Sodium Tripolyphosphate (TPP) Crosslinked Chitosan Membranes and Application in Humic Acid Removal

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Abstract

Macro- or micro-porous chitosan membranes have been utilized as adsorptive membrane for the removal of metal ions, organic macromolecules or bioseparation of protein mixtures. The removal or separation mechanism is not based on physical size retention but based on the high adsorption capability of chitosan to the target solutes. For this purpose, it is important that large macro or micro pores and high porosity are achieved for the membrane. However, the study on chitosan membrane for this purpose is very limited due to the difficulty in forming macro/micro pores and also the poor mechanical and chemical properties of chitosan. In order to form desired pores, we utilized polyethylene glycol (PEG) as porogen in the study. Coarse filter paper was employed to provide support. In order to improve the chemical stability of the resultant membranes, crosslinking reactions of chitosan with sodium tripolyphosphate (TPP) was carried out. The surface morphology, DI water flux, and anti-acid ability of the resultant membrane was investigated. The results showed chitosan membrane prepared in the study can achieve the goal of adsorptive membrane as microporous surface and high porosity were successfully achieved. The crosslinking reaction successfully improved the anti-acid ability of chitosan membrane to pH 2. The application of chitosan adsorptive membrane in water treatment was carried out through removal of humic acid from water. The results showed efficient removal of humic acid was obtained. The effect of humic acid solution pH on removal efficiency and desorption of humic acid were also investigated.

Keywords

sodium tripolyphosphate (TPP), chitosan, adsorptive membrane, PEG, humic acid

1 Introduction

Chitosan, a deacytelated form of chitin and resourceful biopolymer in nature, has been widely studied in water and wastewater treatment recently. The chemical structure of chitosan and chitin is shown in Figure1. Chitin and chitosan are of commercial interest due to their high percent nitrogen content compared to synthetically substituted cellulose and this makes chitin and chitosan a useful binding agent [1]. The free amine groups on chitosan molecules can be easily protonated to $-NH_3^+$ at acid solutions and can bind negatively charged substances. At alkali solutions, chitosan is negatively charged due to the dissociation of CH_2OH groups or the adsorption of OH^- from the solution and can be used to remove positively charged substances. In addition to the charge characteristics, chitosan can bind valuable or toxic metals ions [2-8] at acid solutions from dilute aqueous solutions due to the chelating function between N atoms and metal ions. Chitosan can also be employed to separate hydrophobic substances such as proteins [9-11] due to the hydrophobic interaction between them. Owing to these above characteristics, chitosan demonstrates great potential in water treatment and is becoming an excellent adsorbent material in water treatment. Until now, chitosan has been widely studied in removal or concentration of dyes [12-17], metal ions and proteins and so on in water treatment.
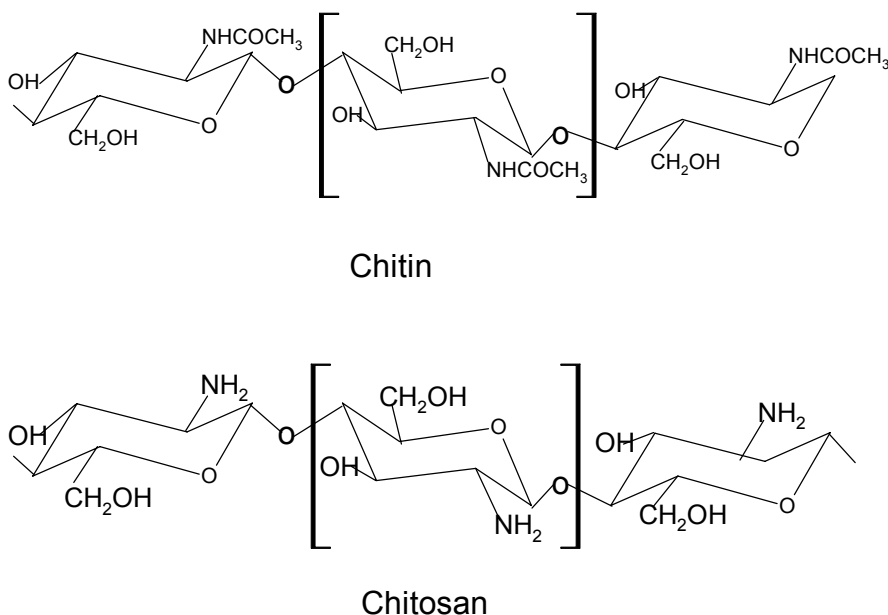

Chitin

Chitosan

Figure 1 chemical structure of chitin and chitosan

Until now, there are many reports which study the successful preparation of chitosan beads, film and membrane, but the products are normally non porous on surface. With the development of biotechnology, membrane chromatography or adsorptive membrane is becoming the interest of researchers. As membrane process brings solute to adsorption site by convective force, it reduces the processing time significantly. The

requirements for adsorptive membrane are reactive functions groups, micro or macro pores, high porosity, large surface area. The removal or separation mechanism is not based on physical size retention but based on the high adsorption capability of chitosan to the target solutes. For this purpose, it is important that large macro or micro pores and high porosity are achieved for chitosan membrane. However, the study on chitosan membrane for this purpose is very limited due to the difficulty in forming macro/micro pores and also the poor mechanical and chemical properties of chitosan. Until now, there are few reports can be found. Zeng et al. [18-20] have prepared macroporous chitosan membrane using silica gel as porogen. When the film was immersed in a NaOH solution at a raised temperature, silica gel would dissolve while chitosan was solidified and then macroporous solid chitosan films were formed. This method can only be used for developing macroporous membrane. Moreover, the expensive silica gel is a limit for large scale production. Another method is to use polyethylene glycol (PEG) as porogen [21-23], which is soluble in water and then be removed from chitosan layers. This method is done at room temperature and PEG is not expensive. The pore size can be controlled by using PEG with different molecule weights. Freeze drying is another good method to prepare macroporous chitosan membrane. However, the strict control of temperature and the availability of freeze drier bring about a lot of difficulty.

In this study, we preferred to polyethylene glycol method to develop microporous chitosan membranes. But the membrane obtained through this way has a poor anti-acid ability and therefore need to be crosslinked. The commonly used crosslinking agent such as EGDE, ECH, and GA is not efficient because they can make the membrane very brittle and the membrane can break under gentle touch at wet and dry state. Moreover, these chemicals are toxic to human body and not environment friendly. In our study, we employed sodium tripolyphosphate solution (TPP) as crosslinking agent and found it made the membrane flexible and at the same time it can improve the chemical stabilities of chitosan membrane. The membrane properties after crosslinking were studied.

The application of chitosan composite membrane in water treatment was investigated through adsorption of humic acid from aqueous solutions. Humic substances are ubiquitous in almost all the surface and ground waters. Humic substances often cause undesirable color and taste in water. They are very active in binding metal ions and thus facilitate their transportation in water. Humic substances can also react with chlorine in water treatment and result in the generation of trihalomethanes which are known or suspected human carcinogens. Recent studies also showed that humic substances act as a major foulant affecting the various applications of membrane processes. Hence, it is desirable to minimize the presence of humic substances in drinking water and other process waters. One of the major components of humic substances is humic acid. It contains both hydrophobic and hydrophilic moieties as well as many chemical functions such as carboxylic, phenolic, carbonyl and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules. The existence of carboxylic and phenolic groups results in humic acid to predominantly carry negative charges in aqueous solutions.

With the chitosan composite membrane, it is possible to separate humic acid from water because intuitively, the amine groups from chitosan on the composite membrane can react with the functional groups of humic acid and thus enhance humic acid retention by the membrane. The detailed studies include the removal of humic acid from aqueous solutions under different solution pH values at static and dynamic mode. The regeneration of the membrane was also investigated.

2 Experimental

2.1 Materials

Chitosan was obtained from Sigma, produced from crab shell and deacytylation degree is minimum 85%. Polyethylene glycol is product of Merck with MW 10,000. Sodium tripolyphosphate was obtained from Aldrich. The support for preparation of composite membrane is Whatman cellulose filter paper (Grade No. 1. and pore size is 11μm). Humic acid was a salt (sodium) form and provided by Aldrich. Acetic acid, sodium hydroxide, hydrochloride acid were all analytical grade. DI water (MICROMEG filtered water) is used for prepare all solutions.

2.2 Apparatus

The surface morphology of the membrane was investigated through Scanning Electron Microscope, JEOL JSM -6700F FESEM. Amicon stir cell (H8400, effective diameter is 76mm) was used to characterize the DI water flux of composite membrane. It is also used for dynamic filtration of humic acid solution. Other equipments included magnetic stirrer (Heidolph, model MR 3002), pH meter (Thermal Orion; model 420A+), electro balance (Goldbell, model GX-8000) and pure nitrogen gas cylinder.

2.3 Preparation and characterization of chitosan composite membrane

The method has been previously described by Zeng Xianfang et al. [21]. In our study, chitosan solution was produced by stirring 1g chitosan in 100ml 1%v/v HAc aqueous solution at 200rpm at 60ºC for 5 hrs, and then was filtered through a 50μm nylon membrane to remove insoluble impurities. 5g polyethylene glycol (PEG) was added to the solution and the solution was stirred for about 1hr at room temperature at 200rpm. Then, the mixture solution was sonicated to remove air bubbles. 5.2ml chitosan and PEG mixture solution was poured onto cellulose coarse filter paper (Diameter is 76mm). After vaporizing for 2hrs, the membrane was immersed into a 5m/v% NaOH solution for overnight. Finally the composite membrane was washed with DI water until neutral.

Non crosslinked membrane has poor chemical stability and will dissolve in acid environment and therefore it need to be crosslinked. The crosslinking reaction was carried out at sodium tripolyphosphate (TPP) concentration of 10%m/v. HCl aqueous solution was used to adjust TPP solution pH to 4. The membrane was immersed in sodium tripolyphosphate solution for 2hrs and washed with DI water until neutral.

The structure and morphology of the composite membranes were observed through scanning electron microscope (SEM). Before SEM analysis, the membrane was treated with 20% aqueous glycerol solution for 1hr before the membrane was dried. This was to prevent the shrinkage of chitosan layer as glycerol can adsorb moisture from air. The treated membrane was firstly dried in air for about 3 days and finally placed in a vacuum desiccantor for at least one day. To measure the thickness of dried composite membrane, the glycerol treated membrane was broken in liquid nitrogen and software in SEM was used.

The test of DI water flux of the composite membrane was done through an Amicon Stir Cell. Nitrogen gas cylinder provided the driving force across the membrane. Digital pressure meter was used to control applied transmemrbane pressure accurately. The filtrate was collected by a beaker and weighed by an electro balance. The filtration test was done at room temperature.

In order to know the anti acid ability of crosslinked chitosan membrane, we cut the membrane into small pieces and immerse them into dilute acetic acid solution with different pH values respectively for 24hrs and saw whether the coated layer was dissolved. We took the greatly swelled chitosan layer as soluble.

2.4 Static adsorption of humic acid

Static adsorption test was conducted to evaluate the reactivity of the composite membrane in removing humic acid. The store humic acid solution was obtained by dissolving solid sodium humic acid into DI water. One piece of composite membrane was cut into four pieces and they were placed into a beaker containing 50mL 40mg/L HA solution and was shaken in a water bath shaker at 150 rpm at room temperature. At desired time, measure the concentration of the solution. For adsorption experiments under different pH values, dilute NaOH and HCl solutions were used to adjust the solution pH. The concentration of HA was determined from calibration curve drawn by UV absorbance at 254nm. All the experiments were done at room temperature.

2.5 Dynamic adsorption

The dynamic adsorption was also carried out in the Amicon Stir Cell using one piece of composite membrane at a constant transmembrane pressure difference of 3psi. 200mL 40mg/L sodium humic acid solution was loaded to the membrane cartridge before filtration and the filtrate was collected at desired time until the membrane cartridge is saturated. The experiment is also done at room temperature.

2.6 Desorption process

After the adsorption of one piece of the membrane in 50 mL HA solution (40mg/L) for 24 h, the membrane was removed from the solution and washed with DI water to remove the loosely attached humic acid. the membrane was then placed into 50 mL 0.1 M NaOH solution for desorption of HA. At desired time intervals, 4 mL of samples was taken for concentration analysis.

3 Results and discussion

3.1 Morphology studies

The surface structures of the resultant chitosan membrane are shown in Figure 2. It is clear the membrane has microporous surface which is necessary for adsorptive membrane. The porous surface is caused by selective dissolution of PEG in water. The pore size and porosity of the membrane depends on the molecular weight and amount of PEG used. With increase in PEG molecular weight, the pore size will increase. The more PEG is used, the higher the porosity is.

Compared with the results of previous work done by other researchers [23, 24], the membrane prepared in this study showed unique three dimensional network structure. The network can be explained by the crosslinking mechanism between chitosan and TPP. At acid TPP solutions, both H^+ and multivalent tripolyphosphate ions are present in the solution. Free amine group on chitosan molecule will be protonated when chitosan contacts acid TPP solution and then the protonated amine groups on different or same chitosan molecules can be crosslinked by negative charged multivalent TPP ions. The crosslinking reaction is schematically shown by FWU-LONG MI [25] in Figure 3. The other characteristics of composite membrane are listed in Table 1.
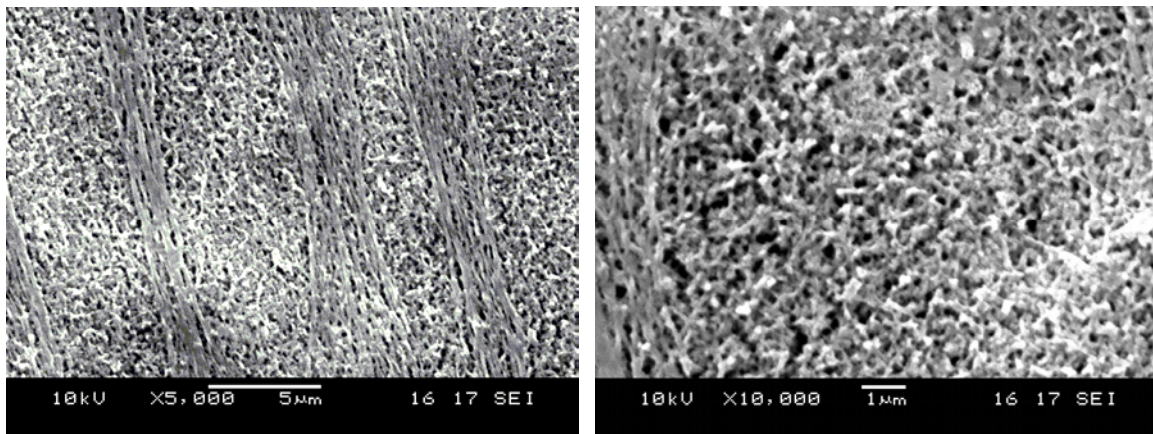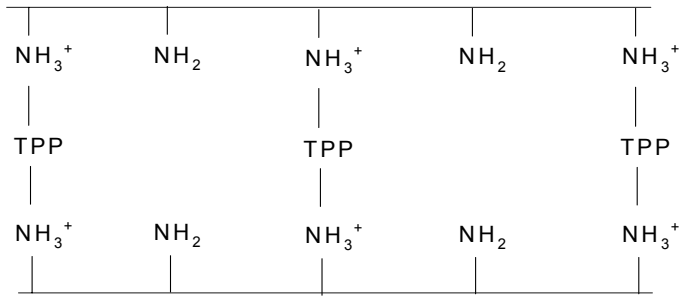

Figure 2 Surface structure of crosslinked chitosan membrane. Left: Magnification=5,000. Right: Magnification=10,000.

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  |             |             |             |             |             |
NH₃⁺         NH₂         NH₃⁺         NH₂         NH₃⁺
  |                         |                         |
TPP                       TPP                       TPP
  |                         |                         |
NH₃⁺         NH₂         NH₃⁺         NH₂         NH₃⁺
  |             |             |             |             |
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cross-linking between cationized chitosan and TPP ions

Figure 3 Mechanism of crosslinking between chitosan and TPP ions

Table 1 Characteristics of chitosan composite membrane

Support thickness/weight (provided by supplier)	180µm; 87 g/m^2
chitosan composite membrane thickness/weight in dry state	195µm; 103g/m^2
Coated chitosan thickness/ weight in dry state	15µm; 16g/m^2
Porosity of composite membrane	68%

3.2 DI water flux

One of the most important advantages of the adsorptive membrane is a high volumetric throughput that results in extremely short process times. The DI water flux (pH 6.6) of chitosan composite membrane is shown in Figure 4. It is apparent the resultant membrane showed almost linear relationship between DI water flux and applied pressure in studied pressure range although it actually deviated from the straight line slightly at higher pressure. The may be caused by the compaction of coated chitosan layer as the mechanical strength of chitosan is relatively poor. The DI water flux is 555kg/m^2.hr at pressure drop of 10psi when the filtered water has pH about 6.6. Actually, the water flux and water resistance depends on water pH since chitosan will change its water contact angle and hydrophilicity significantly with filtered solution pH.
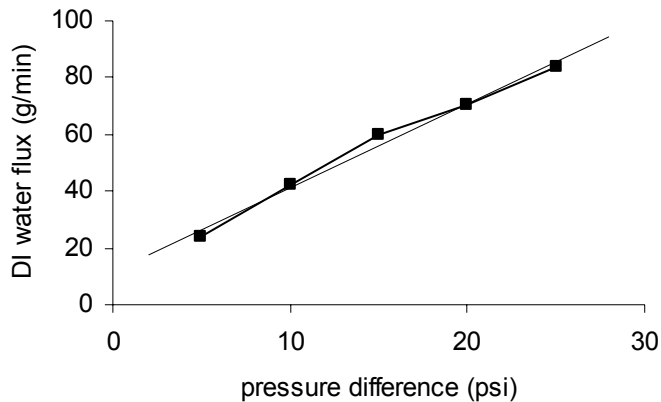
Figure 4 DI water flux of crosslinked chitosan membrane

3.3 Anti-acid ability of chitosan membrane

One of the objectives of crosslinking is to improve the anti-acid ability of chitosan membrane as chitosan can dissolve easily in acid solution. It limits the practical use of chitosan beads or membrane. There are many crosslinking methods, and most frequently used are EGDE and others include ECH, GA, alginate salt, sulfuric ions, surfactant solution and so on. TPP is a new crosslinking reagent. The main advantage of TPP is non toxic and it can easily control the crosslinking ratio by adjusting TPP solution pH. At lower pH the cross linking ratio is higher. FWU-LONG MI [25] had studied in detail the crosslinking between chitosan and TPP including anti acid ability, swelling ratio, cross linking mechanism and their performance in drug delivery.

The results in this study showed non crosslinked chitosan membrane dissolves in pH 4.5 while the crosslinked membrane can resist acid solution with pH 2. It implies that TPP crosslinking is effective to improve chemical stability of chitosan membrane. According to FWU-LONG MI [25], the swelling properties of chitosan can be reduced also by TPP crosslinking.

3.4 Effect of humic acid solution pH on static adsorption of humic acid

The changes of HA concentrations in the solution due to adsorption on the membrane and the corresponding adsorption amount of HA adsorbed on the membranes are shown in Figure 5, 6. The original cellulose coarse filter paper did not adsorb HA noticeably while the chitosan composite membranes had significantly improved adsorption capability for humic acid although the adsorption capacity changed with HA solution pH. With the increase of solution pH values, the adsorption capacity decreased slightly. For example, after 24 h, the concentrations decreased to 12.5%, 17.5% and 25.8% of the initial value (40 mg/L) at pH=4, 6.5, and 9.5, respectively. This corresponds to adsorption amounts of 1.75, 1.65, 1.484 mg humic acid for one piece of

membranes at pH 4, 6.5, and pH=9.5, respectively. If we estimate the total amount of chitosan on the membranes is 52 mg per composite membrane, the adsorption capacities after 24 h adsorption can be converted to 33.7, 31.7, and 28.5 mg HA per gram chitosan under the three different pH values. In other word, chitosan significantly increased the surface reactivity and adsorption capability of the composite membranes for HA molecules.

The slight difference in adsorption capability at different pH can be explained by the different surface charge characteristics of chitosan polymer. Chitosan molecules will be positively charged at pH<6.6 and negatively charged at pH>6.6, and for humic acid in the solution, they will carry negative surface charges at pH>2. Therefore, at pH above 6.6, both the membrane surface and humic acid molecules are negatively charged. So they would repel each other due to the electrostatic repulsions. The results in Figure 5 & 6 however showed that the membranes still had good adsorption capabilities. This may be caused by the hydrophobic interaction which exists regardless of the solution pH values. It is well kown humic acid contains both hydrophobic and hydrophilic moieties as well as many chemical functions such as carboxylic, phenolic, carbonyl and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules. The hydrophobic parts in the molecule can make it be adsorbed by chitosan as chitosan are reported has a contact angle about 60°-90°.

However, at pH from 2-6.6, the composite membrane surface was positively charged and HA was negatively charged. So, except hydrophobic interaction, humic acid can also be adsorbed on the membrane surface through electrostatic attraction. This led to an enhanced adsorption capacity of HA at a lower solution pH. The adsorption mechanisms on the composite membrane can therefore involve at least the electrostatic and the hydrophobic interactions. The former one mainly exists in acid solutions while the latter one exists in any pH solutions.
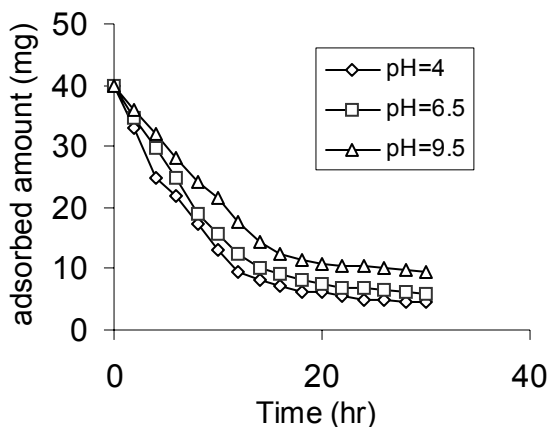

Figure 5 Concentration change of HA solution. C_0=40mg/L.
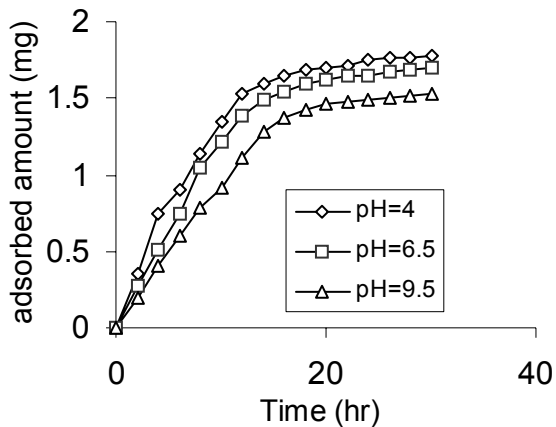
Figure 6 HA adsorption amount by one piece of chitosan composite membrane. C_0=40mg/L.

3.5 Dynamic adsorption

Adsorbent column has been widely used as a powerful tool in separations because of its widespread applicability, and high capacity, but slow internal diffusion is a major problem. In contrast to the column process, the membrane process brings solute into the proximity of the adsorb sites by convection, thus largely reduces the resistance to mass transfer and allows lower pressure drops and higher flow rates. The filtrate concentrations with time for membrane filtration behave like those of an adsorbent column. Figure 7 shows three typical breakthrough curves for the filtration of HA solution at different solution pH values. It can be seen that the filtrate concentrations increased initially like that of an adsorbent column, and then reached a maximum concentration (i.e., break through point). At the beginning, the membrane surface had many available adsorption sites and HA molecules can be removed from the solution due to their adsorption on the membrane. So, initial HA concentrations in the filtrate were almost zero. But with the increase of time, the number of available reactive sites decreased and more HA molecules passed through the membrane, resulting in filtrate concentration increasing with time and reaching a maximum.

The flow through curve was also dependent on solution pH as that of static adsorption. The breakthrough volume (the total collected volume from beginning to membrane is saturated) were 81, 97, 106g filtrate for pH=9.5, 6.5 and 4 respectively. It is obviously breakthrough volume increased with decreasing solution pH, indicating the adsorption amount increases with decreasing solution pH. The time for getting to break through point were 12.5, 15.6, 17 mins respectively for pH 9.5, 6.5 and 4 respectively. It indicated that membrane filtration process can process larger volume solutions in a short time than adsorbent column.
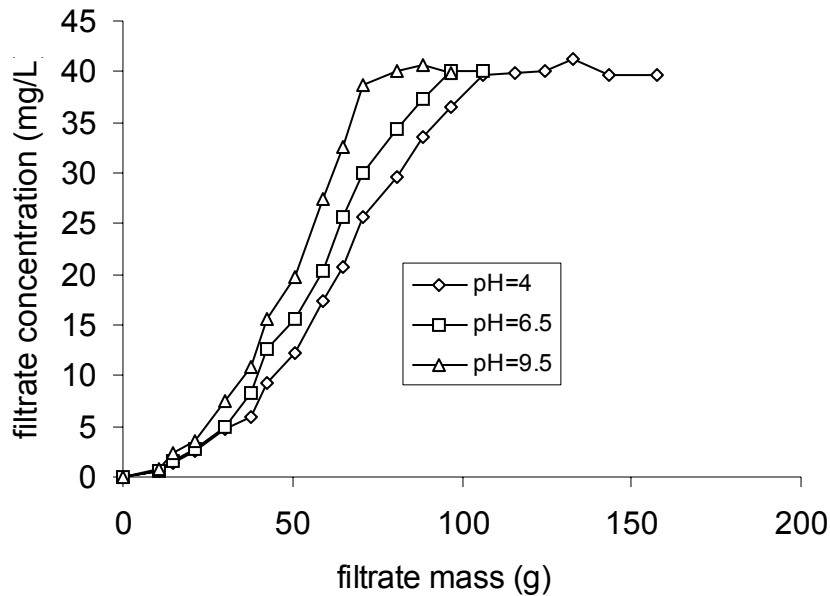
Figure 7 Dynamic removal of humic acid. C_0=40mg/L.

3.6 Desorption of HA from chitosan composite membrane

It is desirable that the retained substances on the membrane can be effectively removed so that the membrane can be used again. Therefore, desorption of the HA from the composite membrane was studied. Usually, desorption reagent is NaOH because it can dissolve humic acid while not dissolve the chitosan layer. Speaking in detail, in a NaOH solution, the COO^- groups in HA bond to the NH_3^+ groups on the composite membrane may be replaced by the OH^- from the solution because of its high concentration and smaller size (than COO^-). This can result in the release of the adsorbed HA from the membrane into the solution. In this part, we examined the desorption efficiency for pre adsorbed membrane at various humic acid solution pH values.

As discussed earlier, the adsorption mechanisms may include electrostatic and hydrophobic interactions, and, at lower pH solution, both of the two mechanisms may take place, but at higher pH solution, the latter one may probably play more important role. For humic acid adsorbed through hydrophobic interaction, they are difficult to be desorbed. Therefore, from the adsorption mechanisms, it can be inferred that desorption performance will also largely depend on the pH values of humic acid solution before adsorption.

The preadsorbed membrane in section 3.4 was tested for desorption experiment. The results in Table 2 showed that the desorbable percent approaches to 70-75% after 2hrs desorption process. The undesorbable humic acid is adsorbed through hydrophobic interaction. The humic acid solution pH indeed played an important role in the desorption performance. Preadsorbed membrane at lower humic acid solution pH values have been found to have better desorption of HA from the composite membrane.

For example, 70% of the adsorbed HA can be desorbed in less than 20 min at pH 4, but it took more than 20 min or even up to 2 h at pH 6.5 and pH 9.5, respectively. This may be due to the higher percent of preadsorbed humic acid by hydrophobic interaction at higher pH. Desorption also appeared to be much fast in the first several minutes but slowed down with time.

Table 2 Desorption percent from preadsorbed chitosan membrane with time

Humic aicd solution pH	4	6.5	9.5
5min	56.4%	54.2%	50.7%
10min	66.0%	62.8%	59.6%
20min	70.6%	67.5%	64.5%
30min	72.3%	69.8%	67.1%
60min	74.1%	70.8%	68.5%
90min	74.9%	71.1%	69.4%
120min	75.3%	71.5%	69.8%

4 Conclusions

From the study, chitosan composite membranes crosslinked by TPP were successfully prepared. They have desired microporous surface, high porosity and large water flux which is necessary for adsorptive membrane. The anti-acid ability was improved to pH 2 from original pH resistance of 4.5. Since the surfaces of the composite membranes were reactive and more adsorptive, they can retain polarized or electrically charged substances such as humic acid more effectively. This makes it possible to use chitosan membranes as adsorptive membrane to treat water or wastewater as retention of substances is no longer based on size exclusion as in conventional membrane separation systems. The study shows that humic acid solution pH can affect the surface properties of the chitosan membrane and the interactions between the composite membrane and the substances to be separated. This provides the possibility to tune the membrane properties to achieve better separation for different types of substances.

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