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Fabrication of Porous Chitosan Affinity Membranes - A Kinetic Study

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Abstract

Affinity membranes with surface functional groups that can be used as adsorptive sites for separation, are of great interest in many industrial and environmental applications. Among the various reactive functional groups, the amino-groups are more reactive than others, such as the hydroxyl groups, and can therefore be used directly as affinity adsorption sites. Recently, chitosan (CS) biopolymer has been increasingly studied as an adsorptive material due to its abundance in the free amino groups for various applications, in the form of powders, flakes or gel beads. In the present study, novel semi-permeable affinity membranes were fabricated from CS to be used in the adsorption of Cu(II) ions from aqeous solutions. Porogens including polyethylene glycol (PEG) and NaCl, were tested for their effect on the membranes' affinity for Cu(II) ions from aqueous solutions. Batch shake flask tests were conducted at different temperatures, and the equilibrium-, Freudlich-, and Langmuir-isotherms were constructed. The CS-NaCl membrane adsorbed almost 500 mg/g of CS. The kinetics of the adsorption were determined according to Lagergren's models and the adsorption process was best described by the pseudo-second-order kinetic equation. The activation energy and thermodynamic parameters were also determined and the negative value of ΔG° suggested the feasibility of adsorption. SEM examinations were conducted to determine the membranes' morphologies.

Keywords: Adsorption, Affinity membrane, Chitosan, Copper, Kinetics

Introduction

CS is the deacetylated form of chitin, which is the second most abundant available biopolymer in nature after cellulose. It is an extremely hydrophilic material for which the reactive amino and hydroxyl groups owe their hydrophilic nature and endow it with a great capability in sorption of heavy metal ions (Boricha and Murthy, 200). Contamination of water and soil with heavy metals is detrimental to human beings and the environment, and is a major concern worldwide (Zhang et al., 2011). Technologies for heavy metal removal in water and wastewater treatment in particular, have bloomed in the last few decades, for which adsorption appears to be an effective way by which heavy metal ions are removed from aqueous solutions. Adsorptive membranes are a type of porous membranes bearing specific functional groups on their surfaces, which include $-NH_2$, $-SO_3$, –OH or -COOH, that can bond with the heavy metal ions through either ion exchange or surface complexation.

CS is biodegradable, cheap and wholly available from shells of crustaceans such as shrimps in seafood processing waste (Guibal, 2004). Amino groups make CS a cationic polyelectrolyte, that is soluble in aqueous acidic media, and when dissolved possesses a high positive charge on $–NH_3$ groups, that adheres to negatively charged surfaces, and chelates heavy metal ions with excellent gel-forming properties (Minoru et al., 2002; Monteiro and Airoldi, 1999; Mi, 2000; Peniche, 2003; Kas, 1997; Felt, 1998; Illum, 1998; Madihally and Matthew, 1999; Krajewska, 2001; Modrzejewska and Eckstein, 2004; Zeng and Ruckenstein, 1996). The preparation of pure CS membranes has been largely limited due to the poor mechanical strength and chemical stability of CS. However, Naim (Naim, 2006) has prepared adsorptive membranes made from CS, which efficiently adsorbed Cu(II) ions from aqueous copper sulfate solutions.

CS has been coated on supports such as flat PES membranes (Zeng and Ruckenstein, 1998) and cellulose membranes (Yang et al., 2002; Liu and Bai, 2005a) 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 (Dufresne et al., 1999; Isogani and Atalla, 1992; Hasegawa et al., 1994; Rogovina et al., 2001; Twu et al., 2003; Jin and Bai, 2002) 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. (Wu et al., 2004). Yang et al. (2002) prepared a composite CS-cellulose membrane by coating CS on a filter paper, and examined it as an affinity membrane. Wan et al. (2006) prepared CS-based immobilized electrolyte porous composite membranes using glutaraldehyde as cross-linking agent. Ren et al. (2006) reviewed the CS binary blend membranes fabricated by solvent casting of CS solution containing highly deacetylated CS and moderately deacetylated CS with different ratios. Carvera and Arnah (2003) evaluated the removal of heavy metals from wastewater by using CS.

Beppu et al. (2004) reviewed the ability of CS to form complexes with bivalent metal ions. Zheng and Ruckenstein (1996) described a procedure for the preparation of membranes with a tailored pore size using a silica porogen. Guibal (2004) reviewed the adsorption of metal cations by chelation on amine groups of CS in near neutral solutions in which sorption proceeds by electrostatic attraction on protonated amine groups. Shi et al. (2005) prepared affinity membranes by coating CS on nylon membranes. CS was employed as an excellent adsorbent for the sorption of phenols and poly-chlorinated biphenyls (Wu et al., 2004) and proteins (Sun et al., 1992; Magalhaˇes and Machado, 1998) and in pollution control as a chelating polymer for binding harmful metal ions (Zeng and Ruckenstein, 1998; No and Meyers, 2000; Juang et al., 2001).

Many publications have reported the performance of adsorptive membranes (Monteiro and Airoldi, 1999; Roper and Lightfoot, 1995). Krajewska (2005) pointed out how chitin/CS materials can contribute to the development of membrane-based processes classified as supportive in the sustainability of our life. There is abundant literature concerning the preparation of flat membranes (Urbanczyk and Lipp-Symonowicz, 1994; Krajewska et al., 1996; Kubota, 1997; Moderzejewska and Kaminski, 1999; Tual et al., 2000; Mi et al., 2001). Zeng et al. (2004) developed a method to prepare a microporous CS membrane by the selective dissolution of its blend. CS macro-porous membranes with asymmetric morphology by using an inorganic porogen agent (SiO_2) were prepared by Santos et al. (2008). A methodology to obtain asymmetric membranes with control of porosity and the average pore size was proposed. Verbych et al. (2005) reviewed the efficiency of heavy metals removal from simulated ground water containing humic substances by means of enhanced ultrafiltration blend CS-CA membranes, in which 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. The properties of the membranes were characterized through water flux measurements, surface and cross-section examinations, and adsorption performances to Cu(II) ions. They displayed good tensile strength even though the latter was reduced with an increase in the CS content in the blend. Han et al. (2007) described a new method for preparing CS and CA blend hollow fibers with high a CS content as adsorptive membranes. Novel CS/CA blend hollow fibers were prepared by Liu and Bai (2005b) by the wet spinning method to obtain adsorptive membranes. Naim and Abdel Razek (2012) prepared affinity membranes from CA, and CA/CS blends, and investigated the effect of the type and ratio of the solvents used in forming the casting solution, mass ratio of CA to CS, and source of CS (shrimp or crab) on the chelation and permeation of Cu(II) ions.

In the present work, porous CS membranes are prepared via the addition of NaCl or PEG (as porogens) to CS, and are compared to the CS membrane. A blend of CA/CS is prepared for comparison. The membranes are tested for their ability to adsorb Cu(II) ions from aqueous solution. Different isotherms are constructed, and the kinetics of adsorption are also determined, at different

temperatures, then the activation energy and the thermodynamic parameters are determined. The surface topology and cross-section morphology of all the membranes are determined by SEM examination.

Experimental

Materials

Analar CS powder (Alpha Chemica, India) and CA flakes (Panreac, Egypt) were used in membrane fabrication, and glacial acetic acid (AA) (Chemica jet, Egypt) was used as a solvent. PEG 4000 (Carbowax 4000 SRL, India) and sodium chloride (Alpha, India) were used as porogens, and sodium hydroxide (Chemica jet, Egypt) was used for neutralization.

Methods

Preparation of Casting Solution

A 3% aqueous acetic acid was added to 4gm CS and stirred while heating until complete dissolution. The solution was poured into several petri-dishes to a certain level, then left to completely air-dry for 48 hours. A 4% aqueous sodium hydroxide solution was poured on the air-dried membrane in order to neutralize the acetic acid and prevent the redissolution of the membrane in water. The membrane was washed efficiently with distilled water until the salt formed upon neutralization was totally removed.

Addition of Porogen

PEG and NaCl were used as porogens. Each porogen was added to the CS solution separately, and the method continued as aforementioned.

Batch Adsorption Experiments

Adsorption experiments were conducted, batchwise, using shake flask tests in order to evaluate the adsorption capacity of the membranes in adsorbing Cu(II) ions from aqueous solution. The membrane was cut into very tiny pieces before the adsorption tests. 20ml of $CuSO_4$ solution was added to each of the numerous conical flasks which contained different weights of CS, then shaken mechanically at different temperatures for two hours. Initially, adsorption experiments were conducted and analyzed for Cu(II) ions at different time intervals for the determination of the minimum time required for equilibrium adsorption to take place.

Construction of Adsorption Isotherms

Numerous adsorption isotherms namely: equilibrium-, Freundlich-, and Langmuir- isotherms were constructed.

Determination of Adsorption Kinetics

The adsorption kinetics and thermodynamic parameters were determined. An exact amount of finely cut CS membranes were weighed in a stoppered

conical flask. 100 ml of 1g Cu(II)/l solution were added to the membrane fragments and the flask was shaken in an automatic shaker equipped with a thermostatically controlled water bath. 1ml of the clear supernatant solution was pipetted, at different time intervals, and analyzed for Cu(II) ions with standard thiosulphate solution, using KI to liberate the iodine, and starch as an indicator. The pseudo -first and -second order Lagergren's diagrams relating $\ln(q_e-q_t)$ versus t, and t/q_t versus t in a respective order were constructed, where q_t is the mass of Cu(II) in mg biosorbed per gram of CS at time t (minutes), and q_e is the quantity biosorbed at equilibrium.

Scanning Electron Microscopy

All membranes were examined by scanning electron microscopy (SEM) to determine their morophology.

Results and Discussion

Adsorption Isotherms

Figures indicating the equilibrium isotherms for the different membranes are presented in Figures 1 and 2. The values of the constants pertaining to both Langmuir and Freundlich models (Eq. 1 and 2) are clarified in Tables 1 and 2. Figure 1 illustrates the equilibrium isotherms for the adsorption of Cu(II) ions with the CS membranes at different temperatures shown on the figure. It is clear that CS membrane chelates Cu(II) significantly reaching almost 250 mg/g of CS, and that adsorption is exothermic since heating decreases x/m.

Langmuir:

$$\frac{C_e}{q} = \frac{C_e}{q_m} + \left(\frac{1}{K_L\, q_m}\right) \qquad (1)$$

Freundlich:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (2)$$

Figure 1. *Equilibrium Isotherm for Adsorption of Cu(II) ions (1 g/L) with CS Membrane*

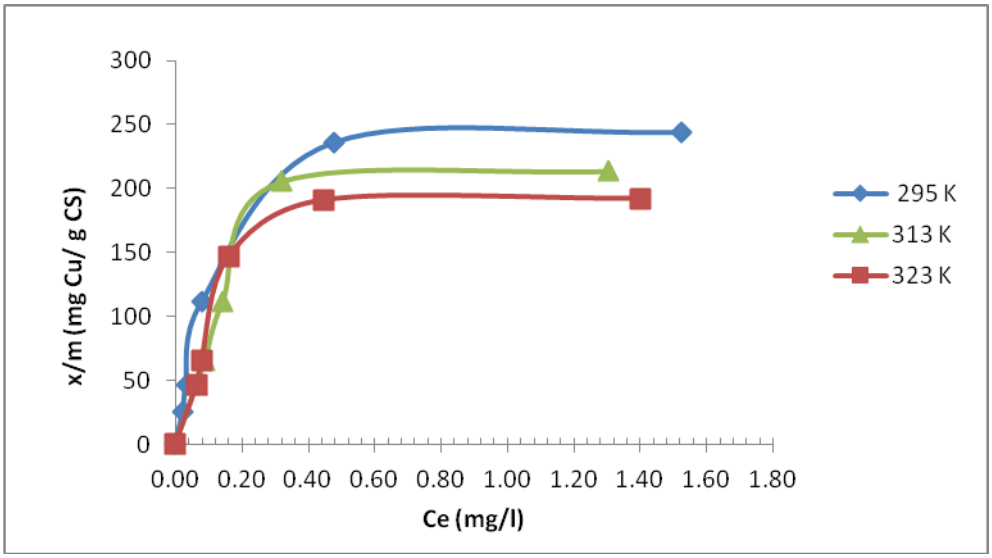


Table 1 presents the adsorption isotherms'constants for the adsorption of Cu(II) ions on CS at different temperatures. However, the figures are not shown. The table clarifies that the Langmuir isotherm model applies strictly since the correlation coefficient is always higher than 0.93. This indicates that the monolayer adsorption takes place and that the binding energy on the whole surface of the membrane was uniform. In other words the chelation of the Cu(II) ions to the $-NH_2$ functional groups takes place due to the lone pair of electrons available on the nitrogen atom. Moreover, it is observed that qm (maximum adsorption capacity) and K_L (Langmuir constant) vary inversely with temperature i.e. adsorption is exothermic. On the other hand, the Freundlich model does not fit the experimental data; however, despite this, 1/n is less than one, which denotes favorable adsorption.

Table 1. *Adsorption Isotherm Constants for Adsorption of Cu(II) Ions on CS at Different Temperatures*

Temp (K)	Langmuir isotherm parameters			Freundlich isotherm parameters		
	q_m (mg g^{-1})	K_L (Lmg^{-1})	R^2	K_F (mg g^{-1}) (Lmg^{-1})$^{1/n}$	1/n	R^2
295	243.8301	2.41248	0.9602	7.65773	0.5147	0.8765
313	213.7864	2.22741	0.9686	7.33669	0.5071	0.8054
323	192.2605	1.92639	0.9306	10.1976	0.4423	0.7586

Figure 2 presents the equilibrium isotherm for the adsorption of the Cu(II) ions with CS membrane blends with NaCl and PEG, and for CS alone for comparison. It is clear that the CS-NaCl blend membrane gave the highest pick-up of Cu(II) ions, which is double that of the CS membrane without

porogen, and about quadriple that of the CS-PEG membrane. These results have been explained on examining the SEM micrographs, since the CS-NaCl membrane exhibited nano-pores covering the entire matrix that led to this exceptional adsorptive capacity.

Figure 2. *Equilibrium Isotherm for Adsorption of Cu(II) Ions (1 g/L) with Membrane Blends at 22°C*

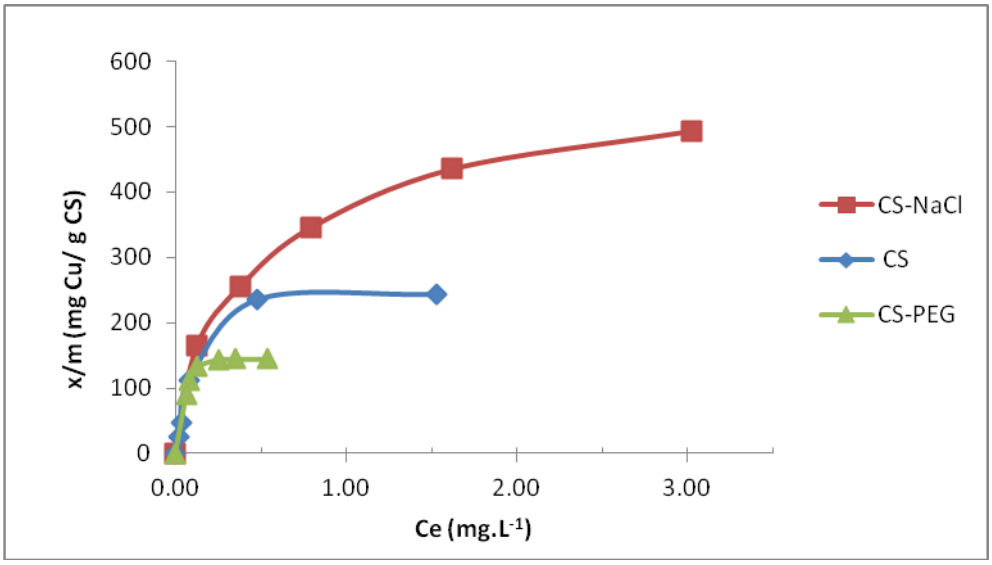


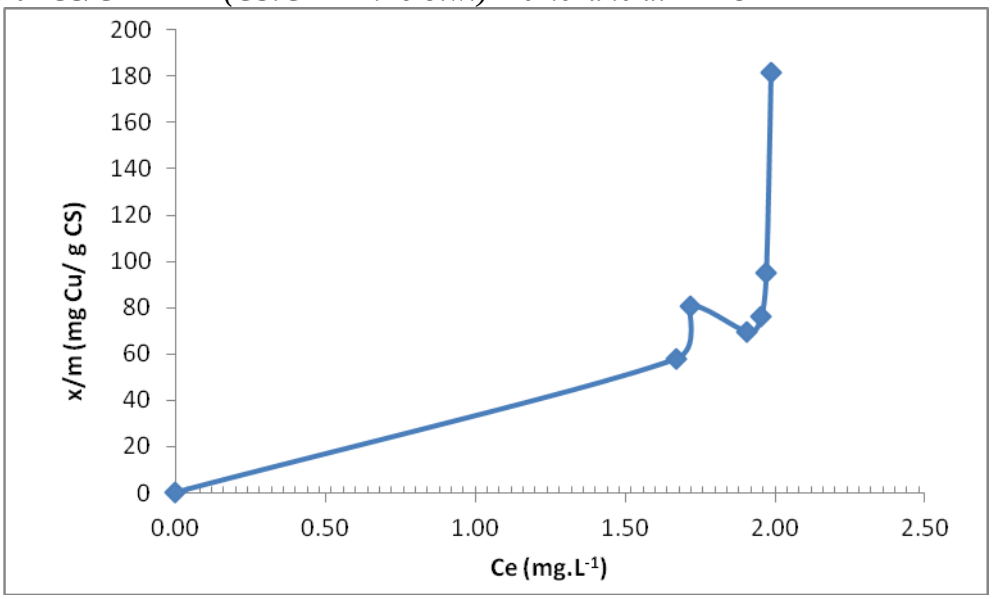
Table 2 clarifies that the Langmuir isotherm model is obeyed for the blend membranes as well, since R^2 varies from 0.9 to 0.97. However, the CS-NaCl membrane only, follows the Freundlich model.

Table 2. *Adsorption Isotherm Constants for Adsorption of Cu(II) Ions on Different CS Membrane Blends*

Membrane	**Langmuir isotherm parameters**			**Freundlich isotherm parameters**		
	q_m (mg g^{-1})	**K_L (Lmg^{-1})**	**R^2**	**K_F (mg g^{-1}) (Lmg^{-1})$^{1/n}$**	**1/n**	**R^2**
CS-NaCl	492.8886	0.96612	0.9716	30.78931	0.3539	0.9877
CS	243.8301	2.41248	0.9602	7.65773	0.5147	0.8765
CS-PEG	145.00	1.16891	0.9011	44.84355	0.1999	0.7675

Figure 3 indicates that the adsorption of the blend CS-CA membrane gives a type 2 (S-shaped) equilibrium isotherm, which signifies that the Cu(II) ions slowly penetrate within the pores. As expected, neither Langmuir nor Freundlich adsorption models were obeyed, since the relationships were far from linear, and the correlation coefficients were both less than 0.5 (figures are not shown).

Figure 3. *Equilibrium Isotherm for Adsorption of Cu(II) Ions from 1 g Cu/L with CS/CA in AA (CS:CA ≈1:20 b.w.) Membrane at 22 °C*



Adsorption Kinetics

The kinetics of the adsorption process were studied by applying Lagergren's pseudo-first-order (Reddy et al., 2010, and Russo et al., 2010), pseudo-second-order (Reddy et al., 2010, Sari et al., 2010) kinetic models.

Pseudo-first-order:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

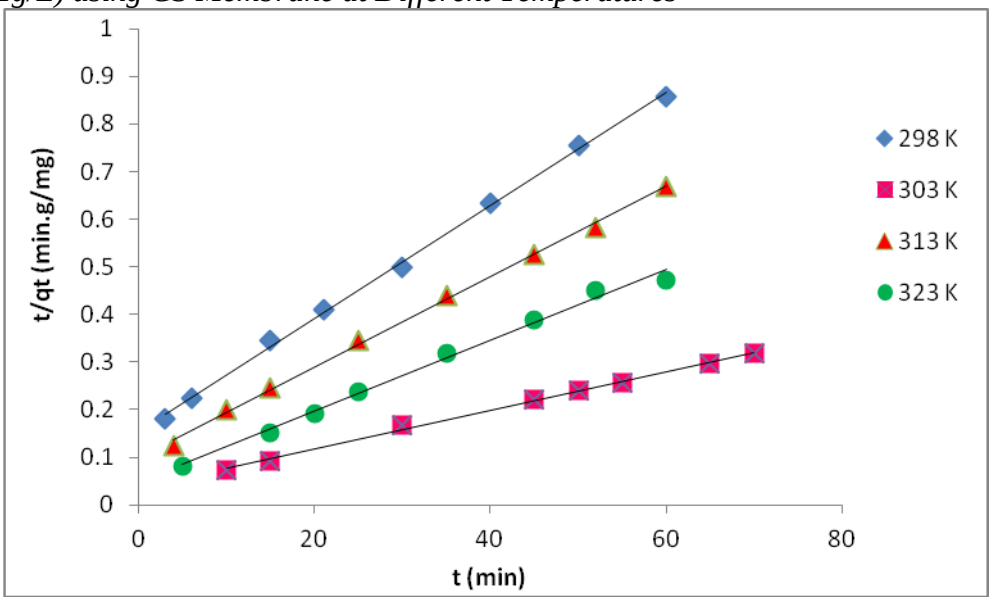
Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad (4)$$

They were applied in order to obtain the rate constants, equilibrium adsorption capacity, and the adsorption mechanism at different temperatures. The pseudo-first-order rate constant (k_1), and the equilibrium adsorption capacity (q_e) at different temperatures were computed from the slope and the intercept of the plots of log ($q_e - q_t$) versus t (figure not shown), however, the correlation coefficient (R^2) was far from unity indicating the poor fitting of the pseudo-first order kinetic model to the results.

The kinetic data was further analyzed using the pseudo-second-order equation (Eq. 4), of which the constants were determined from the slope and intercept of the plot of t/qt versus t. The latter are illustrated at different temperatures in Figure 4 and their values are presented in Table 3.

Figure 4. *Pseudo-second Order Kinetics Plot for Biosorption of Cu(II) Ions (1g/L) using CS Membrane at Different Temperatures*



The fitting of the kinetic data showed a good linearity with very high R^2 over the studied temperature range. Accordingly, the data can be explained accurately by the pseudo-second-order kinetic model. It is also observed from Table 3 that the rate constant (k_2) varied directly with a temperature indicating adsorption, is endothermic in the range 298 to 323 K, except at 303K, which suggests that the rate-limiting step of the adsorption process is physical adsorption. However, this anomaly (related to temperature) was verified and confirmed by conducting the experiments in duplicates.

Table 3. *Kinetic Parameters for Adsorption of Cu(II) Ions onto CS Membrane*

Temp (K)	Pseudo-second-order kinetic model			
	qe,cal (mg g^{-1})	k_2 (gmg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
298	84.745	0.000898	6.451613	0.9986
313	105.263	0.000906	10.04016	0.9982
323	133.333	0.001202	21.36752	0.9937
303	243.902	0.000487	28.98551	0.9936

The initial adsorption rate (h), was calculated at different temperatures using Eq. (5) (Sari et al., 2010) and is presented in Table 3.

$$h = k_2 \, q_e^2 \qquad (5)$$

It is clear that h increased with the increase in the temperature suggesting that the adsorption was favourable at a high temperature. However, it was reached its maximum at 303K, as seen in Table 3, then declined as the temperature increased.

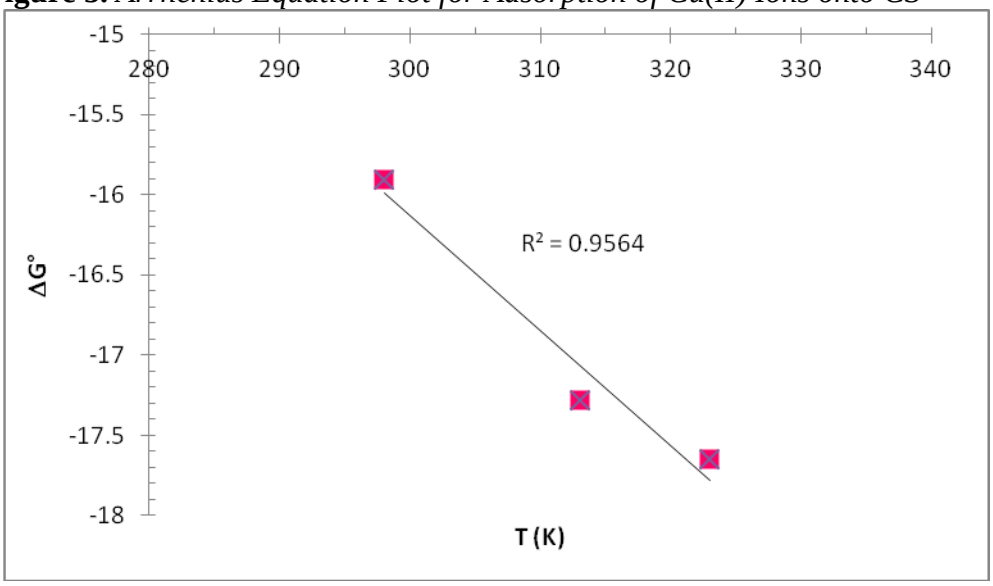
Activation Energy

From the pseudo-second-order rate constant k_2 (Table 3), the activation energy E_a for the adsorption of Cu(II) ions onto CS was determined using the Arrhenius equation (Eq. 6). (Chowdhury and Saha, 2010; Mohapatra et al., 2009):

$$\ln(k_2) = \ln A - \frac{E_a}{RT} \qquad (6)$$

By plotting $\ln(k_2)$ versus 1/T (Figure 5), Ea was obtained from the slope of the linear plot, of which the value of E_a for the adsorption of Cu(II) on CS was found to be 36.88 kJ/mol. The value of E_a gives an idea about the type of sorption, which is either physical or chemical. The value of E_a for physical adsorption is less than 40 kJ/mol, since the forces involved in physical adsorption are weak. On the other hand, higher values represent a chemical reaction since chemisorption is specific, and involves much stronger forces than physical adsorption does (Anirudhan, and Radhakrishnan, 2008). Accordingly, the value of E_a in the present work confirms that the nature of adsorption onto CS is physical adsorption, which indicates that the CS can be easily regenerated for reuse.

Figure 5. *Arrhenius Equation Plot for Adsorption of Cu(II) Ions onto CS*



Thermodynamic Parameters

The thermodynamic behaviour of the adsorption of Cu(II) ions on the CS membrane was evaluated by the thermodynamic parameters – Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), which were calculated using the following equations (Senturk et al., 2010; Tsai and Chen, 2010):

$$\Delta G^\circ = -RT \ln K_c \qquad (7)$$

$$K_C = \frac{C_a}{C_e} \quad (8)$$

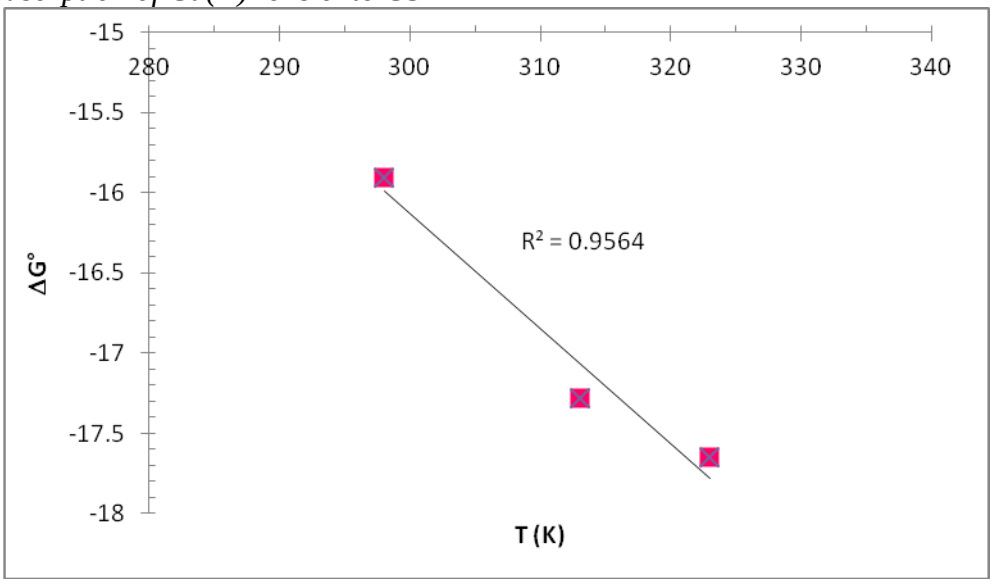
$$\Delta G° = \Delta H° - T\Delta S° \quad (9)$$

where K_C is the distribution coefficient for adsorption, and C_a and C_e are the equilibrium concentrations (mg/l), on the CS fragments, and in the solution, respectively. A plot of ΔG° versus temperature T, shown in Figure 6, is linear, from which ΔS° and ΔH° were computed from the slope and intercept, and were equal to -0.0715 (kJ/mol.K) and 5.316 (kJ/mol), in respective order (Table 4). Negative values of $\Delta G°$ indicate the feasible nature of the adsorption process and a decrease in its value with an increase in temperature suggests that higher temperature makes adsorption easier. The positive value of ΔH° implies that the adsorption phenomenon is endothermic. The magnitude of ΔH° may give an idea about the type of sorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e. 2.1–20.9 kJ/mol, while the heats of chemisorption generally fall into a range of 80–200 kJ/mol. Moreover, the negative value of ΔS° suggests that the process is enthalpy-driven and reflects the affinity of the CS towards the Cu(II) ions (Liu and Liu, 2008).

Table 4. *Activation Energy and Thermodynamic Parameters for Adsorption of Cu(II) Ions onto CS*

Ea (kJ/mol)	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/ mol. K)
	298	313	323		
36.89	-15.9023	-17.2834	-17.6457	5.316	-0.0715

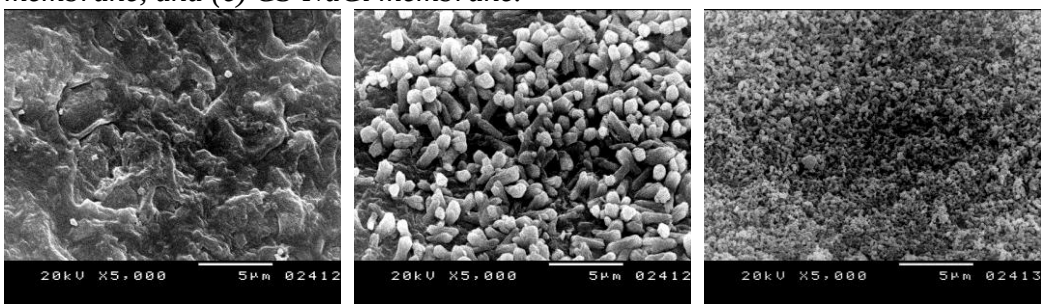
Figure 6. *Plot of Gibb's Free Energy Change versus Temperature for Adsorption of Cu(II) Ions onto CS*



SEM Examination

SEM micrographs are depicted in Figures 7-12 in which it is clear that the surfaces are all porous, in fact the pores are mainly in the nano range, particularly the membrane which was treated with NaCl. Figure 7(a, b, c) demonstrates the surface micrographs of the CS, CS-PEG and CS-NaCl membranes, respectively, in which the PEG and NaCl functioned as porogens. It is observed from Figure 7(a) that a pure CS membrane contains some micro-pores on its surface. Moreover, the surface is rough and contains plenty of hills and valleys. Figure 7(b) illustrates the CS-PEG membrane from which it is observed that the surface contains more pores, slightly larger than the CS membrane. The micrograph emphasizes the formation of some micro-pores due to the leaching of some of the PEG molecules that have been rinsed away from the surface leaving pores behind. Figure 7(c) on the other hand, shows fine pores in the nano range which are manifested as dark spots, due to the leaching of the NaCl from the CS membrane matrix. It proves that the NaCl functioned as an efficient porogen and in addition the surface is smoother than the original CS without porogens, and the pores are much finer than the case of CS-PEG (Figure 7(b)) in which the pores were much wider.

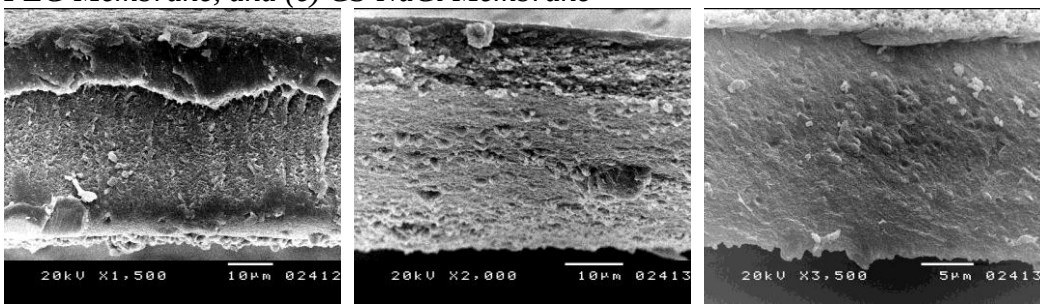
Figure 7. *SEM surface micrographs of: (a) CS membrane, (b) CS-PEG membrane, and (c) CS-NaCl membrane.*



(a) (b) (c)

Figure 8(a, b, c) on the other hand, illustrates the micrographs of the cross-sections of the same three membranes, in the same previous order, from which Figure 8(a) clarifies the very fine pores in the CS membrane matrix, representing a magnified view at 10,000 X, of the matrix cross-section, which will be clarified in the following Figure 9(a). On the other hand, Figure 8(b) indicates that the cross-section of the CS-PEG membrane in which scattered irregular and uneven pores are distributed all over the membrane cross-section. However, it is worth mentioning that the top layer is more porous and exists on the membrane surface. Moreover, Figure 8(c) proves that the cross-section contains pores, contrary to its surface.

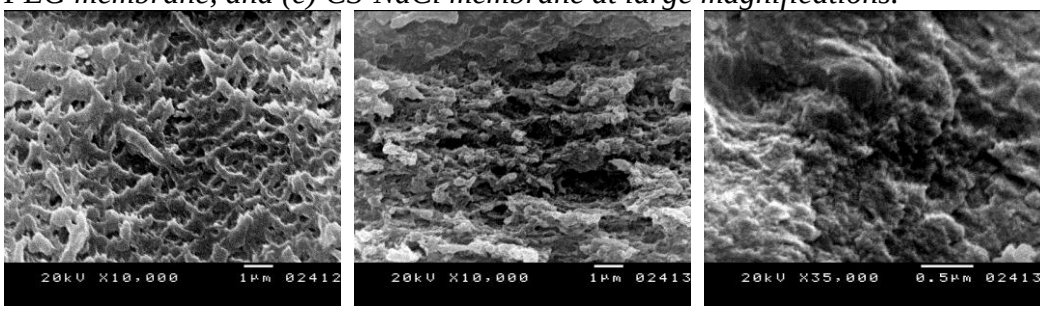
Figure 8. *SEM Cross-section Micrographs of: (a) Pure CS Membrane, (b) CS-PEG Membrane, and (c) CS-NaCl Membrane*



(a) (b) (c)

Figure 9(a, b, c) depicts a close-up of the three aforementioned membranes' matrices, in the same order as before. Figure 9(a) shows a portion of the membrane clarified in Figure 9(a), enlarged 10,000 X, it shows that the matrix is porous to a great extent and the pores vary in their sizes from a nano to a micro scale as shown in the figure, in fact, scaffolds are apparent. However, the pores are mainly in the nano range. On the other hand, Figure 9(b) clarifies the presence of numerous scattered micro-pores which are generally incompletely interconnected. This may be attributed to the link of the PEG molecule which on being leached leaves larger voids behind. Moreover, the pores are of unequal size. However, Figure 9(c) shows a part of the CS-NaCl membrane matrix, which has been magnified to 35,000 X, showing numerous interconnected pores which are in the nano range and are scattered within the matrix, while some NaCl molecules are shown to be trapped inside the membrane matrix (left corner).

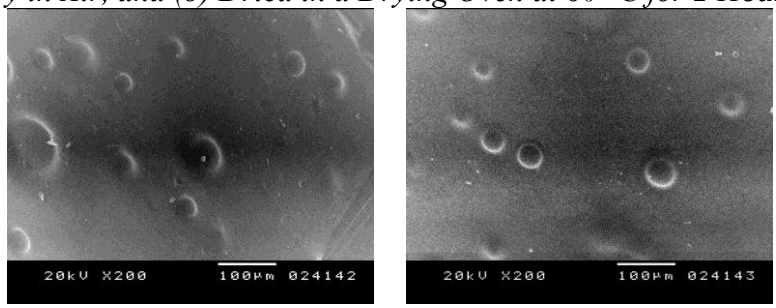
Figure 9. *SEM cross-section micrographs of: (a) pure CS membrane, (b) CS-PEG membrane, and (c) CS-NaCl membrane at large magnifications.*



(a) (b) (c)

Figure 10(a) illustrates the surface micrograph of the CA-CS (20:1 b.w.) membrane which has been left to dry in air, while figure 10(b) was another membrane of the same composition but which has been dried in a drying oven at 60 °C for 2 hours. The 2 micrographs show that the topology of the two surfaces are similar, as expected, and that they are different from the former ones, since they are much smoother and less porous, which explains why adsorption follows a type-2 isotherm.

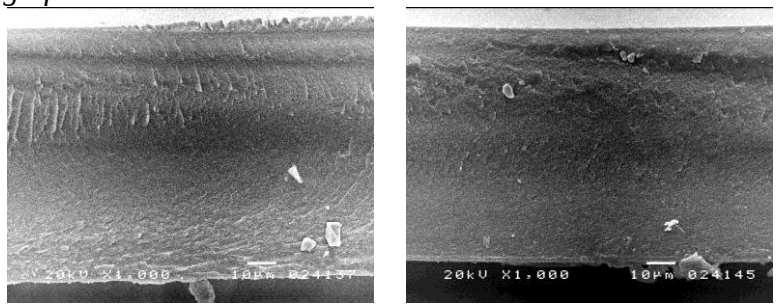
Figure 10. *SEM Surface Micrographs of CA-CS Membrane (20:1 b.w.): (a) Left to Dry in Air, and (b) Dried in a Drying Oven at 60 °C for 2 Hours*



(a) (b)

However, Figure 11(a, b) present the cross-sections of the same aforementioned membranes, in a respective order. It is realized that the matrices are non-porous to a great extent and that the two micrographs which are magnified 1000X appear to be identical.

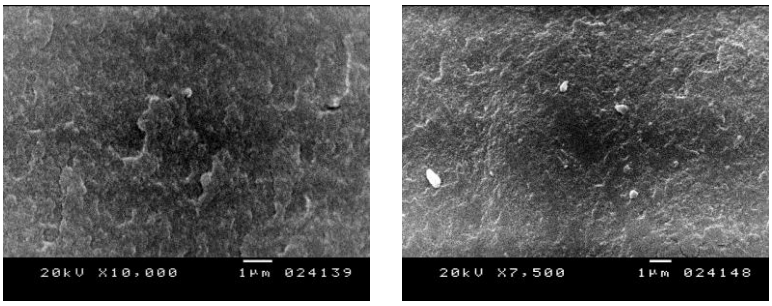
Figure 11. *SEM Cross-section Micrographs of CA-CS Membrane (20:1 b.w.): (a) Left to Dry in Air, and (b) Dried in a Drying Oven at 60 °C for 2 Hours at Small Magnifications*



(a) (b)

On the other hand, Figure 12(a, b) clarifies a magnified view (10,000 X) of the two same membranes respectively, from which it is emphasized that the membranes are both almost devoid of pores. This result is attributed to the presence of CA which does not form porous membranes except under specified conditions. However, CA gives strength to the CS membrane but renders it less suitable for adsorption. Accordingly a lower ratio of CA:CS in the thereabouts of 2:1 b.w. should be attempted in the near future, in order to combine merits of both biopolymers.

Figure 12. *SEM Cross-section Micrographs of CA-CS Membrane (20:1 b.w.): (a) Left to Dry in Air, and (b) Dried in a Drying Oven at 60°C, at Large Magnifications*



(a) (b)

Conclusions

Porous CS membranes with exceptional affinity to Cu(II) ions have been successfully prepared. PEG and NaCl were used as porogens for the CS membranes. Batch adsorption studies proved that NaCl provided the best adsorption capacity compared to the CS-PEG and CS membranes, for which q_m approached 500 mg/g which is much higher than the values reported in the literature for different adsorbents. It was confirmed that a monolayer adsorption took place, since the Langmuir model was obeyed. The adsorption increased with temperature until 30°C then declined with the further increase in temperature. Adsorption kinetics followed the pseudo-second order Lagergren's model and the rate constant was found to decrease with the increase in temperature above 30°C, indicating exothermic adsorption. This was also proven from batch adsorption experiments of the CS membrane. The value of Ea indicated physical adsorption, which allows the reuse of the membrane after regeneration with acid. Negative values of $\Delta G°$ indicated the feasible nature of the adsorption process and the decrease in its value with the increase in temperature suggests that lower temperature makes adsorption easier. The positive value of $\Delta H°$ implied that the adsorption phenomenon is exothermic. Moreover, the negative value of $\Delta S°$ suggests that the process is enthalpy-driven and reflects the affinity of the CS towards the Cu(II) ions. SEM micrographs revealed the nanoporous nature of the CS-NaCl membrane, followed by the CS membrane which in addition contained scaffolds, then the CS-PEG which contained larger pores that led to least adsorption capacity, due to the minimum surface area to volume ratio.

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