Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2013 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.700035

51 (2013) 644–657
January

Taylor & Francis
Taylor & Francis Group

Chelation and permeation of heavy metals using affinity membranes from cellulose acetate–chitosan blends

M.M. Naim*, H.E.M. Abdel Razek

Department of Chemical Engineering, Faculty of Engineering, Alexandria University, Alexandria, Egypt
Email: monanaim66@yahoo.com

Received 15 April 2012; Accepted 29 May 2012

ABSTRACT

Affinity membranes have attracted the attention of membrane researchers especially in the field of wastewater treatment specifically in removing heavy metals by chelation from aqueous solutions. In the present work, several membranes are made from either cellulose di-acetate (CA) or CA together with chitosan (CS) solutions, the CS prepared in our lab from shrimp shells or from readymade shrimp or crab shells. The variables investigated included type and ratio of solvents forming the casting solutions, mass ratio of CA to CS in the casting solution, type of CS (shrimp or crab shells), and initial concentration of Cu(II) ions. The membranes were fabricated by casting on a glass plate of a casting assembly using a surgical blade by the phase inversion technique. The permeation and adsorption capacity of each membrane were examined in a plexiglass two compartment diffusion cell in which the membrane was placed between the two compartments to separate the copper ion solution from an equal volume of distilled water. The two compartments were stirred either magnetically or mechanically. The results were presented as concentration–time curves and ln (C_o/C_t) vs. time from which the overall mass transfer coefficient was computed in each case. It was found that the presence of CS obtained from shrimps acted as a better affinity membrane in high CA to CS ratios as well as high concentration of Cu(II) ions, and that crab CS has a poor affinity to Cu(II) ions compared to that obtained from shrimps. It was also realized that the composition of the casting solution markedly affected the properties of the fabricated affinity membrane. In addition, scanning electron microscopic examination revealed the morphology of the membrane surfaces (upper, lower, and cross-section). It is worth mentioning that membrane thickness has a profound effect on both permeability and extent of chelation of the heavy metal examined.

Keywords: Affinity membrane; CS; Cellulose di-acetate; Cu(II) ions; Heavy metals; Wastewater

1. Introduction

In view of growing public health and environmental awareness accompanied by an increasing number of even stricter environmental regulations on discharged wastes, attention has been focused on the use of biopolymers from renewable resources as alternatives to synthetic polymers [1,2]. Biopolymers are compounds that are produced in nature by living organisms and plants, participate in the natural biocycle and are eventually degraded and reabsorbed in nature. The most widespread biopolymers are polysaccharides, cellulose, starch, chitin, and lignin, whose

---

*Corresponding author.

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

swellability in water and viscous solution/gel-forming properties are utilized to manufacture a number of industrial and consumer products. Among the commercially available polysaccharides that are prevailingly neutral or acidic, chitin and its primary derivative CS are special in that they are basic in nature [2,3]. This basicity gives chitin/CS singular chemical and biological characteristics, biocompatibility, antibacterial properties, heavy metal ion chelation ability, gel-forming properties, hydrophilicity, and remarkable affinity to proteins. Owing to these characteristics, the polymers, thus far underutilized, are predicted to be widely exploited in the near future in environmentally benign applications, notably in systems working in biological environments, among others in membrane-based processes.

Chitin is counted among the most plentiful, renewable organic resources in nature. It is found in shells of crustaceans, the exoskeletons of insects, and the cell walls of fungi where it plays a structural role [4–7]. Chemically, it is composed of N-acetylglucosamine forming a long-chain linear polymer. It is a hydrophilic, tough and inert solid, insoluble in water and most ordinary solvents. CS, the primary derivative of chitin, is obtained by N-deacetylation to a varying extent that is characterized by the degree of deacetylation, and is consequently a copolymer of N-acetylglucosamine and glucosamine. Insoluble in water, CS readily dissolves in acidic solutions, which is due to the presence of amino groups in its molecules, the degree of deacetylation necessary to obtain a soluble product being 80–85% or higher. Fully acetylated chitin and CS can be chemically considered as analogs of cellulose, in which the hydroxyl at carbon-2 has been replaced by acetamido and amino groups, respectively.

Commercially, chitin and CS are obtained at a relatively low cost from the shells of shell fish (mainly crabs, shrimps, prawns, lobsters, and krills), the wastes of the seafood processing industry. Basically, the process consists of the deproteinization and removal of lipids of the raw shell material with a dilute NaOH solution and decalcification with a dilute HCl solution. To afford CS, the obtained chitin is subjected to N-deacetylation by treatment with a 40–45% NaOH solution in which pigments are also removed, followed by purification procedures. Depending on the origin and manufacture process the obtained products may vary in composition and properties [2].

CS possesses singular chemical and biological properties [4–9] attributable to the presence of amino and hydroxyl groups, which allow chemical modifications of CS. Additionally, amino groups make CS a cationic polyelectrolyte ($pK \approx 6.5$), due to which CS is soluble in aqueous acidic media at $pH < 6.5$ and when dissolved possesses a high positive charge on $-NH_3$ groups, it adheres to negatively charged surfaces, it aggregates with polyanionic compounds, and chelates heavy metal ions with excellent gel-forming properties [10–20].

Preparation of pure CS membranes has been largely limited due to the poor mechanical strength and chemical stability of CS. However, Naim [21] has prepared adsorptive membranes made from CS, which efficiently adsorbed Cu(II) ions from an aqueous copper sulfate solution to a high degree (59.8%) which followed a pseudo-second order reaction kinetics. CS has been coated on supports such as flat PES membranes [22] and on cellulose membranes [23,24] to make composite CS membranes. More recently, blending CS with other polymers has been found to be an effective way to overcome the shortcomings of CS [25–30], because blending may form additional chemical bonds at the microscopic level due to chemical interactions. CS/cellulose blend membranes suitable to be used as a wound dressing with antibacterial properties were prepared by Wu et al. [31]. Yun and Shin [32] adsorbed tannic acid, humic acid, and dyes from water using composite beads of CS and activated clay in an effort to improve the CS's mechanical properties. Yong et al. [33] managed to adsorb acid dyestuff onto polyurethane–chitosan blends, which were prepared by a complex multistep method. Core-shell type CS/calcium phosphate composite fibers were prepared by Matsuda et al. [34] by a facile wet spinning method, in which the CS aqueous solution with phosphate ions was dropped and coagulated in the ethanol/calcium hydroxide solutions at different mixed ratio. Steenkamp et al. [35] manufactured a tubular alumina/CS composite membrane with a porous alumina support by a centrifugal casting technique. Yang et al. [36] prepared a composite CS-cellulose membrane by coating CS on a filter paper. They examined the physical properties of the composite membrane and its application as affinity membrane. Preparing CS-based immobilized electrolyte composite membranes with a three-layer structure that has a porous intermediate layer and two solid surface layers using glutaraldehyde as cross-linking agent was reviewed by Wan et al. [37]. Ren et al. [38] reviewed on the CS binary blend membranes fabricated by solvent casting of CS solution containing highly deacetylated CS and moderately deacetylated CS with different ratio. Hongming et al. [39] prepared chitin derivatives for use as flocculants and membranes for water purification. Carvera and Arnah [40] evaluated the removal of heavy metals from wastewater by using adsorption on alumina or CS, whereby, the adsorption of Cd(II) and Cr(III) ions onto the two adsorbents was studied as a function of pH, time, amount of adsorbent, and concentration of metal ions. Zhou and Zhang [41] prepared cellulose/chitin beads by coagulating a blend of cellulose and chitin in 6% NaOH, 5 wt.% thiourea aqueous solution with 5% H_2SO_4 as coagulant and investigated the adsorption of heavy metals (Pb(II), Cd(II), and Cu(II) ions) from aqueous solution on the beads. Chlorophenols were removed from ground water by sorption onto CS flakes and highly swollen beads [42]. A fundamental investigation on the removal of cadmium ions from aqueous solutions by chitin was conducted in batch conditions by Benguella and Benaissa [43], in which kinetic data and equilibrium removal isotherms were measured. Hirano et al. [44] demonstrated that wet spinning is a suitable method of preparing novel chitin-silk fibroin fibers and chitin fibers. Aqueous solution of sodium chitin(N-acetyl CS) salt and its blends of silk fibroin in aqueous 14% sodium hydroxide was spun through a viscose-type spinnerate.

Beppu et al. [45] reviewed on the ability of CS to form complexes with bivalent metal ions. They investigated the influence of functionalization of macroporous CS membranes with histidine on their ability to remove copper ions from aqueous solution in the range of pH 4–6. Chao et al. [46] reviewed on preparing of macroporous CS membranes by using NaCl particles as porogen and genipin as cross-linking agent. Other genipin cross-linked CS membranes were prepared by either freeze drying or by using silica particle as porogen. The mean pore diameter, the porosity, the crystallinity index as well as the effect of the drying procedures of these CS membranes were examined. Also, Zheng and Ruckenstein [47] described a procedure for the preparation of membranes with tailored pore size using a porogen. Silica as porogen, is added with CS to acetic acid (AA) solution. The mixed suspension is spread on a plate, and the solvent is evaporated. Gümüşderelioğlu and Agi [48] demonstrated macroporous CS membranes prepared by solvent evaporation method in the presence of silica particles, which were used as a porogen. These membranes were cross-linked under alkaline conditions, using epichlorohydrin as the cross-linking agent. The macroporous chitin membranes were obtained by acetylating the CS membranes with acetic anhydride in methanol.

Guibal [49] reviewed that metal cations can be adsorbed by chelation on amine groups of CS in near neutral solutions. In the case of metal anions, the sorption proceeds by electrostatic attraction on protonated amine groups in acidic solutions. However, the presence of ligands and the pH strongly control sorption performance (sorption isotherm) and the uptake mechanism. Several examples were discussed with precious metals (Pd, Pt), oxo-anions (Mo, V), and heavy metals (Cu, Ag). Sorption performance is also strictly controlled by other structural parameters of the polymer (degree of acetylation, crystallinity for example) that control swelling and diffusion properties of CS.

It is interesting to observe that CS has very limited affinity for alkaline and alkaline-earth metals due to the absence of d and f unsaturated orbitals [50]. However, these metals can be sorbed on CS derivatives when phosphorylated groups are grafted on the polymer [51–55]. It has been stated by Mckay et al. [56] that in the case of the sorption of metal cations, the chelation mechanism is very sensitive to pH and usually sorption does not occur at low pH. However, to prevent the polymer from dissolving, it will be necessary to use sulfuric acid. It would also be possible to use a strong chelating agent such as EDTA: the complexation of the metal by the ligand can displace the metal from the sorbent [57]. CS has been employed as an excellent adsorbent for sorption of phenols and polychlorinated biphenyls [58] and proteins [59,60], and in pollution control as a chelating polymer for binding harmful metal ions [61–63]. Many publications have reported the performance of adsorptive membranes [64,65]. A novel application of the nontoxic cationic biopolymer-CS was evaluated as a substitute for CMC by Selmer-Olsen et al. [66]. In a review by Krajewska [67], she pointed out how chitin/CS materials can contribute to the development of membrane-based processes classified as supportive in the sustainability of our life. Roux et al. [68] reviewed on the suitability of CS as an antifouling agent. The ability of CS to be molded into globules, microspheres, membranes, and fibers has been verified by many researchers [69–75]. Torres et al. [76] obtained CS membranes with self-organized lines on their surface. SEM and laser diffraction techniques showed that structures with peak-valley periods of about $5 \pm 2\,\mu m$ were observed in both porous and dense CS membranes. These unique patterns may be of special interest for applications where micro–mechanical interactions are important such as for biomaterials.

There is abundant literature concerning the preparation of flat membranes [18,77–83]. Wang et al. [84] developed membrane emulsification technique to prepare CS microspheres. Zeng et al. [85] developed a method to prepare microporous CS membrane by selective dissolution of its blend, while Zeng and Feng [86] made a cross-linked CS membrane with submicrometer porous structure prepared by extraction of poly ethylene glycol.

CS macroporous membranes with asymmetric morphology by using an inorganic porogen agent (SiO_2) were prepared by Santos et al. [87]. A methodology to obtain asymmetric membranes with control of porosity and average pore size was proposed. The porous membranes were obtained taking advantage of the opposite solubility characteristics of CS and silica (4–20 m). The results showed that the methodology was very efficient to yield asymmetric membranes with good mechanical resistance, control of pore size, and dense layer thickness and that these membranes can potentially be used to the transport of drugs.

Membrane-based affinity chromatography has been extensively investigated for biomolecule purification and immune adsorption. However, recently developed composite membranes have been found to be limited in their liquid flow rates. A CS/cellulose composite membrane that provides a large liquid flow rate through the membrane and good mechanical properties were investigated by Yang and Chen [88]. This new membrane was prepared by coating a 0.5% CS solution containing 1% AA and 15% polyethylene glycol onto coarse filter paper.

Novel natural polymer CS/cellulose blend beads were prepared by Twu et al. [89] via homogeneous dissolution of CS and cellulose in N-methyl morpholine-N-oxide. They also demonstrated that spray drying process is a suitable method of preparing CS microspheres.

The removal of divalent metal ions including Cu(II), Co(II), Ni(II), and Zn(II) ions from aqueous solutions by membrane filtration with the help of water soluble CS was described by Juang and Shiau [90]. Verbych et al. [91] reviewed on the efficiency of heavy metals removal from simulated ground water containing humic substances by means of enhanced ultrafiltration with CS.

Removal of toxic metals from streaming water and ground water is an important task to preserve the environment as mentioned by Seko et al. [92]. Radiation process of grafting and cross-linking can synthesize adsorbent having high performances. Graft adsorbent can be synthesized by using the conventional polymer like polyethylene having variety of shapes such as membrane, cloth, and fiber.

A mathematical model including convection, diffusion, and Freundlich adsorption is developed by Shi et al. [93]. To examine the validity of the model, the affinity membranes were prepared by coating CS on the nylon membranes, a ligand of poly-l-lysine was bound to the chitosan-coated membranes, and the adsorption behavior of bilirubin through the stacked affinity membranes was investigated.

Novel CS/cellulose acetate blend hollow fibers by the wet spinning method to obtain adsorptive membranes were prepared by Liu and Bay [94]. In the hollow fiber membranes, CA acted as a matrix polymer and CS as a functional polymer to provide the membrane with coupling or reactive sites for affinity-based separations. Formic acid (FA) was used as the co-solvent for both CA and CS to prepare the dope solution and NaOH solution was used as the external and internal coagulants in the wet spinning fabrication process. The properties of the blend hollow fibers were characterized through water flux measurements, surface and cross-section examinations,and adsorption performances to Cu(II) ions and bovine serum albumin on the surfaces, and were compared with those for CA hollow fibers. The blend hollow fibers displayed good tensile stress even though the tensile stress reduced with the increase in the CS content in the blend. The blend hollow fibers achieved significantly better adsorption performance as compared to that of CA hollow fibers, indicating the benefit in adding CS into CA to make novel blend hollow fibers in improving the performance of the traditional CA hollow fibers, especially for the affinity-based separation applications. They also reported the study on the effect of fabrication factors influencing the structures and morphologies of these membranes to achieve highly porous and macrovoid free structures with different pore sizes [95].

Han et al. [96] described a new method for preparing CS and CA blend hollow fibers with high CS contents as adsorptive membranes through the use of a nonacidic organic dope solvent. The new preparation method provides the great advantage of making high CS content blend hollow fiber membranes with potentially more choice of polymers as the matrix polymer to achieve enhanced adsorption capacity, improved material property, and reduced preparation cost.

Low-density vanillin-modified thin CS membranes were synthesized and characterized by Cestari et al. [97]. The membranes were utilized as adsorbent for the removal of Cu(II) from aqueous solutions. The modification of CS by introducing phosphonic acid group, which was confirmed by Fourier transform infrared and proton nuclear magnetic resonance and preparation of its composite membranes with poly (vinyl alcohol) of different compositions was described by Binsu et al. [98]. Blends of the naturally occurring polysaccharides, cellulose, and CS, obtained in the solid phase by the combined action of high pressure and shear deformation using various equipments were studied by Rogovina et al. [99]. A new cotton fiber with a CS coating by the oxidation of a cotton thread with potassium periodate at 60°C in water and subsequent treatment with a solution of CS in aqueous AA, was prepared by Liu et al. [100].

In the present work, a membrane consisting of a blend of CA and CS in different ratios was investigated for its ability to adsorb cupric ions from aqueous solution using a batch membrane cell constructed in our lab. Various factors were studied in order to evaluate their effect on the %Cu(II) ions chelated, permeated, extracted, and remained in the solution compartment.

2. Experimental

2.1. Materials

Shrimp shells were obtained from the local fish market, and constituted the source of chitin. The shells were cleaned from any adhering meat, washed well with soap and water, and rinsed efficiently with tap water followed by distilled water and left to air dry. AA and FA (Femico, Egypt) were used as solvents. Sodium hydroxide flakes (El-Salam Chemical Co., Egypt) were used for the deacetylation of chitin to CS. CS from crab was a product of Sigma Co., USA. CA powder (Panreac, Egypt) and potassium iodide (El Gomhouria Co., Egypt) were used in membrane fabrication and analysis of Cu(II) ions, respectively. Copper sulfate pentahydrate (El Nasr Pharmaceutical Chemical Co., Egypt) was used as the source of copper ions. Sodium thiosulfate (Chema Jet Co., Egypt) and soluble starch (Fisher Chemical Fisher Scientific, USA) were used in the determination of the Cu(II) ions.

2.2. Methods

2.2.1. Conversion of chitin to chitosan

A 100 ml of 40% aqueous sodium hydroxide solution was added to 22 g of the cleaned air-dried shrimp shells in a beaker. The mixture was heated at constant volume while stirring for 2 h, after which the mixture was washed successively with distilled water by decantation until neutrality. The beaker contents (CS flakes) were then filtered on a filter paper and the solids were spread on kitchen paper towels and left to air dry from dust.

2.2. Preparation of casting solutions

Weighed amounts of CA and CS in different ratios were mixed in a clean glass bottle then dissolved in either FA or AA by stirring with a mechanical mixer until complete dissolution. The closed bottle then was left aside at room temperature for two days to get rid of the air bubbles.

2.3. Casting of membrane

The solution was cast on a smooth uniform glass plate of a specially devised casting assembly equipped with a doctor's blade. The blade was preset to various clearances above the glass sheet by a set of new shaving blades to give an approximate desired as—cast thickness. The membranes were measured for their thickness by an Abbe vertical metroscope available in our workshop.

2.4. Adsorption experiments

2.4.1. Apparatus

A specially devised membrane cell was constructed from plexiglass which contained two compartments one for the copper solution while the other contains an equal volume of distilled water with the membrane separating the two. Constant stirring was used in the two compartments using either mechanical or magnetic stirring. Fig. 1 illustrates an isometric view of the membrane cell.

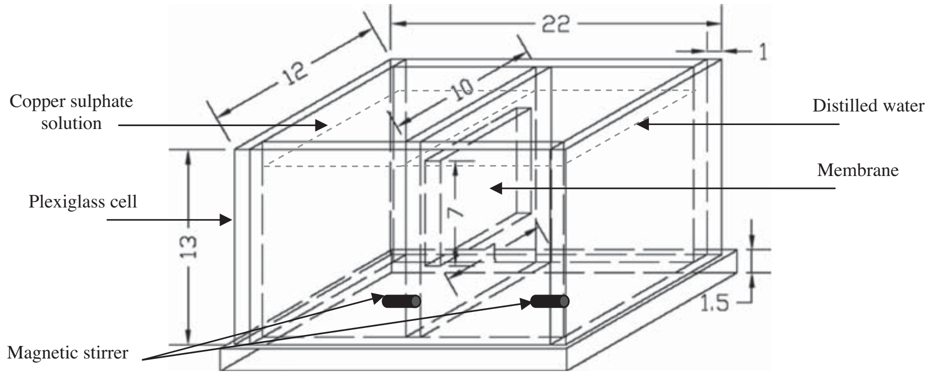


Fig. 1. Isometric view of the membrane cell (dimensions in cm).

2.4.2. Procedure

Batch experiments were used to determine the efficiency of each membrane under study. The membrane was cut into a square (7 × 7 cm) and made to fit in place. For every 30 min, 1 ml of the solution was analyzed for Cu(II) ions. The water compartment was analyzed in the same way whereby the residual, adsorbed, and permeated copper could be determined.

2.5. Variables investigated

The variables investigated in the present work were

(1) Mass ratio of CA to CS.
(2) Initial copper ion solution concentration.
(3) Type of CS (from shrimp or crab).
(4) Type of solvent (formic or acetic acid).
(5) Type of stirring (mechanical or magnetic).
(6) Stirring speed.
(7) Membrane thickness.

3. Results and discussion

Affinity membranes have recently played an important role in abating aqueous pollution due to heavy metals. In the present work, affinity membranes consisting of a blend of CA and CS in different ratios were fabricated and tested for their ability to chelate Cu(II) ions from copper sulfate solutions of different concentration. The results are presented in Figs. 2–11 as well as micrographs of SEM examination of the membranes after being submitted to adsorption experiments (Figs. 12–17) in which a, b, and c represent the upper, lower, and cross-section view, respectively. Also, com-

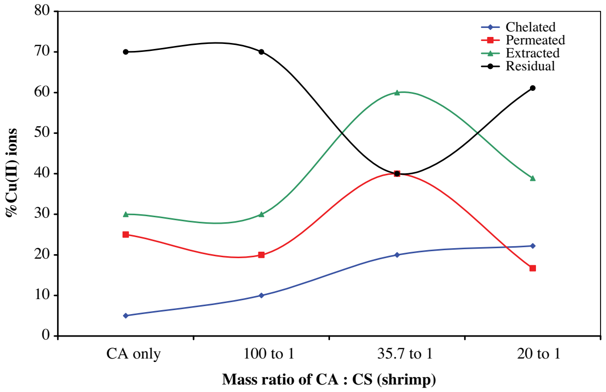


Fig. 2. Effect of mass ratio of CA:CS (shrimp), $C_i = 2.65$ g copper ion/l, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.7201$ mm.

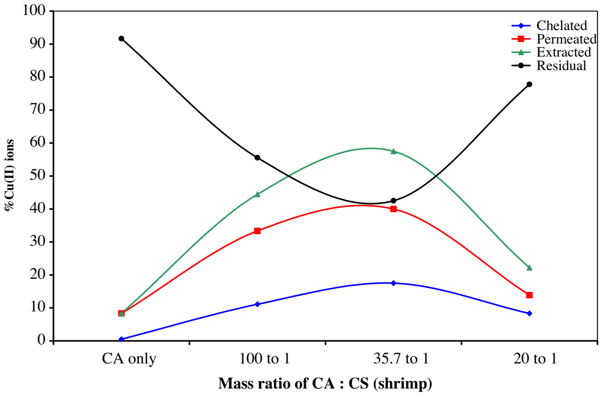


Fig. 3. Effect of mass ratio of CA:CS (shrimp), $C_i = 5.3$ g copper ion/l, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.6536$ mm.

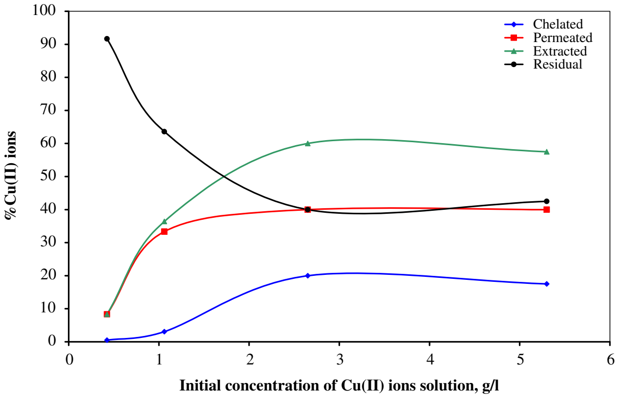


Fig. 4. Effect of initial concentration of Cu(II) solution, mass ratio of CA:CS (shrimp) = 35.7:1, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.6956$ mm.

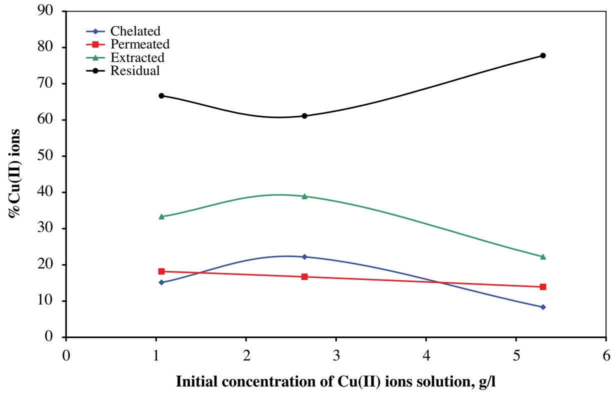


Fig. 5. Effect of initial concentration of Cu(II) solution, mass ratio of CA:CS (shrimp) = 20:1, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.7391$ mm.

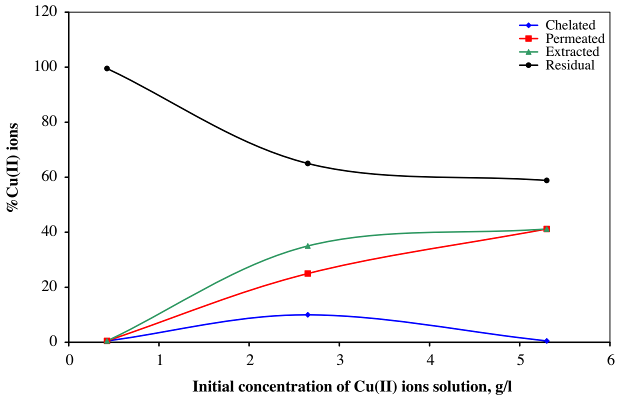


Fig. 6. Effect of initial concentration of Cu(II) solution, mass ratio of CA:CS (crab) = 35.7:1, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.6763$ mm.

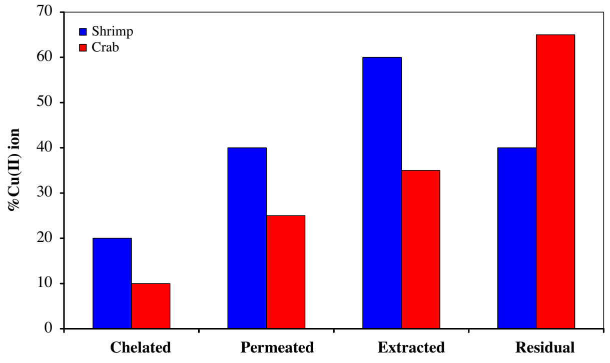


Fig. 7. Effect of type of CS, $C_i = 2.65$ g Cu(II) ion/l, mass ratio of CA:CS = 35.7:1, FA solvent, magnetic stirring (500 rpm), and $\lambda = 0.6708$ mm.

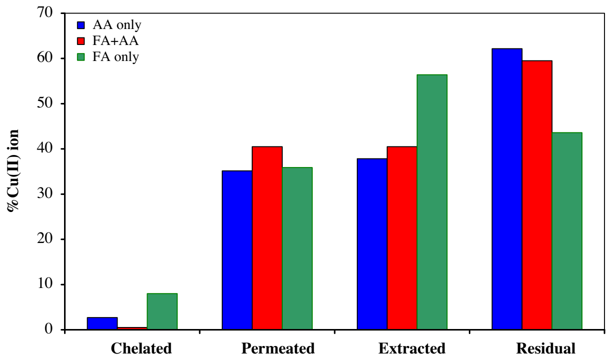


Fig. 8. Effect of type of solvent, mass ratio of CA:CS (mixture of shrimp and crab) = 62.5:1, $C_i = 1.06$ g Cu(II) ion/l, magnetic stirring (500 rpm), and $\lambda = 0.6719$ mm.

puted overall mass transfer coefficients were obtained from Fig. 18 and Table 1 presents their values.

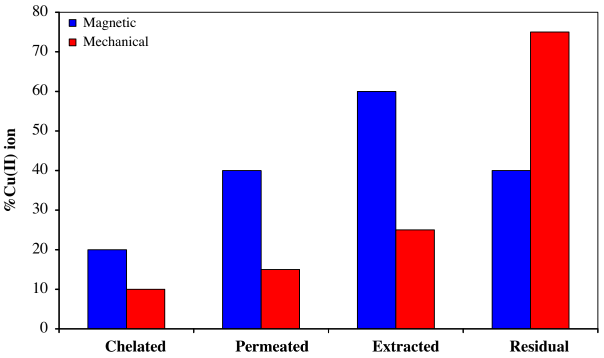


Fig. 9. Effect of stirring type, $C_i = 2.65$ g Cu(II) ion/l, mass ratio of CA:CS (shrimp) = 35.7:1, FA solvent, stirring speed = 500 rpm, and $\lambda = 0.7201$ mm.

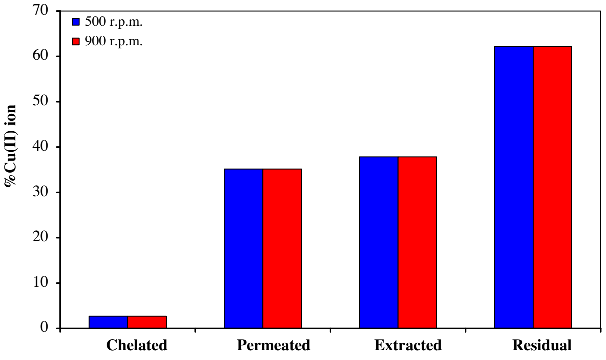


Fig. 10. Effect of stirring speed, $C_i = 1.06$ g Cu(II) ion/l, mass ratio of CA:CS (mixture of shrimp and crab) = 62.5:1, magnetic stirring, AA solvent, and $\lambda = 0.6719$ mm.

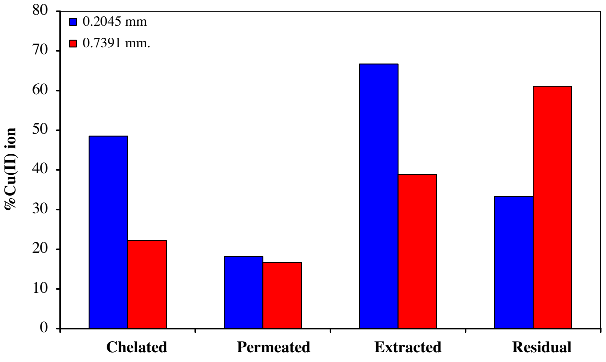
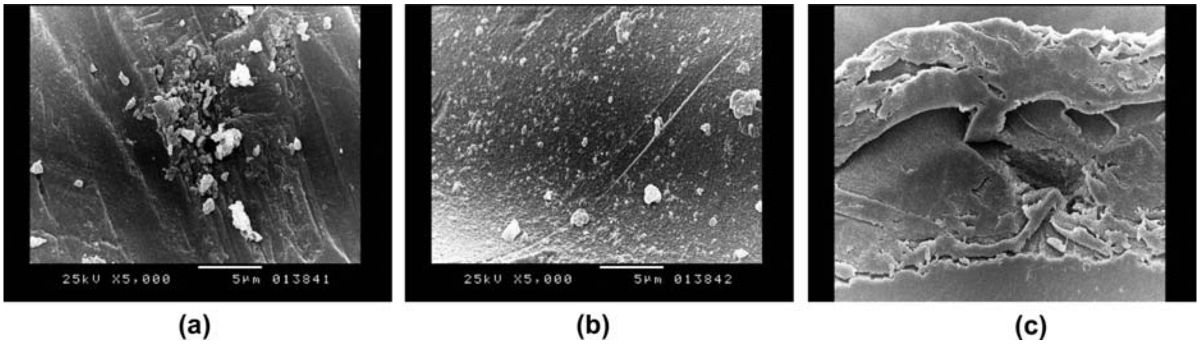


Fig. 11. Effect of membrane thickness, mass ratio of CA:CS (shrimp) = 20:1, FA solvent, and magnetic stirring (500 rpm).

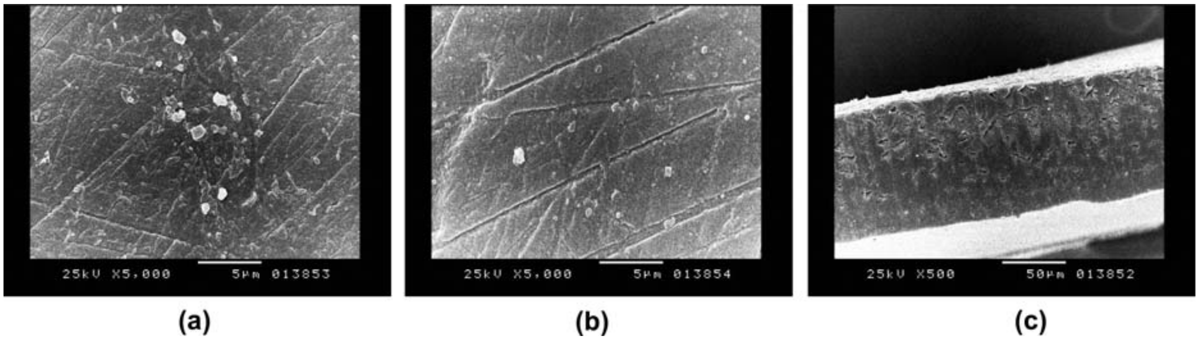
3.1. Effect of mass ratio

From Fig. 2 which shows the effect of mass ratio of CA to CS from shrimp shells and in which the % of



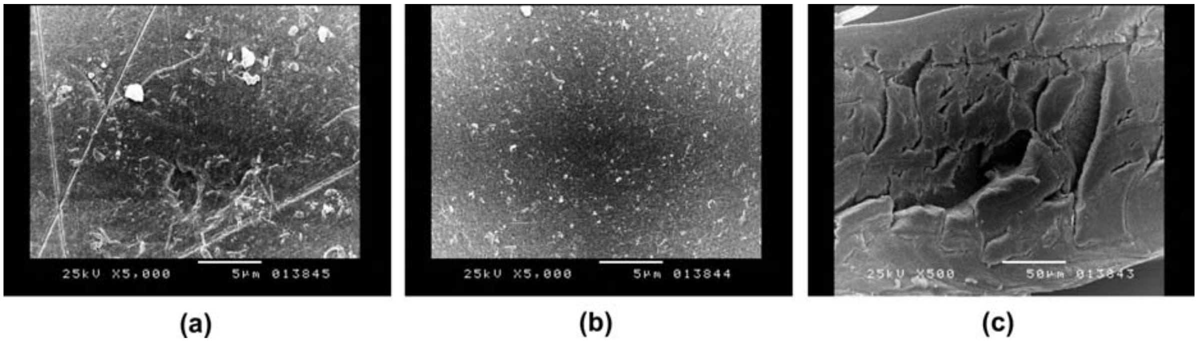
(a) (b) (c)

Fig. 12. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA only membrane of $\lambda = 0.647$ mm after adsorption experiment in solutions of $C_i = 2.65$ then 5.3 g Cu(II)/l.



(a) (b) (c)

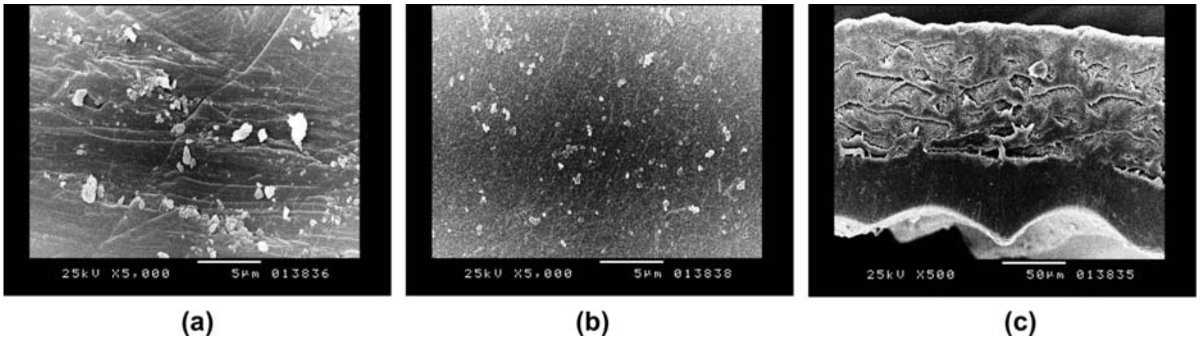
Fig. 13. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA:CS (shrimp) = 100:1 membrane of $\lambda = 0.5995$ mm after adsorption experiment in solutions of $C_i = 2.65$ then 5.3 g Cu(II)/l.



(a) (b) (c)

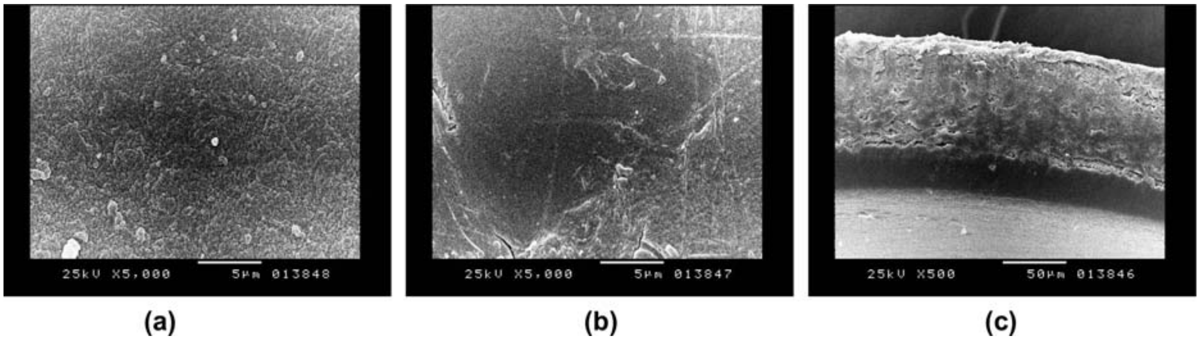
Fig. 14. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA:CS (shrimp) = 35.7:1 membrane of $\lambda = 0.7201$ mm after adsorption experiment in solutions of $C_i = 2.65$ then 5.3 g Cu(II)/l.

Cu(II) ions chelated, permeated, extracted, and residual (remaining) are indicated, it is observed that in case of CA membrane the % extracted (chelated + permeated) Cu(II) ions is 30% of the Cu(II), whereas 70% of ions remain in the solution compartment. This is expected since CA does not have strong binding ions such as CS. However, the % adsorbed to the free (OH^-) in secondary CA is only 5% of the ions while 25% of the ions permeate through the membrane in spite of its asymmetric nature (Fig. 12(c)). However, when CA is blended with CS in a ratio 100:1, it is realized that the chelated ions increased to 10% and those permeated were less than in case of CA. The reason is the presence of the amino group which caused an increased adsorption of the Cu(II) ions. However, the permeated amount is decreased due to the trapping



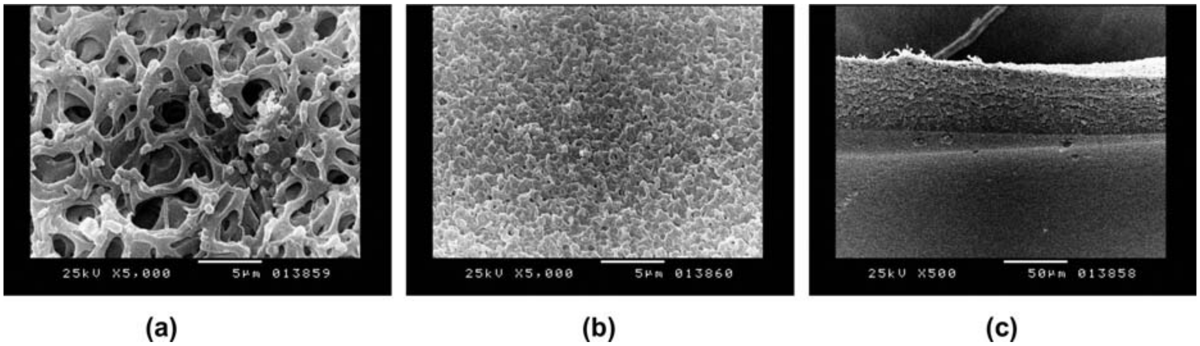
(a) (b) (c)

Fig. 15. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA:CS (shrimp) = 20:1 membrane of $\lambda = 0.6536$ mm after adsorption experiment in solutions of $C_i = 2.65$ then 5.3 g Cu(II)/l.



(a) (b) (c)

Fig. 16. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA:CS (crab) = 35.7:1 membrane of $\lambda = 0.6763$ mm after adsorption experiment in solutions of $C_i = 2.65$ then 5.3 g Cu(II)/l.



(a) (b) (c)

Fig. 17. Micrographs of SEM examination of upper, lower, and cross-section views, respectively, for CA:CS (shrimp) = 20:1 membrane of $\lambda = 0.2045$ mm after adsorption experiment in solution of $C_i = 1.06$ g Cu(II)/l.

effect of the primary amino group, which allows less Cu(II) ions to permeate and due to the dense membrane matrix (Fig. 13(c)). However, the total amount extracted is the same in the CA membrane and the aforementioned blend membrane. Accordingly, the remaining Cu(II) ions in the solution compartment are identical in the two cases. On increasing the ratio of CS in the blend membrane to 35.7:1 as expected, the amount chelated reached 20% and that permeated reached 40%, which is due to a larger amount of CS present and due to the dense nature of the membrane. The microvoid present in the membrane are clear from the micrograph (Fig. 14(c)), which are responsible for allowing more ions to permeate. Accordingly, the total extracted ions reached 60%, while only 40% of the 2.65 g Cu(II)/l remained in the original solution. This

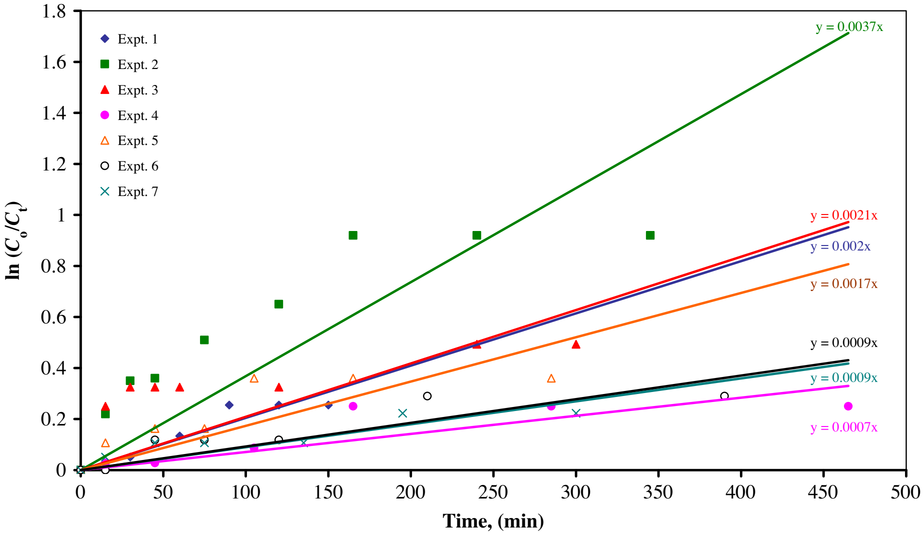


Fig. 18. Determination of mass transfer coefficient.

Table 1
Values of overall mass transfer coefficients for some experiments

Experiment number	C_i (g/l)	Mass ratio of CA to CS (shrimp)	λ (mm)	Slope	K (cm/min) × 10^2
1	5.3	35.7:1	0.7201	0.002	4.90
2	2.65	35.7:1	0.7201	0.0037	9.06
3	2.65	20:1	0.6536	0.0021	5.14
4	5.3	20:1	0.6536	0.0007	1.71
5	2.65	100:1	0.5995	0.0017	4.16
6	5.3	100:1	0.5995	0.0009	2.20
7	2.65	CA only	0.647	0.0009	2.20

is an important observation since it means that 60% of the 2.65 (1.2) g is extracted, which is a big amount relative to the mass of the membrane subjected to the solution. The last ratio which is the highest (20:1), however, resulted in about 22.2% chelation and only 16.7% permeation which means about 38.9% extraction and therefore 61.1% residual Cu(II) remained. One observation which is of importance is that the % chelation increased gradually from CA membrane to low, medium, and high ratios of CS in the membrane, which is expected; however, maximum extraction was achieved in case of the medium ratio (35.7:1).

Fig. 3 also presents the effect of mass ratio of CA to CS, but at a higher concentration (5.3 g Cu(II) ions/l). It is noteworthy that the membranes used in the experiments denoted by Fig. 2 were the same used in in Fig. 3. It is obvious that CA membrane almost did not chelate any ions and that the blend membrane with a medium ratio of CA to CS adsorbed about 17.5% of the Cu(II) ions followed by that membrane with less CS followed by that with the greatest ratio. This could be explained to be due to the fact that CS is expected to have a greater ability to adsorb Cu(II) ions much better than CA alone. However, in case of the smallest ratio CA:CS (20:1) the % Cu(II) ions chelated less than the other lower two ratios may be due to the morphology of the membrane, which is shown in Fig. 15(c) to be denser than the other two. In addition, the CA membrane was a dense one and allowed only 8.3% of the Cu(II) ions to permeate, while 91.7% of the ions remained in the solution compartment. The same pattern is shown for the amount of the permeated ions through the membranes in the same Fig. 3. On comparing the extracted amount to the residual ions, it is observed that at the present concentration, the residual amount exceeded that extracted in all cases except that of membrane formed from a ratio of 35.7:1, which suggests it to be a good affinity membrane to Cu(II) ions.

3.2. Effect of initial solution concentration

Fig. 4 illustrates the effect of C_i of Cu(II) solution. Again, a nearly similar trend to that in Fig. 3 is clear for the amount adsorbed, but the highest concentration results in almost 20% chelation. The amount permeated was much greater than that adsorbed. This could be due to the adsorption sites being occupied on increased concentration so that at the highest concentration all of the sites were filled and no more Cu (II) ions can be adsorbed. The same pattern was shown in which the % extracted increased to a maximum level of the highest concentration. In regard to the remaining Cu(II) ions in the solution compartment, it was clear that in the case of the lowest concentration, probably due to a very low driving force being present, almost 91.7% of the Cu(II) remained in the solution compartment. On increased concentration, the residual Cu(II) ions decreased steadily except at the highest concentration which was almost equal to the one with a lower C_i. This result was discussed in the aforementioned lines.

The effect of C_i was examined for the (20:1) membrane in Fig. 5 for three different C_is. It was realized that the medium concentration resulted in 22.2% chelation by the affinity membrane which was greater than a similar range of concentration in Fig. 4, but slightly higher probably due to the higher ratio of CS in the membrane. However, the amount adsorbed decreased at the highest concentration tested, which may be attributed to the free sites being filled, in addition to the dense nature of the membrane attributed to FA solvent as shown in Fig. 15(c). The amount permeated decreased as the concentration was increased. However, the residual amount in the three cases were between 61.1 and 77.8% which proved that the present membrane with bigger quantity of CS than that presented in Fig. 4 was not as efficient as the latter. It is worth noting that the intermediate ratio of CA:CS resulted in best results from Fig. 2 and especially Fig. 3, again, confirming the fact that the morphology of the membrane may be a dominating factor.

From Fig. 5, the effect of C_i on the membrane made from (35.7:1) CS obtained from crab and not from shrimp, it is clear that the amount chelated of Cu(II) ions is trivial if not equal to zero in two cases, which stressed that CS made from crab was worse than that of shrimps which has been stated by Krajewska [2]. Another reason might be the difference in the degree of deacetylation of the crab and shrimps which was not stated on the crab container. Accordingly, in the case of very low concentration Cu(II) ions neither permeated nor were chelated by the blend membrane using crab as a source for CS, and as a result, the remaining amount was 100%. On the other hand, the moderate concentration permeated 25% while almost 65% remained, and in case of the highest concentration 41.2% permeated and 58.8% remained in the solution, however, the membrane was less efficient affinity membrane.

3.3. Effect of source of chitosan

The effect of type of CS, whether from shrimp or crab shells was clarified on analyzing Fig. 7. It was noticed that CS from shrimp shells was double as efficient in adsorbing Cu(II) ions than that obtained from crab shells. Additionally, the permeated Cu(II) ions were almost double in case of shrimps shells. Therefore, as a result, the residual Cu(II) ions was only 40%, whereas in the other case it reached up to 65%, under the conditions mentioned in the figure caption.

Fig. 16(c) indicates the dense membrane structure obtained from crab CS which led to poor chelation and moderate permeation. Fig. 16(a) shows very little adsorption of Cu(II) ions on the upper membrane surface which verified the obtained results.

3.4. Effect of type of solvent

The effect of type of solvent is illustrated in Fig. 8 in which either AA or FA was used alone or together in equal volume. The figure proved that under the conditions mentioned in the figure caption, it was clear that FA was a better solvent than AA, and that FA + AA in equal proportions resulted in no chelation whatsoever. However, in case of % Cu(II) ions permeation, the figure showed that the two acids allowed the same amount of Cu(II) ions to permeate through the membrane, and on mixing the two acids an increase of about 5% permeated Cu(II) ions was obtained. This may be due to a synergism between the two acids which improved the porosity of the resulting membrane.

3.5. Effect of type of stirring

As to the effect of stirring type, it is clear from Fig. 9 under the conditions mentioned in the caption that magnetic stirring was more efficient than mechanical stirring probably due to the flow pattern during magnetic stirring being smoother next to the membrane, whereas in mechanical stirring the propeller was positioned more or less near the membrane surface which resulted in slicing of the solution along the membrane surface causing the Cu(II) ions to rapidly pass through the membrane not giving the ions the opportunity to diffuse to the inside of the membrane. Therefore, the residual Cu(II) ions in the solution compartment were almost twice that in case of the magnetic stirring. Accordingly, magnetic stirring was recommended and used in all the aforementioned experiments. It is noteworthy that there is a region of high turbulence in the vicinity of the propeller [101].

3.6. Effect of stirring speed

The effect of stirring speed using magnetic stirring proved as shown in Fig. 10 that stirring at 500 rpm gave identical results to stirring at 900 rpm, as long as swirling does not take place [101].

3.7. Effect of membrane thickness

Fig. 11 clarifies the effect of membrane thickness which proved that a thinner membrane resulted in more than double the result in case of the much thicker membrane. This may be attributed to the higher porosity of the membrane which led to higher amount of Cu(II) ions adsorbed. The large amount of Cu(II) ions chelated by the aforementioned membrane was most probably due to the very high porous structure of this thin membrane which is shown in Fig. 17 (a)–(c).

It is worth noting that if the previous experiments had been done using thinner membranes, the results would have even been better than those arrived at in the present study. To this end, future work should be done using thinner membranes in order to optimize the results regarding increasing the amount of Cu(II) ions adsorbed by the membrane. Also, desorption is still to be studied in the near future.

Fig. 18 presents the values of the overall mass transfer coefficients for different membranes under different initial Cu(II) ion solution concentrations for almost identical membrane thicknesses. It is clear that the experiments in which the concentration was 2.65 g Cu(II) ions resulted in the highest mass transfer coefficients which suggest that moderate concentrations used in the present study led to the best affinity membranes regarding % chelation and permeation (experiments 2, 3 then 5).

4. Conclusions

From the present work it was shown that:

(1) Blending CS with CA resulted in stronger membranes since CS alone is known to produce rather weak membranes, at the same time, CS, due to the presence of NH_2 groups, can function as a chelating agent for heavy metal ions (copper in particular). These blend membranes can have the advantage combining useful properties from each constituent.

(2) Using AA and FA could have been replaced by aqueous FA or AA had the CS been used alone. But the use of concentrated acids resulted in forming more or less dense membranes, which were difficult to penetrate as shown from the scanning electron microscopic examinations.

(3) Use of thinner membranes could result in better affinity to Cu (II) ions which was proven in our work, the pure FA used as solvent emphasizing the dense structure of the resulting membranes.

(4) It was found that the presence of CS obtained from shrimp shells had a better affinity than that obtained from crab shells.

(5) An optimum copper solution concentration existed at which maximum affinity to the Cu(II) ions was attained after which it declined due to the amount of available chelating sites being occupied.

(6) The composition of the casting solution markedly affects the properties of the fabricated affinity membranes, so that FA was better than AA, while an equivolume mixture of the two solvents deteriorated the adsorbing nature of the membrane. On the other hand, it resulted in improved permeation compared to each solvent alone.

(7) It was concluded that magnetic stirring resulted in improved chelation and permeation through the membrane since high turbulence in case of mechanical stirring near the propeller caused the liquid to slice quickly along the membrane surface not giving an opportunity for the Cu (II) ions to diffuse through the surface to the other side of the membrane.

Nomenclature

CA — cellulose diacetate
CS — chitosan
C_i — initial concentration of Cu(II) ion solution (g/l)
FA — formic acid
AA — acetic acid
λ — membrane thickness (mm)

References

[1] E. Chiellini, F. Chiellini, P. Cinelli, in: Gr. Scott (Ed.), Degradable Polymers: Principles and Application, Kluwer Academic publishers, ISBN 1-4020-0790-6, 2002.
[2] B. Krajewska, Membrane-based processes performed with use of chitin/CS materials, Sep. Purif. Technol. 41 (2005) 305–312.

[3] K. Kurita, Controlled functionalization of the polysaccharide chitin, Prog. Polym. Sci. 26 (2001) 1921–1971.

[4] J.A. Howell, Desalination 144 (2002) 127.

[5] S.M. Hudson, C. Smith, in: D.L. Kaplan (Ed.), Biopolymers from Renewable Resources, Springer-Verlag Berlin Heidelberg, New York, ISBN 3-540-63567-X, 1998.

[6] Q. Li, E.T. Dunn, E.W. Grandenaison, M.F.A. Goosen, J. Bioact. Comp. Polym. 7 (1992) 379.

[7] M.G. Peter, Applications and environmental aspects of chitin and chitosan, J. Macromol. Sci. Pure Appl. Chem. A(32) (1995) 629–640.

[8] W. Paul, C.P. Sharma, STP Pharma. Sci. 10 (2000) 5.

[9] A.K. Singla, M. Chawla, Pharm. Pharmacol. 53 (2001) 1047.

[10] M. Minoru, S. Hiroyuki, S. Yoshihiro, Trends Glycosci. Glycotechnol. 14 (2002) 205.

[11] O.A.C. Monteiro, C. Airoldi, Int. J. Biol. Macromol. 26 (1999) 119.

[12] F.L. Mi, C.Y. Kuan, S.S. Shyu, S.T. Lee, S.F. Chang, Carbohydr. Polym. 41 (2000) 389.

[13] C. Peniche, W. Argüelles-Monal, H. Peniche, N. Acosha, Macromol. Biosci. 3 (2003) 511.

[14] H.S. Kaş, J. Microencapsul. 14 (1997) 689.

[15] O. Felt, P. Buri, R. Gurny, Drug Dev. Ind. Pharm. 24 (1998) 979.

[16] L. Illum, Pharm. Res. 15 (1998) 1326.

[17] S.V. Madihally, H.W.T. Matthew, Biomaterials 20 (1999) 1133.

[18] B. Krajewska, Diffusion of metal ions through gel CS membranes, React. Funct. Polym. 47 (2001) 37–47.

[19] Z. Modrzejewska, W. Eckstein, CS hollow fiber membranes, Biopolymers 73 (2004) 61–68.

[20] X. Zeng, E. Ruckenstein, Supported CS-dye affinity membranes and their protein adsorption, J. Membr. Sci. 117 (1996) 271–278.

[21] M. Naim, Preparation of an adsorptive membrane from crude CS obtained from shrimp shells, in: 6th International Conference on Role of Engineering Towards a Better Environment, RETBE, Alexandria, 2006.

[22] X. Zeng, E. Ruckenstein, Cross-linked macroporous CS anion-exchange membranes for protein separations, J. Membr. Sci. 148 (1998) 195–205.

[23] L. Yang, W.W. Hsiao, P. Chen, CS-cellulose composite membrane for affinity purification of biopolymers and immunoadsorption, J. Membr. Sci. 197 (2002) 185–197.

[24] C.X. Liu, R.B. Bai, Recovery of bovine serum albumin (BSA) by tripolyphosphate (TPP) cross-linked CS membrane, in: Presented at Recent Advances in Separation & Pharmaceutical Products Development, NTU, Singapore, 21–23 February, 2005.

[25] A. Dufresne, J.Y. Cavaillé, D. Dupeyre, M. Garcia-Ramirez, J. Romero, Morphology, phase continuity and mechanical behavior of polyamide 6/CS blends, Polymer 40 (1999) 1657–1666.

[26] A. Isogani, R.H. Atalla, Preparation of cellulose-CS polymer blends, Carbohydr. Polym. 19 (1992) 25–28.

[27] M. Hasegawa, A. Isogai, S. Kuga, F. Onabe, Preparation of cellulose-CS blend film using chloral/dimethyl formamide polymer, 35 (1994) 983–987.

[28] S.Z. Rogovina, T.A. Akopova, G.A. Vikhoreva, I.N. Gorbacheva, Solid state production of cellulose-CS blends and their modification with the diglycidyl ether of olögo (ethylene oxide), Polym. Degrad. Stab. 73 (2001) 557–560.

[29] Y.K. Twu, H.I. Huang, S.Y. Chang, S.L. Wang, Preparation and sorption activity of CS/cellulose blend beads, Carbohydr. Polym. 54 (2003) 425–430.

[30] L. Jin, R.B. Bai, Mechanisms of lead adsorption on CS/PVA hydrogel beads, Langmuir 18 (2002) 9765–9770.

[31] Y.-B. Wu, S.-H. Yu, F.-L. Mi, C.-W. Wu, S.-S. Shyu, C. Peng-Chao, Preparation and characterization of mechanical and anti-bacterial properties of CS/cellulose blends, Carbohydr. Polym. 57 (2004) 435–440.

[32] C.M. Yun, J.R. Shin, Adsorption of tannic acid, humic acid and dyes from water using the composite of CS and activated clay, J. Colloid Interface Sci. 278(1) (2004) 18–25.

[33] S.C. Yong, C.C. Wen, H.K. Shein, Adsorption of color dyestuffs on polyurethane–CS blends, J. Appl. Polym. Sci. 91(6) (2004) 3991–3998.

[34] A. Matsuda, T. Ikoma, H. Kobayashi, J. Tanaka, Preparation and mechanical property of core-shell type CS/calcium phosphate composite fiber, Mater. Sci. Eng. C 24(6–8) (2004) 723–728.

[35] G.C. Steenkamp, K. Keizer, H.-W.-J.-P. Neomagus, H-M. Krieg, Copper (II) removal from polluted water with alumina/CS composite membranes, J. Membr. Sci. 197 (2002) 147–156.

[36] L. Yang, W.W. Hsiao, P. Chen, CS-cellulose composite membrane for affinity purification of biopolymers and immuno adsorption, J. Membr. Sci. 197 (2002) 185–197.

[37] Y. Wan, K.A.M. Creber, B. Peppley, V.-T. Bui, CS-based electrolyte composite membranes-mechanical properties and ionic conductivity, J. Membr. Sci. 284 (2006) 331–338.

[38] D. Ren, H. Yi, H. Zhang, W. Xie, X. Ma, A preliminary study on fabrication of nanoscale fibrous CS membranes *in situ* by biospecific degration, J. Membr. Sci. 280 (2006) 99–107.

[39] W. Hongming, Y. Liansheng, Z. Manchang, Preparation of chitin and its application in water treatment, Guangxi Huangog 26(4) (1997) 40–43.

[40] L. Cervera, C. Arnal, Removal of heavy metals by using adsorption on aluminum or CS, Anal. Bional. Chem. 375(6) (2003) 820–825.

[41] D. Zhou, L. Zhang, Cellulose/chitin beads for adsorption of heavy metals in aqueous solution, Water Res. 38(11) (2004) 2643–2650.

[42] S. Zheng, Z. Yang, D.H. Job, Y.H. Park, Removal of chlorophenols from ground water by CS sorption, Water Res. 38(9) (2004) 2315–2322.

[43] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res. 36(10) (2002) 2463–2474.

[44] S. Hirano, T. Nakahira, M. Nakagawa, S.K. Kim, The preparation and applications of functional fibres from crab shell chitin, Biotechnology 70 (1999) 373–377.

[45] M.M. Beppu, E.J. Arruda, R.-S. Vieira, N.N. Santos, Adsorption of Cu(II) on porous CS membranes functionalized with histidine, J. Membr. Sci. 240 (2004) 227–235.

[46] A.-C. Chao, S.-H. Yu, G.-S. Chuang, Using NaCl particles as porogen to prepare a highly adsorbent CS membranes, J. Membr. Sci. 280 (2006) 163–174.

[47] X. Zheng, E. Ruckenstein, Control of pore sizes in macroporous CS and chitin membranes, Ind. Eng. Chem. Res. 35 (1996) 4169–4175.

[48] M. Gmşderelioğlu, P. Agi, Adsorption of concanavalin A on the well-characterized macroporous CS and chitin membranes, React. Funct. Polym. 61 (2004) 211–220.

[49] E. Guibal, Interactions of metal ions with CS-based sorbents: a review, Sep. Purif. Technol. 38 (2004) 43–74.

[50] T.-Y. Hsein, G.L. Rorrer, Sep. Sci. Technol. 30 (1995) 2455.

[51] T. Sakaguchi, T. Horikoshi, A. Nakajima, Nippon Nôgeigaku Kaishi 53 (1979) 149.

[52] N. Nishi, A. Ebina, S.-I. Nishimura, A. Tsutsumi, O. Hasegawa, S. Tokura, Int. J. Biol. Macromol. 8 (1986) 311.

[53] N. Nishi, Y. Mackita, S.-I. Nishimura, O. Hasegawa, S. Tokura, Int. J. Biol. Macromol. 9 (1987) 109.

[54] K.S. Choi, H.S. Ahn, Polym. Korea 14 (1990) 516.

[55] A. Heras, N.M. Rodriguez, V.M. Ramos, E. Agullo, Carbohydr. Polym. 44 (2001) 1.

[56] G. McKay, H.S. Blair, S. Grant, J. Appl. Polym. Sci. 40 (1987) 63.

[57] V.W.D. Chui, K.W. Mok, C.Y. Ng, B.P. Luong, K.K. Ma, Environ. Int. 22 (1996) 463.

[58] Y.-B. Wu, S.-H. Yu, F.-L. Mi, C.-W. Wu, S.-S. Shyu, C.-K. Peng, A.-C. Chao, Preparation and characterization of mechanical and anti-bacterial properties of CS/cellulose blends, Carbohydr. Polym. 57 (2004) 435–440.

[59] W.Q. Sun, G.F. Payne, M.S.G.L. Moas, J.H. Chu, K.K. Wallace, Biotechnol. Prog. 179 (1992) 8.

[60] J.M.C.S. Magalhães, A.A.S.C. Machado, Talanta 47 (1998).
[61] X. Zeng, E. Ruckenstein, J. Membr. Sci. 148 (1998) 195.
[62] H.K. No, S.P. Meyers, Rev. Environ. Contam. Toxicol. 163 (2000) 1.
[63] R.S. Juang, F.C. Wu, R.L. Tseng, Biores. Tech. 80 (2001) 187.
[64] O.A.C. Monteiro, Jr., C. Airoldi, J. Colloid Interface Sci. 212 (1999) 212.
[65] D.K. Roper, E.N. Lightfoot, J. Chromatogr. 702 (1995) 3.
[66] E. Selmer-Olsen, H.C. Ratnaweera, R. Pehrson, A novel treatment process for dairy wastewater with CS produced from shrimp-shell waste, Water Sci. Technol. 34(11) (1996) 33–40.
[67] B. Krajewska, Membrane-based processes performed with use of chitin/CS materials, Sep. Purif. Technol. 41(3) (2005) 305–312.
[68] I.L. Roux, H.M. Krieg, C.A. Yeates, J.C. Breyten Bacha, Use of CS antifouling agent in a membrane bioreactor, J. Membr. Sci. 248 (2005) 127–136.
[69] M.M. Beppu, E.J. Arruda, C.C. Santana, Synthesis and Characterization of Dense and Porous Structures from Chitosan Polymers: Science and Technology - Nov/Dec 4 (1999) 163–169.
[70] M.M. Beppu, C.C. Santana, Key Eng. Mater. 192 (2001) 31–34.
[71] M. Gingras, I. Paradis, F. Berthod, Biomaterials 24 (2003) 1653–1661.
[72] K.L. Shantha, D.R.K. Harding, Carbohydrate Polym. 48 (2002) 247–253.
[73] E.B. Denkbaş, E. Kiliçay, C. Birliksaven, E. Öztürk, React Funct. Polym. 50 (2002) 225–232.
[74] H. Ping, S.S. Davis, L. Illum, Euro. J. Pharm. 4 (1996) 173.
[75] Y. Wan, K.A.M. Creber, B. Peppley, V.T. Bui, Polymer 44 (2003) 1057–1065.
[76] M.A. Torres, C.G. Aimoli, M.M. Beppu, J. Frejlich, CS membrane with patterned surface obtained through solution drying, Colloids Surf. A: Physio Chem. Eng. Aspects 268 (1) (2005) 175–179.
[77] W. Kaminski, Z. Modrzejewska, Z. Sroda, CS flat and hollow-fiber membranes in: Z.S. Karnicki, A. Wojtasz-Pajak, M.M. Brzeski, P. Bykowski (Eds.), Chitin World, Wirtschafts-Verlag NW, Bremerhaven, 1995, p. 600.
[78] G.W. Urbanczyk, B. Lipp-Symonowicz, The influence of processing terms of CS membranes made of differently deacetylated chitin on the crystalline structure of membranes, J. Apply. Polym. Sci. 51 (1994) 2191–2194.
[79] B. Krajewska, A. Olech, Pore structure of gel CS membranes. I. Solute diffusion measurements, Polym. Gels Ntwk. 4 (1996) 33–43.
[80] N. Kubota, Permeability properties of CS—transition metal complex membranes, J. Appl. Polym. Sci. 64 (1997) 819–822.
[81] Z. Moderzejewska, W. Kaminski, Separation of Cr(VI) on chitosan membranes, Ind. Eng. Chem. Res. 38 (1999) 4946–4950.
[82] C. Tual, E. Espuche, M. Escoubes, A. Domard, Transport properties of CS membranes: influence of crosslinking, J. Polym. Sci. Polymn. Phys. 378 (2000) 1521–1529.
[83] F.-L. Mi, S.-S. Shyu, Y.-B. Wu, S.-T. Lee, J.-Y. Shyong, R. Huang, Fabrication and characterization of a sponge-like asymmetric CS membrane as a wound dressing, Biomaterials 22 (2001) 165–173.
[84] L.-Y. Wang, G.-H. Ma, Z.-G. Su, Preparation of uniform sized CS microspheres by membrane emulsification technique and application as a carrier of protein drug, J. Controlled Release 106 (2005) 62–75.
[85] M. Zeng, Z. Fang, C. Xu, Effect of compatibility on the structure of the microporous membrane prepared by selective dissolution of CS/synthetic polymer blend membrane, J. Membr. Sci. 230 (2004) 175–181.
[86] M. Zeng, Z. Fang, Preparation of sub-micrometer porous membrane from CS/polyethylene glycol semi-IPN, J. Membr. Sci. 245 (2004) 95–102.
[87] D.E.S. Santos, C.G.T. Neto, J.L.C. Fonseca, M.R. Pereira, CS macroporous asymmetric membranes—preparation, characterization and transport of drugs, J. Membr. Sci. 325 (2008) 362–370.
[88] L. Yang, P. Chen, CS/coarse-filter paper composite membrane for fast purification of IgG from human serum, J. Membr. Sci. 205 (2002) 141–153.
[89] Y.-K. Twu, H.-I. Huang, S.-Y. Chang, S.-L. Wang, Preparation and sorption activity of CS/cellulose blend beads, Carbohydr. Polym. 54 (2003) 425–430.
[90] R.-S. Juang, R.-C. Shiau, Metal removal from aqueous solutions using CS-enhanced membrane filtration, J. Membr. Sci. 165 (2000) 159–167.
[91] S. Verbych, M. Bryk, A. Alpatova, G. Chornokur, Ground water treatment by enhanced ultrafiltration, Desalination 179 (2005) 237–244.
[92] N. Seko, M. Tamda, F. Yoshii, Current status of adsorbent for metal ions with radiation grafting and cross linking techniques, NIMB 236 (2005) 21–29.
[93] W. Shi, F. Zhang, G. Zhang, Mathematical analysis of affinity membrane chromatography, J. Chromatogr. A1081 (2005) 156–162.
[94] C. Liu, R. Bai, Preparation of CS/cellulose acetate blend hollow fibers for adsorptive performance, J. Membr. Sci. 267 (2005) 68–77.
[95] C. Liu, R. Bai, Preparing highly porous CS/cellulose acetate blend hollow fibers as adsorptive membranes: effect polymer concentrations and coagulant compositions, J. Membr. Sci. 279 (2006) 336–346.
[96] W. Han, C. Liu, R. Bai, A novel method to prepare high CS content blend hollow fiber membranes using a non-acidic dope solvent for highly enhanced adsorptive performance, J. Membr. Sci. 302 (2007) 150–159.
[97] A.R. Cestari, E.F.S. Vieira, C.R.S. Mattos, Thermodynamics of the Cu(II) adsorption on thin vanillin-modified CS membranes, J. Chem. Thermodynam. 38 (2006) 1092–1099.
[98] V.V. Binsu, R.K. Nagarale, V.K. Shahi, P.K. Ghosh, Studies on N-methylene phosphonic CS/poly (vinyl alcohol) composite proton-exchange membrane, React. Funct. Polym. 66 (2006) 1619–1629.
[99] S.Z. Rogovina, S.Z. Akopova, G.A. Vikhoreva, I.N. Gorbacheva, Solid state production of cellulose—CS blends and their modification with the diglycidyl ether of oligo(ethylene oxide), Polym. Degrad. Stab. 73 (2001) 557–560.
[100] X.D. Liu, N. Nishi, S. Tokura, N. Sakairi, CS coated cotton fiber preparation and physical properties, Carbohydrate Polym. 44 (2001) 233–238.
[101] J.M. Coulson, J.F. Richardson, Chemical Engineering, 5th ed., vol. 2, Butterworth Heinemann, Oxford, 1969.