

# **EVALUATION OF THE MEMBRANES BASED ON THE MIXTURE BIOPOLYMERS FOR THE REMOVAL OF AMMONIA AND AMMONIUM IONS FROM WASTE WATERS**

Y. ANGAR, N. E. DJELALI

*Laboratoire de traitement et mise en forme des polymères fibreux, université M'Hammed Bougara, Boumerdes 35000, Algérie.*

Corresponding author: Anessma@gmail.com

## **Abstract**

High concentrations of ammonia are commonly present in industrial wastewaters and fertilizer wastewaters which can promote the eutrophication phenomena. Although the removal of ammonium from contaminated water via polyelectrolyte was investigated in this work using a sodium poly acrylate supported on the chitosan membrane on a batch adsorption experiments. The concentration of ammonium in the receiving solution is essentially zero. Total ammonia removal could be accelerated by the driving force using the electrodes in each compartment for this liquid-liquid membrane contactor operation is the difference in ammonium partial pressure between the feed and the receiving solution. The results indicate that as prepared mixture adsorbent has faster adsorption kinetics and higher adsorption capacity than the chitosan membrane and other mixture polymers such as sodium alginate and polyvinyl alcohol/ chitosan at different ratio. All information obtained give an indication that the mixture polyelectrolyte/chitosan can be used as a novel type, fast-responsive and high-capacity sorbent material for  $\text{NH}_4^+$ -N removal.

**Keywords:** mixture polymer, membrane, sodium polyacrylate, chitosan, ammonium, biopolymer.

## **1- INTRODUCTION**

Eutrophication of water body is a major, global environmental problem. Its main cause is disposal of nutrients (N and P) directly from wastewater plants or indirectly from agriculture runoff and leaching from sludge deposited in landfill fields [1]. Nitrogen compounds are very essential elements for living organisms. However, when they are more than needed, they can contribute to accelerated eutrophication of lakes and rivers, dissolved

oxygen depletion and fish toxicity in receiving water, leading thus a number of health problems involving living species such as humans and animals [2]. Therefore, it is desirable that these nutrients should be removed before they are returned to the environment. Ammonium nitrogen ( $\text{NH}_4^+$ ) is the most commonly encountered nitrogenous compounds in wastewaters. In order to remove  $\text{NH}_4^+$ , several technologies have been tested, namely biological treatment [3], chemical precipitation [4], supercritical water oxidation [5], steam-stripping [6], microwave radiation

[7], ion exchange [8] and adsorption [9]. Among these recipes, adsorption technology has received much attention and is considered to be a robust and effective technique used in water and wastewater treatments due to its economical advantages, low energy input and easy operation. The success of an adsorption technology depends on the choice of an appropriate adsorbent [10]. Due to the comparable low cost of application, most clays, which are hydrated aluminum-silicate minerals, have been used in removing  $\text{NH}_4^+$  contaminant, such as sepiolite [11, 12]. Natural zeolites are important inorganic cation exchangers that exhibit higher affinity for  $\text{NH}_4^+$  and then are investigated widely for  $\text{NH}_4^+$  removal [8, 13]. Thanks to highly developed porous structure and large specific area, activated carbons show also considerable adsorption capacity towards  $\text{NH}_4^+$  [9]. These adsorbents have been developed and studied for  $\text{NH}_4^+$  removal, but the adsorption kinetics are slow and the adsorption capacity is also limited only via ion exchange or porous adsorption. In addition, only under optimum pH condition, the higher adsorption capacity for  $\text{NH}_4^+$  would be obtained. The regeneration of developing adsorbents is also a limiting factor governing the adsorption cost.

Hydrogels exhibit the ability to swell in water and retain a significant fraction of water within its structure without dissolving. It has physical properties similar to those of human tissues and possesses excellent tissue compatibility. The main disadvantage of hydrogels is their poor mechanical properties after swelling. In order to eliminate the disadvantage, hydrogels can be modified by physical blending [14–18] or/and chemical modification by grafting [19–23], interpenetrating polymer networks [24, 25] and crosslinking method [18, 26, 27].

Chitosan (poly- $-(1,4)$ -d-glucosamine), a cationic polysaccharide, is obtained by alkaline deacetylation of chitin, the principal exoskeletal component in crustaceans. As the combination of properties of chitosan such as water binding capacity, fat binding capacity, bioactivity, biodegradability, nontoxicity, biocompatibility, and antifungal activity, chitosan and its

modified analogs have shown many applications in medicine, cosmetics, agriculture, biochemical separation systems, tissue engineering, biomaterials and drug controlled release systems [18–34].

In this study the preparation of several membranes based on the polyvinyl alcohol, chitosan and sodium alginate respectively and the membranes based on the mixed polymers as chitosan/sodium alginate at differentes ratio together with chitosan/polyacrylic acid blended hydrogel membranes were also reported. Consequently, the aim of this study is; (i) to prepare a series of polymeric membranes; (ii) to evaluate the potential of prepared membrane for ammonium ions removal; (iii) to test its water resistivity for treatment of wastewater containing ammonia and ammonium ions for long term.

## **2- MATERIELS AND METHODS**

### **2.1- Reagents**

Polyacrylic acid (aquakeep D60, Atofina), chitosan (CTS, >75% deacetylated, sigma alderich Germany), Polyvinyl Alcohol (PVA Mw 89,000-98,000, sigma alderich), sodium alginate ( sigma alderich, Germany)

A 1000 mg/L stock standard solution of  $\text{NH}_4^+$  was prepared by dissolving an appropriate amount of ammonium chloride (dried to constant mass at 100–105 °C) in 1000mL of distilled water. All solutions were prepared with distilled water.

### **2.2- Preparation of membranes based on one polymer.**

All membranes were prepared by solution casting and solvent evaporation technique. The corresponding solution of each polymer was prepared as follows; 1,5 % (w/v) of PVA were dissolved in distilled water , stirred at 200 RPM for 1 hour.

1,5% (w/v) of sodium alginate were dissolved in distilled water, stirred at 200 RPM for 5 hours.

Chitosan, 1.5% (w/v), was dissolved in water containing 2% (w/v) of acetic acid solution and

stirred overnight using a magnetic stirrer at 200rpm. After drying, the films were carefully

peeled off. The average surface area of the obtained films was 63,58 cm<sup>2</sup> and the thickness was 200 ± 30 µm. The films were stored in tightly sealed glass containers maintained at room temperature until required for further investigations

### 2.3- Preparation of chitosan–alginate blend films

Chitosan–alginate blend was prepared by mixing the corresponding prepared solutions, at different weigh ratio of sodium alginate:chitosan, 20:80, 40:60 and 50:50 and then stirring at high speed. When alginate was blended with chitosan solution the polycationic nature of chitosan led to a strong interaction with negatively charged alginate. Finally, the mixtures were then transferred to Teflon plates and dried in an incubator at 45°C for 24 h. After drying, the films were carefully peeled off. The average surface area of the obtained films was 63,58 cm<sup>2</sup> and the thickness was 200 ± 30 µm. The films were stored in tightly sealed glass containers maintained at room temperature until required for further investigations

### 2.4- Preparation of chitosan/polyacrylic acid blended hydrogel membranes

The chitosan solutions were prepared by dissolving chitosan in 1% acetic acid solution at ambient temperature with stirring for overnight. The solution was filtered by filter before use. 10 wt.% polyacrylic acid solutions were prepared by dissolving polyacrylic acid solution in 1% (w/v) NaOH solution in distilled water with stirring for 4 h. Then the mixture of chitosan and polyacrylic acid solution were stirred for 24 h and cast in petri-dish at ambient temperature for 5 days. The membranes were pelled off, neutralised and washed with distillated water and then dried in oven at 45° for overnight.

### 2.5- Analytical methods.

The concentration of ammonium nitrogen was measured by spectrophotometric method at a wave number of 630 nm using aThermo Scientific GENESYS™ 10S UV-Visible Spectrophotometer USB Six-Position Cell Holders.

## 3- RESULTS AND DISCUSSIONS

### 3.1- Preparation of the range of the films

The prepared films showed a durability, stress resistant, flexibility, pliability, and elasticity at different colors; PVA are transparent, chitosan and sodium alginate are pale yellow in its colors. It was easy to apply and remove without upset the recipient.

The membranes of PVA and sodium alginate presents a high water solubility on account, however, for this propriety , it cannot be used in the wastewater treatment.

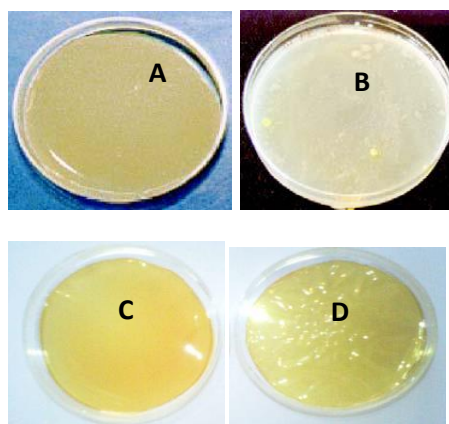


Fig .01: Prepaperd membranes polymeric; A. Sodium alginate, B. blended membrane of chitosan/polyacrylic acid., C. Chitosan, D. blended membrane of chitosan/sodium alginate.

The membranes were prepared at different concentration of desired solution including 0.5%, 1%, 2.5% of each biopolymers (chitosan and sodium alginate), as well as, for the mixture polymers, the amounts ratio of both chitosan/sodium alginate and chitosan/acrylic acide were 50/50 and 80/20. The physical form of these mixture polymers membrane were presented in the fig. 01 B and D, it wasn't uniformed like the single membrane but it had some suppleness and flexibility.

### 3.2- Ammonium adsorption capacity of chitosan and sodium alginate films

Different ratio of singles membranes were tested for the removal of ammonium in a sample of synthetic wastewater at neutral pH and at room temperature of 25°C. The capacity

of ammonium adsorption does not exceed 10% as rate for all three chitosan membranes concentrations (Fig. 02) during 24 hours as a time of the reaction.

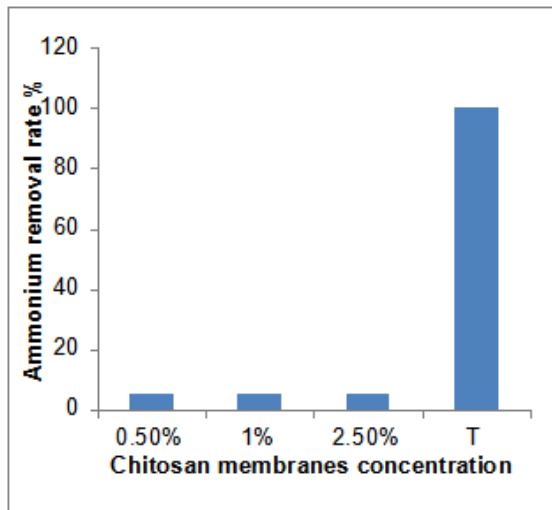


Fig. 02: Ammonium removal rate as a function of chitosan membranes concentration during 24 hours.

The same membranes were immersed in the same synthetic wastewater for 48 hours as the time of the adsorption (Fig. 03), the results indicated that these membranes cannot adsorb more than 10% of ammonium at this operating conditions.

The results suggested that the elimination of ammonium ions by chitosan membrane is low, the diminution of the initial ammonium concentration during 24 hours and even after 48 hours was very small compared by other membranes reported by other researchers, which can allowed to 90% as a rate of elimination.

In the other hand, for the sodium alginate membrane, the adsorption was more important compared with that obtained for the chitosan membranes at the membranes concentrations high than 1%, it could attain until 46,92% as rate of adsorption at a concentration of 2,5% of the sodium alginate, like shown in the (fig. 04).

However at the concentration less than 1%, the membrane were completely dissolved and even at the times more than 24 hours of the reaction, for all membrane concentrations, for

this reason these membranes are not recommended for the wastewater treatment.

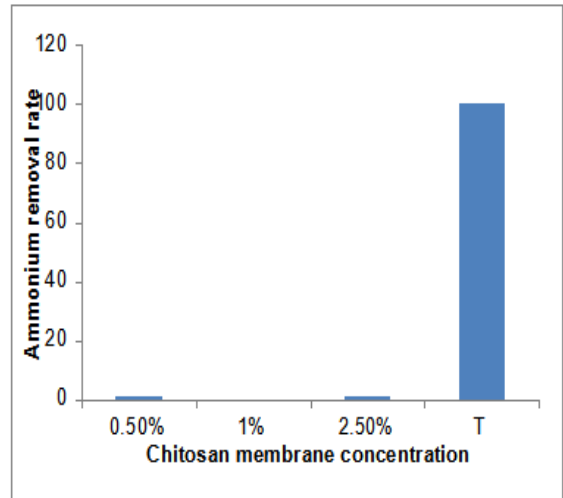


Fig. 03: Ammonium removal rate as a function of chitosan membrane concentration during 48 hours

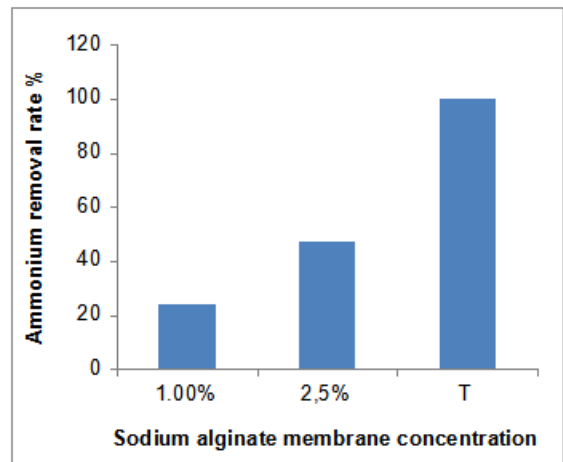
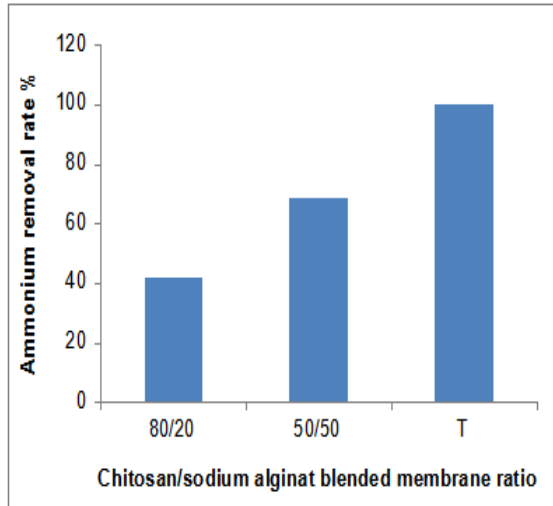


Fig. 04: Ammonium removal rate as a function of sodium alginate membrane concentration during 24 hours

### 3.3- Ammonium adsorption capacity of the blended films

The ammonium, removal by the films of Chitosan/Sodium alginate, was presented in the (fig. 05). The adsorption was more importante with a mixture polymer compared with previous tests, it increased as a function

of increasing of sodium alginate concentration until a definite concentration, so the best ratio was 50/50, the rate of the ammonium removal was 68,44%. However, at the values, of membrane ratio, higher than 50/50 the membrane loses its physical form and it was completely deformed.

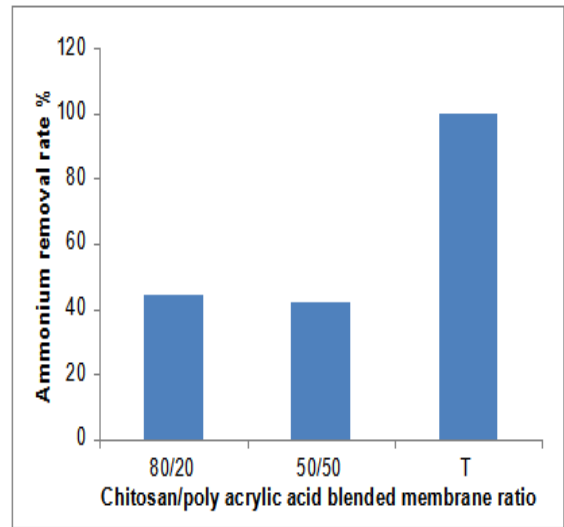


*Fig. 05: Ammonium removal rate as a function of chitosan/sodium alginate blended membrane concentrations ratio during 24 hours.*

The adsorption of  $\text{NH}_4^+\text{-N}$  onto CTS/PAA as a function of contact time showed that the adsorption was very rapid and could be achieved within 5min. For a ratio of 80/20, the adsorption rate were slightly greater compared with obtained at ratio of 50/50 (fig. 06), the rate obtained was around 42% for both ratio.

This fast kinetics between adsorbent and  $\text{NH}_4^+\text{-N}$  was attributed to the well-formed three-dimensional polymeric networks. As-prepared adsorbent belongs to hydrogels whose main feature is the ability to absorb water quickly due to the hydrophilic networks. After the initial faster hydration of the polymer network, concentration gradient of  $\text{NH}_4^+\text{-N}$  is formed at gel-water interface, thereby the diffusion of  $\text{NH}_4^+\text{-N}$  from the aqueous solution into the gel is started and bound immediately to the swollen polymeric networks as a result of electrostatic attraction. Then, the adsorbate  $\text{NH}_4^+\text{-N}$  outward is moved at once into the swollen polymeric networks, leading the adsorption system to reach equilibrium within a

few minutes.



*Fig. 06: Ammonium removal rate as a function of chitosan/polyacrylic acid membrane ratio during 24h*

#### 4- CONCLUSION

The adsorption of ammonium by the chitosan/sodium alginate blended membrane was more important compared with chitosan/polyacrylic acid blended membrane which could attain 68,44% as a rate of ammonium removal. The results obtained for the both blended membrane were more significant compared with chitosan membrane. However the PVA membrane and sodium alginate membrane had a high solubility in water which limited its application in wastewater treatment.

The results may be very advantageous for some specific applications of wastewater treatment considering the ammonium concentrations of interest are quite specific to the source of the wastewater and some applications such as aquaculture requires ammonia removal at levels of  $1\text{g L}^{-1}$ . Therefore, membrane contactors coupled with a reaction in the receiving phase converting ammonia to an ammonium salt are a good candidate for removal of ammonia from specific wastewater streams with very low concentrations.

## REFERENCES

- [1] L.-E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), *Water Res.* 38 (2004) 4222–4246.
- [2] L. Guo, Doing battle with the green monster of Taihu Lake, *Science* 317 (2007) 1166.
- [3] U. Welander, T. Henrysson, T. Welander, Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process, *Water Res.* 32 (1998) 1564–1570.
- [4] S. Uludag-Demirer, G.N. Demirer, S. Chen, Ammonia removal from anaerobically digested dairy manure by struvite precipitation, *Process Biochem.* 40 (2005) 3667–3674.
- [5] N. Segond, Y. Matsumura, K. Yamamoto, Determination of ammonia oxidation rate in sub- and supercritical water, *Ind. Eng. Chem. Res.* 41 (2002) 6020–6027.
- [6] M.K. Ghose, Complete physico-chemical treatment for coke plant effluents, *Water Res.* 36 (2002) 1127–1134.
- [7] L. Lin, J. Chen, Z. Xu, S. Yuan, M. Cao, H. Liu, X. Lu, Removal of ammonia nitrogen in wastewater by microwave radiation: A pilot-scale study, *J. Hazard. Mater.* (2009) 113, doi:10.1016/j.jhazmat.2009.02.
- [8] D. Karadag, S. Tok, E. Akgul, M. Turan, M. Ozturk, A. Demir, Ammonium removal from sanitary landfill leachate using natural Gordes clinoptilolite, *J. Hazard. Mater.* 153 (2008) 60–66.
- [9] P. Vassileva, P. Tzvetkova, R. Nickolov, Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation, *Fuel* 88 (2008) 387–390.
- [10] M.S. Onyango, D. Kuchar, M. Kubota, H. Matsuda, Adsorptive removal of phosphate ions from aqueous solution using synthetic zeolite, *Ind. Eng. Chem. Res.* 46 (2007) 894–900.
- [11] S. Balci, Y. Dinc, el, Ammonium ion adsorption with sepiolite: use of transient uptake method, *Chem. Eng. Process.* 41 (2002) 79–85.
- [12] S. Balci, Nature of ammonium ion adsorption by sepiolite: analysis of equilibrium data with several isotherms, *Water Res.* 38 (2004) 1129–1138.
- [13] Z.-Y. Ji, J.-S. Yuan, X.-G. Li, Removal of ammonium from wastewater using calcium form clinoptilolite, *J. Hazard. Mater.* 141 (2007) 483–488.
- [14] M.M. Amiji, Permeability and blood compatibility properties of chitosan-poly(ethyleneoxide) blend membranes for haemodialysis, *Biomaterials* 16 (1995) 593–599.
- [15] M.G. Cascone, B. Sim, S. Downes, Blends of synthetic and natural polymers as drug delivery systems for growth hormone, *Biomaterials* 16 (1995) 569–574.
- [16] T. Koyano, N. Koshizaki, H. Umehara, M. Nagura, N. Minoura, Surface states of PVA/chitosan blended hydrogels, *Polymer* 41 (2000) 4461–4465.
- [17] W.Y. Chuang, T.H. Young, C.H. Yao, W.Y. Chiu, Properties of the poly(vinyl alcohol)/chitosan blend and its effect on the culture of fibroblast in vitro, *Biomaterials* 20 (1999) 1479–1487.
- [18] T. Chandy, C.P. Sharma, Prostaglandin E1-immobilized poly(vinyl alcohol)-blended chitosan membranes: blood compatibility and permeability properties, *J. Appl. Polym. Sci.* 44 (1992) 2145–2156.
- [19] J.M. Yang, C.P. Chang Chian, K.Y. Hsu, Oxygen permeation in SBS-g-DMAEMA copolymer membrane prepared by UV photografting without degassing, *J. Membr. Sci.* 153 (1999) 175–182.
- [20] J.M. Yang, M.J. Huang, T.S. Yeh, Preparation of poly(acrylic acid) modified

polyurethane membrane for biomaterial by UV radiation without degassing, *J. Biomed. Mater. Res.* 45 (1999) 133–139.

[21] J.M. Yang, M.C. Wang, Y.G. Hsu, C.H. Chang, S.K. Lo, Preparation of heparin containing SBS-g-VP copolymer membrane for biomaterial usage, *J. Membr. Sci.* 138 (1998) 19–27.

[22] J.M. Yang, Y.J. Jong, K.Y. Hsu, C.H. Chang, Preparation and characterization of heparin containing SBS-g-DMAEMA copolymer membrane, *J. Biomed. Mater. Res.* 39 (1998) 86–91.

[23] J.M. Yang, Y.J. Jong, K.Y. Hsu, Preparation and properties of SBS-g-DMAEMA copolymer membrane by ultraviolet radiation, *J. Biomed. Mater. Res.* 35 (1997) 175–180.

[24] C. Peniche, W. Arguelles-Monal, N. Davidenko, R. Sastre, A. Gallardo, J.S. Roman, Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: preparation, characterization and interpolymer complexation, *Biomaterials* 20 (1999) 1869–1878.

[25] P. Gong, L. Zhang, L. Zhuang, J. Lu, Synthesis and characterization of polyurethane-chitosan interpenetrating polymer networks, *J. Appl. Polym. Sci.* 68 (1998) 1321–1329.

[26] V.B. Kushwaha, Permeation of molecules through different polymeric membranes, *J. Appl. Polym. Sci.* 74 (1999) 3469–3472.

[27] C.K. Yeom, K.H. Lee, Pervaporation separation of water–acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde, *J. Membr. Sci.* 109 (1996) 257–265.

[28] J. Ge, Y. Cui, Y. Yan, W. Jiang, The effect of structure on pervaporation of chitosan membrane, *J. Membr. Sci.* 165 (2000) 75–81.

[29] D. Knorr, Dye binding properties of chitin and chitosan, *J. Food Sci.* 48 (1983) 36–41.

[30] D.K. Kweon, S.B. Song, Y.Y. Park, Preparation of water-soluble chitosan/heparin complex and its application as wound healing accelerator, *Biomaterials* 24 (2003) 1595–1601.

[31] Y. Hu, X. Jiang, Y. Ding, H. Ge, Y. Yuan, C. Yang, Synthesis and characterization of chitosan-poly(acrylic acid) nanoparticles, *Biomaterials* 23 (2002) 3193–3201.

[32] M. Ishihara, K. Nakanishi, K. Ono, M. Sato, M. Kikuchi, Y. Saito, H. Yura, T. Matsui, H. Hattori, M. Uenoyama, A. Kurita, Photocrosslinkable chitosan as dressing for wound occlusion and accelerator in healing process, *Biomaterials* 23 (2002) 833–840.

[33] X.Y. Shi, T.W. Tan, Preparation of chitosan/ethylcellulose complex microcapsule and its application in controlled release of vitamin D<sub>2</sub>, *Biomaterials* 23 (2002) 4469–4473.

[34] S.J.K. Francis, H.W.T. Matthew, Application of chitosan-based polysaccharide biomaterials in cartilage tissue engineering: a review, *Biomaterials* 21 (2000) 2589–2598.