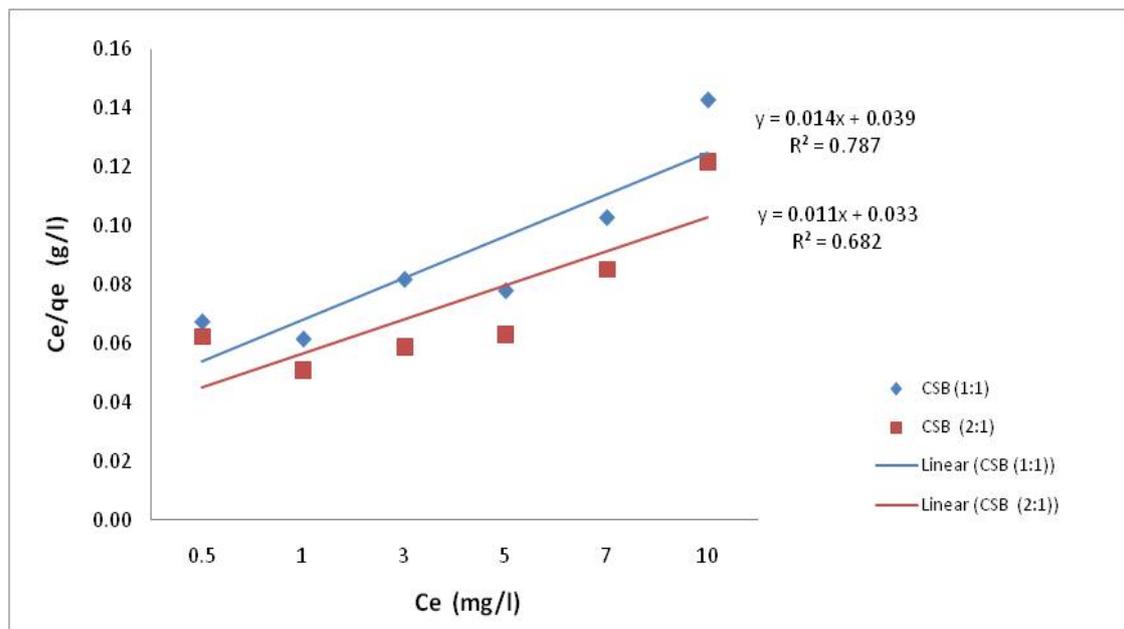


Fig. 9 (a) Freundlich plot of CSB films for iron removal (b) Langmuir plot of CSB films for iron removal

Table 2. Freundlich and Langmuir parameters for the sorption of Fe(II) onto CSB films

	Adsorbent	Freundlich			Langmuir		
		<i>k</i>	<i>n</i>	<i>R</i> <sup>2</sup>	<i>b</i>	<i>q<sub>m</sub></i>	<i>R</i> <sup>2</sup>
Fe(II)	CS:PEG 1:1	0.050	15.6	0.832	0.359	71.4	0.787
	CS:PEG 2:1	0.040	16.4	0.703	0.333	90.9	0.682

#### 4. Conclusion

In this study, adsorptive cross-linked chitosan/poly(ethylene glycol) blend (CSB) films with sub micro porous structure were directly prepared from extraction of poly(ethylene glycol) (PEG) from chitosan/PEG blend films. DSC analysis confirmed that the thermal stability of CSB films were higher than that of chitosan powder, and the stability of blend films decreases by increasing CS:PEG ratio in the blend film. XRD patterns showed that the crystallinity of CSB is higher than that of CS. Batch adsorption experiments confirmed that CSB films were highly adsorptive for iron ions and the chitosan contents

in the blend films provided the functionality and hence determined the adsorption capacity of the films. Under the conditions investigated, CSB films showed adsorption capacities of up to 38 mg/g for iron ions at pH 5 within 60 min. The iron ions adsorbed on the films were effectively desorbed by 0.1 mol/L HCl, and the regenerated CSB films can be reused almost without much loss of adsorption capacity for up to four cycles. An implication of the present study is that the CSB films have great potentials to be used for removing iron ions from aqueous solutions.

### Nomenclature

CS	Chitosan
CSB	Chitosan blend
DSC	Differential scanning calorimeter
IPN	Inter-penetrating network
PEG	Poly(ethylene glycol)
XRD	X-ray diffraction

### Acknowledgments

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### References

- [1] Yang QW, Shu WS, Qiu JW, Wang HB, Lan CY. Lead in paddy soils and rice plants and its potential health risk around lechang lead/zinc mine, Guangdong, China. *Environ. Int.* 2004; 30: 883-889.
- [2] Mayer MG, Wilson DN. Healthy and safety-the downward trend in lead levels. *J. Power Sources* 1998;73:17-22.
- [3] Mbareck C, Nguyen QT, Alaoui OT, Barillier D. Elaboration, characterization and application of polysulfone and polyacrylic acid blends as ultrafiltration membranes for removal of some heavy metals from water. *J. Hazard. Mater.* 2009;171:93-101.
- [4] Argun ME, Dursun S. A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresour Technol.* 2008;99(7):2516-2527.
- [5] Ulbricht M. Advanced functional polymer membranes. *Polymer* 2006;47:2217-2262.
- [6] Peter-Varbanets M, Zurbrugg C, Swartz C, Pronk W. Decentralized systems for potable water and the potential of membrane technology. *Water Res.* 2009;43:245-265.
- [7] Sikdar SK, Grosse D, Rogut I. Membrane technologies for remediating contaminated soils: a critical review. *J. Membr. Sci.* 1998;151:75-85.
- [8] Liu C, Bai R. Adsorptive Removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes. *J. Membr. Sci.* 2006; 284:313-322.
- [9] Wang LH, Khor E, Wee A. Chitosan-alginate PEC membrane as a wound dressing: assessment of incisional wound healing. *J. Biomed. Mater. Res.* 2002;63:610.
- [10] Mi FL, Shyu SS, Wu YB. Fabrication and characterization of a sponge-like asymmetric chitosan membrane as a wound dressing. *Biomaterials* 2001;22:165.
- [11] Zeng, XF, Ruckenstein, E. Membrane chromatography: preparation and applications to protein separation, *Biotech. Prog.* 1999, 15:1003.
- [12] Ghosh R. Protein separation using membrane chromatography: opportunities and challenges. *J. Chromatogr.* 2002;A952:17.
- [13] Grini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* 2005;30(1):38-70.
- [14] Li J, Chen YP, Yin Y, Yao F, Yao K. Modulation of nano-hydroxy apatite size via formation on chitosan-gelatin network film in situ. *Biomaterials* 2007;28(5):781-790.
- [15] Rodrigues LB, Leite HF, Yoshida MI, Saliba JB, Junior ASC, Faraco AAG. In vitro release and characterization of chitosan films as dexamethasone carrier. *Int. J. Pharm.* 2008;368:1-6.
- [16] Zeng M, Fang Z. Preparation of sub-micrometer porous membrane from chitosan/polyethylene glycol semi-IPN. *J. Membr. Sci.* 2004;245: 95-102.
- [17] Chuang WY, Young TH, Yao CH, Chiu WY. Properties of the poly(vinyl alcohol)/chitosan blend and its effect on the culture of fibroblast in vitro. *Biomaterials* 1999;20(16):1479-1487.
- [18] Lee SJ, Kim SS, Lee YM. Interpenetrating polymer network hydrogels based on poly(ethylene glycol) macromer and chitosan. *Carbohydr. Polym.* 2000;41(2):197-205.
- [19] Kantipuly C, Katragadda S, Chow A, Gesser HD. Chelating polymers and related supports for separation and pre-concentration of trace metals. *Talanta* 1990;37(5):491-517.
- [20] Denizli A, Tanyolac D, Salih B, Ozdural A. Cibacron blue F3GA-attached poly vinyl butyral micro beads as novel magnetic sorbents for removal of Cu(II), Cd(II), and Pb(II) ions. *J. Chromatogr. A* 1998;793(1):47-56.
- [21] Cho H, Oh D, Kim K. A study on removal characteristics of heavy metals from aqueous solution by fly ash. *J. Hazard. Mater.* 2005;127:187-195.
- [22] Nasef MM, Yahya AH. Adsorption of some heavy metal ions from aqueous solutions on nafion 117 membrane. *Desalination* 2009;249(2):677-681.
- [23] Deomall I, SanJay T, Nripendra S. Studies on the use of carbon waste generated from fertilizer plant in wastewater treatment. *Proceedings of the 18<sup>th</sup> international conference on solid waste technology and management, Philadelphia, USA, 2003.*
- [24] El Said A, El Serafy MA. Adsorptive Removal of some pesticides using fixed bed columns. *Proceedings of the 13<sup>th</sup> international conference on environmental protection is a must, 2003.*