CHAPTER 5

TRICHLOROACETIC ACID IMPRINTED POLYPYRROLE MODIFIED MICROFILTRATION REGENERATED CELLULOSE (RC) MEMBRANE

5.1. Introduction

The four developed industrial membrane separation processes are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. These processes are all well established, and the market is served by a number of experienced companies (Baker, 2004).

The range of application of the three pressure-driven membrane water separation processes *i.e.*, reverse osmosis, ultrafiltration and microfiltration, is illustrated in Fig. 5.1. Ultrafiltration and microfiltration are basically similar in that the mode of separation is molecular sieving through increasingly fine pores. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μm in diameter. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. The mechanism of separation by reverse osmosis membranes is quite different. In reverse osmosis membranes, the membrane pores are so small, from 3 to 5 Å in diameter, that they are within the range of thermal motion of the polymer chains that form the membrane. The accepted mechanism of transport through these membranes is called the solution-diffusion model. According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubilities and mobilities of different solutes in the membrane. The principal application of reverse osmosis is desalination of brackish groundwater or seawater.

Although reverse osmosis, ultrafiltration and microfiltration are conceptually similar processes, the difference in pore diameter (or apparent pore diameter) produces dramatic differences in the way the membranes are used. A simple model of liquid flow through these membranes is to describe the membranes as a series of cylindrical capillary pores of diameter d. The liquid flow through a pore (q) is given by Poiseuille's law as:

$$q = \frac{\pi d^4}{128\mu\ell} \cdot \Delta p \qquad (5\text{-}1)$$

where Δp is the pressure difference across the pore, μ is the liquid viscosity and l is the pore length. The flux, or flow per unit membrane area, is the sum of all the flows through the individual pores and so is given by:

$$J = N \cdot \frac{\pi d^4}{128 \mu \ell} \cdot \Delta p \qquad (5\text{-}2)$$

where N is the number of pores per square centimeter of membrane. For membranes of equal pore area and porosity (ε), the number of pores per square centimeter is proportional to the inverse square of the pore diameter. That is,

$$N = \varepsilon \cdot \frac{4}{\pi d^2} \qquad (5\text{-}3)$$

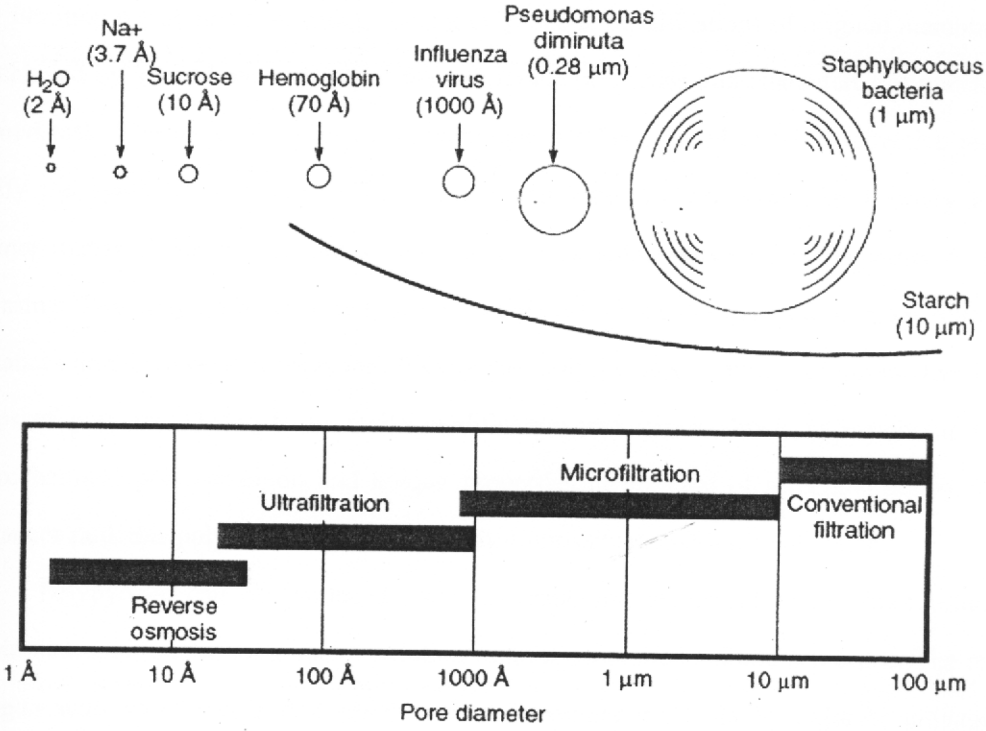


Fig. 5.1. Reverse osmosis, ultrafiltration, microfiltration, and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter. Reverse osmosis membranes are so dense that discrete pores do not exist; transport occurs via statistically distributed free volume areas. The relative size of different solutes removed by each class of membrane is illustrated in this schematic (Baker, 2004).

It follows that the flux, given by combining Equations (5-2) and (5-3), is

$$J = \frac{\Delta p \varepsilon}{32 \mu \ell} \cdot d^2 \qquad (5\text{-}4)$$

From Fig. 5.1, the typical pore diameter of a microfiltration membrane is 10,000 Å. This is 100-fold larger than the average ultrafiltration pore and 1000-fold larger than the (nominal) diameter of pores in reverse osmosis membranes. Because fluxes are proportional to the square of these pore diameters, the permeance, that is, flux per unit pressure difference ($J/\Delta p$) of microfiltration membranes is enormously higher than that of ultrafiltration membranes, which in turn is much higher than that of reverse osmosis membranes. These differences significantly impact the operating pressure and the way that these membranes are used industrially.

Over last few decades, great efforts have been made to develop the modified micro- or ultra-filtration membrane concerning adaptation process. Modifications of original membrane can be achieved by several ways to adjust the membrane properties and characteristics match to the required task. The molecular imprinting technique has been found to be an effective means to modify the synthetic membrane. This process will introduce the molecular memory into the polymer matrix. Recently, interest in the use of conducting polymers in preparing of MIP is increasing. This may be because polymer materials can be easily prepared on many surfaces of substances and have good recognition. Polypyrrole polymer is a dominant representative in these groups of polymer. Owing to its facile modification into various kinds of membrane through electrochemical polymerization and unique properties in the case of screening ability to ionic substances rank this polymer being used in many composite membrane applications.

Polypyrrole can be produced from electropolymerization of the mixture solution of pyrrole monomer and redox initiator solution in an appropriated anionic substance. The reaction is begun with withdrawing first electron from monomer molecule by oxidizer initiator. The propagation of the reaction is governed by resonance of the actively positively charge monomer and its reaction with the other neutral monomer to extend the polymer chain. This manner is repeated until the stable polymer chain is obtained complementary with anionic specie compensation. Such anionic compound is employed to compensate the positively charge surface of polypyrrole backbone generating during continuous reaction. In order to control the polymer deposition occurring only at the membrane, membrane needed to saturate with redox initiator before being soaked in the mixture of pyrrole monomer and counter ion to begin the reaction.

Progressively, whenever the pyrrole monomer moves closely to the membrane surface by the Brownian movement, it is attracted to start the polymerization reaction. After the positively charge surface of polypyrrole backbone produced, according to thermodynamic criteria the anionic compound in the mixture is induced to couple such positively charge surface to maintain the energy of the system at low level.

5.2. Objective

To develop the microfiltration regenerated cellulose membrane modified with imprinted polypyrrole synthesized by electrochemical polymerization for selective separation haloacetic acids in drinking water.

5.3. Method

5.3.1. Preparation

Polypyrrole dispersion was synthesized using poly(ethyleneglycol)methyl ether as a stabilizer and ammonium persulfate as a polymerization initiator. The polymer composition are shown in Table 5.1.

Table 5.1

Order of mixing and content of ingredient used in polypyrrole synthesis.

Order of mixing	Content (%)			
	F1	F2	F3	F4
Poly(ethyleneglycol)methyl ether	20% of pyrrole monomer			
Ammonium persulfate concentration (M)	0.1	0.3	0.5	0.9
Deionized water (ml)	100	100	100	100
Trichloroacetic acid (M)	0.036	0.036	0.036	0.036
Pyrrole monomer (M)	0.145	0.145	0.145	0.145

All ingredients as listed in Table 5.1 were mixed together in 250 ml erlenmeyer flask on a magnetic stirrer. The mixtures were stirred with magnetic bar until homogeneous solution can be observed. N_2 gas was then purged into the flask for 5 min before closure using a parafilm and aluminium foil respectively. Reaction was left for completion for 15 hrs. The resulting particulates were then filtered and washed with 50 ml of deionized water. The polymer powder was dried in the vacuum oven at room temperature and kept in desiccator prior to use.

5.3.2. The characterization of the ready-made polypyrrole particles.

5.3.2.1. IR spectroscopy

The ready-made polypyrrole particles were characterized by using Fourier-Transform Infrared Spectrometer through KBr disk preparation technique. Wavenumbers corresponding with infrared absorption of funtional group were determined from IR spectrum. Some functional group and wavenumber of polypyrrole and trichloroacetic acid IR absorption are shown in Table 5.2.

Table 5.2

Some functional group and IR wavenumber of polypyrrole and trichloroacetic acid spectra

Interested functional group	Wavenumber (cm^{-1})
-C=O- of overoxidized polypyrrole	1669
-C=O- of trichloroacetic acid	1683
-C=C- of polypyrrole	1553

The peak area of those three peaks for polypyrrole when was prepared in the absence and presence of template molecule was calculated using Perkin-Elmer Spectrum Lite software version 1.45bLite. Unfortunately, the absorption peak of –C=O- of trichloroacetic acid was overlapped with the –C=O- absorption peak of over-oxidized polypyrrole, thus haloacetic acid absorption in polypyrrole particle was determined by subtracting peak area at 1669 cm^{-1} of polypyrrole prepared with TCAA template with peak area at 1683 cm^{-1} of control polymer (without template). The peak area that was calculated from control polymer presents the degree of over-oxidation in polypyrrole particles. The relative peak area at 1669 and 1553 cm^{-1} was examined.

5.3.2.2. Binding test

Since the imprinting process of polypyrrole was performed in the aqueous solution, thus recognition ability of the polymer particles was determined in the aqueous solution. In typical binding test, 50 g of polypyrrole powder was weighed into 10 ml vial and then 5 ml of 0.1 mM trichloroacetic acid was pipetted into the same vial. Vigorously shaked for 5 min. and polymer powder was filtered using a small stainless steel filter. Polymer powder was dried in the vacuum oven and leaved it overnight in the desiccator before using in the experiment of trichloroacetic acid absorption content determination via elemental analysis method using a scanning electron microscope (SEM) equipped with microanalyser. Polymer powder was then washed with deionized water to remove reversible absorbed trichloroacetic acid and was analyzed by microanalysis with SEM.

5.3.3. Preparation of trichloroacetic acid imprinted polypyrrole modified-RC membrane

MIP membranes were prepared using the 0.2 μm micro-filtration RC membrane as a supporting membrane and trichloroacetic acid and pyrrole as template and functional monomer, respectively. In typical preparation of MIP-pyrrole membrane, RC membrane was initially immersed in appropriated concentration of ammonium persulfate. The membranes were then transferred to a solution mixture of template and monomer to initiate electrochemical reaction. The reaction was left to complete in a certain time period. Thereby, the membrane was modified by the oxidized polypyrrole. The modified membranes were sequentially washed with methanol, acetonitrile and distilled water, respectively, to remove the excess unreacted monomer and the template. The non-imprinted polymer (NIP)-based membrane was prepared to investigate selectivity of the MIP-based membrane by using the procedure same as the MIP based membrane but the template was omitted.

5.3.4. Template uptake of the modified membrane.

Molecular adsorption of the prepared membranes to TCAA was studied using buffer pH 0.69 as medium. In typical binding test, the tested membrane was immersed in the aqueous solution until saturation and was cut to a size of 4.7 cm diameter. The cut membrane was mounted into the 5 cm diameter dead-end filtration unit, in which a stainless steel sieve support was placed at the bottom of the unit. The membrane was put on the top of support following with rubber O-ring for assured airtight seal of the membrane. A Perspex O-ring was set on the rubber O-ring with the second rubber O-ring placed on the top. A 5 cm Perspex cylinder was situated on the rubber O-ring. The filtration unit was finally closed with Perspex cover having other rubber O-ring inserted between cylinder and cover. A 1.5 L of sample solution was loaded into a Perspex reservoir having the diameter of 15 cm and was gradually driven into filtration unit using N_2 gas pressure in the range of 25-125 KPa. A filtrate was accumulated and weighed corresponding to the pressure used. The amount of TCAA in the sample solutions has been analyzed in triplicate by GC-ECD method as described in the next section and the data shown was the mean value of analysed data.

In addition, the influence of filtration pH on recognition ability to the template and analogs of the modified membranes was investigated. For this purpose, the original and modified membranes, prepared with different pH medium and concentration of ammonium persulfate, were mounted into dead-end microfiltration system. The filtrate composing with template molecule was pressurized passing the membrane with N_2 gas. The membrane was washed with aqueous solution to elute the bound template. The acid template was derivatized to the ester compound and was transferred to the organic phase via micro-extraction procedure for facilitating GC detection. And the organic phase was finally subjected to the GC-ECD analyse method to assay the amount of the template comparing with pre-added internal standard.

5.3.5. The analysis of TCAA amount in the solution samples by LLE-GC-ECD

The water samples collected from binding experiments were analysed by GC-ECD method in combination with liquid-liquid extraction. The sample preparation was carried out using the EPA method [3]. In the present case, 100 ml of water sample was added with 5 ml of concentrated sulfuric acid and 40 g of sodium sulfate and the solution was then extracted with 5 ml of methyl tert-butyl ether (MTBE) spiked with the internal standard, 2,4-dichloro-1-nitrobenzene (10 μg). A 3 μl aliquot of the extract was introduced into the GC by splitless injection at an injection temperature of 200 ^{O}C and the transfer line temperature of 280 ^{O}C. The separations were achieved on a HP-5 capillary column (30 m x 0.25 mm, 0.25 mm film thickness). The carrier gas flow rate was at 1.0 ml/min. The oven temperature was held constant at 35 ^{O}C for 10 min and the ramped to 75 ^{O}C at a rate of 5 ^{O}C /min for 5 min, 135 ^{O}C at a rate of 5 ^{O}C /min for 2 min, and 185 ^{O}C at a rate of 25 ^{O}C /min.

5.4. Material and equipment

5.4.1. Material

Trichloroacetic acid (TCAA) was purchased from Merck K.G. (Darmstadt, Germany). Dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), dibromoacetic acid (DBAA), monobromoacetic acid (MBAA), tribromoacetic acid (TBAA), malonic acid and 2,4-dichloro-1-nitrobenzene were obtained from Fluka Chemie AG (Buchs, Switzerland).

Analytical grade pyrrole was purchased from Fluka Chemie AG (Buchs, Switzerland) and its chemical structure is displayed in the Fig. 5.2.

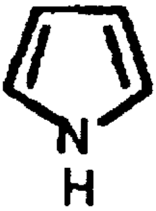


Fig. 5.2. The chemical structure of conducting monomer used to prepare polypyrrole film

Ammonium persulfate was the analytical grade and purchased from Ajax FineChem (Auckland, New Zealand).

The 0.2 μm micro-filtration regenerated membrane (RC) membrane was received from Sartorius AG (Goettingen, Germany).

All chemicals for preparing buffer solution (K_2HPO_4, NaH_2PO_4, NaCl, HCl and KCl) were analytical grade and were obtained from Merck (Darmstadt, Germany).

All solvents used in this work were analytical grade and were dried with 4 A pore sized molecular sieve before use. Working standard solutions were prepared daily.

5.4.2. Equipment

A Hewlett-Packard 6890 Series gas chromatography (Gaithersburg, Germany) (Fig. 5.3) equipped with a ^{63}Ni electron capture detector was used to assay TCAA and analogs (mono- and dichloroacetic acid and mono-, di- and tribromoacetic acid) in bulk solution obtained from the binding experiment.

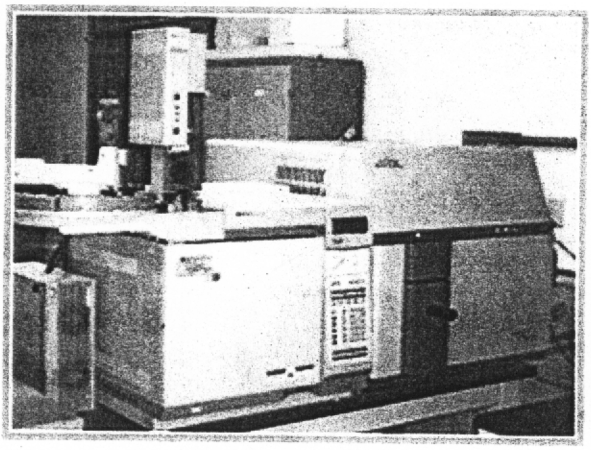


Fig. 5.3. A Hewlett-Packard 6890 Series gas chromatography

A JSM-5800 LV electron microscope (Jeol, MA, USA) equipped with an Oxford Instruments LINK-ISIS 300 X-ray detector and microanalysis system was used to perform elemental analysis of MIP thin-film coated on electrodes (Fig 5.4).

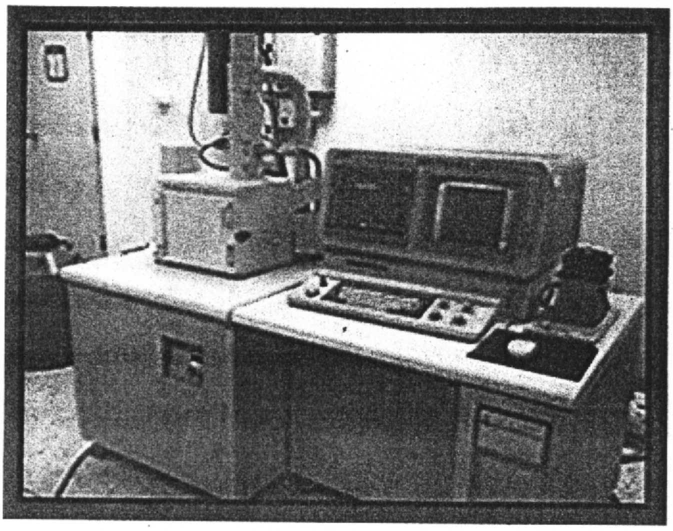


Fig. 5.4. Scanning electron microscope

A Fourier transform infrared spectrometer (FT-IR 2000 system, Perkin Elmer, USA) (Fig. 5.5) was employed to characterize the extraction process of imprinted polymer layer.

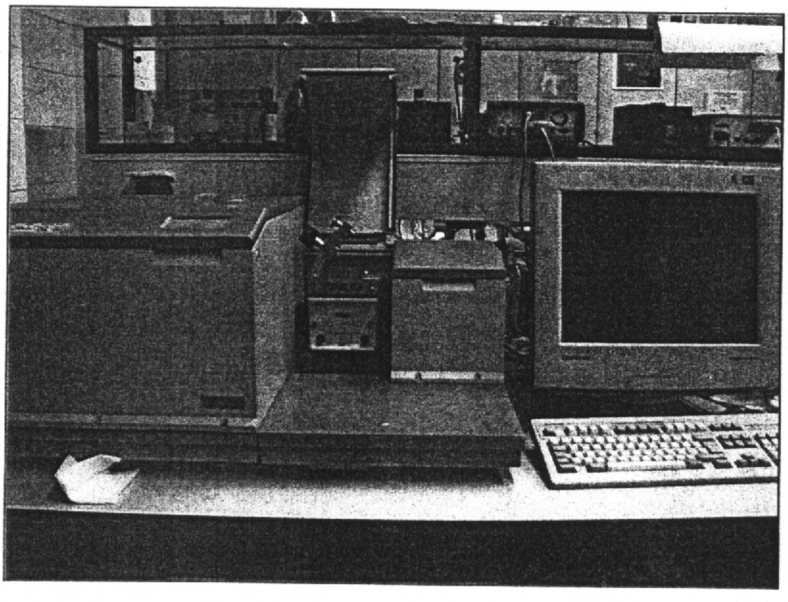


Fig. 5.5. A Fourier transform infrared spectrometer 2000 series

5.5. Results and discussion

5.5.1. The evaluation for the use of polypyrrole particle as recognition material

5.5.1.1. The influence of concentration of ammonium persulfate and synthesis pH used in modification process on recognition ability of imprinted polypyrrole

IR results of polypyrrole synthesized at various conditions (varying pH of solution medium and concentration of ammonium persulfate) were received from KBr disc experiment and interested function group and its wavenumber are shown in the Table 5.3 and spectrum of polypyrrole synthesized varying pH and concentration of ammonium persulfate can be seen in the Fig 5.6 and Fig 5.7, respectively.

Table 5.3

Interested functional group and its IR wavenumber from the spectrum analyzed using FT-IR spectrometer

Interested functional group	Wavenumber (cm^{-1})
-C=O- of overoxidized polypyrrole	1669
-C=O- of trichloroacetic acid	1683
-C=C- of polypyrrole	1553

It can be seen in Fig 5.6, when using higher concentration of ammonium persulfate, the peak at wavenumber ~1670 had higher area. It was attributed to the higher over-oxidation of polypyrrole causing from the reaction of polymer backbone with more excess amount of ammonium persulfate remained in the polymer synthesis. This process created the carbonyl functional group onto the polypyrrole structure causing the repulsive force with trichloroacetic acid. Thus, TCAA can not interact and absorp with polypyrrole. In addition, when using higher pH in polypyrrole synthesis (Fig. 5.7), absorption peak at ~1670 corresponding to the carbonyl functional group of TCAA, was smaller. It was due to that the higher pH of solution medium accommodated oxidation reaction of polypyrrole resulting in the higher amount of carbonyl group onto polypyrrole structure. Hence, higher repulsive force with TCAA was obtained and interaction and absorption between polypyrrole and TCAA is hardly occurred, similarly with using higher concentration of ammonium persulfate in the polypyrrole synthesis.

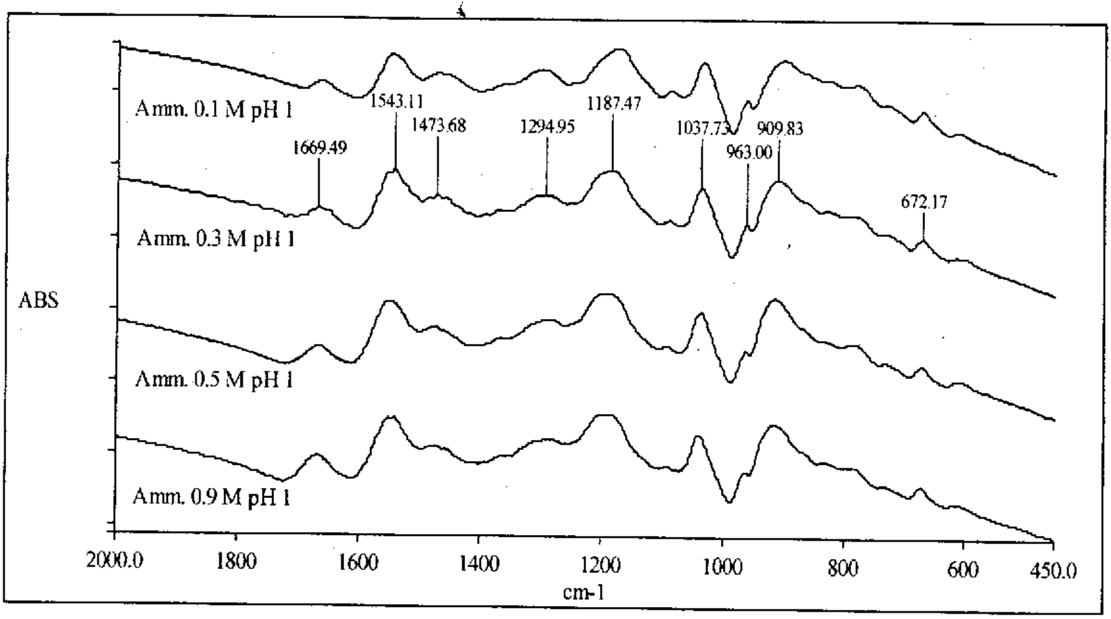


Fig. 5.6. IR spectrum of polypyrrole synthesized in the buffer solution pH1 and ammonium persulfate concentrations were varied at 0.1, 0.3, 0.5, and 0.9 M.

The effect of concentration of ammonium persulfate on template recognition was displayed as the peak area ratio at 1669 cm^{-1} and 1554 cm^{-1} (Fig. 5.8) which was belong to the carbonyl group of trichloroacetic acid and C-H stretching of polypyrrole backbone respectively. It was found that when higher concentration of ammonium persulfate used, lower peak area corresponding with IR absorption content of trichloroacetic acid carbonyl group was received. It was probably owing to using higher amount of ammonium persulfate which was used as polymerization initiator cause polypyrrole had a higher oxidizing state. Hence, the polymer had higher carbonyl group onto its structure and had dominant negative charge repelling with trichloroacetic acid molecule that can be negatively ionized at pH used in polymer synthesis. Therefore, TCAA can not be interacted and absorbed to the recognition site.

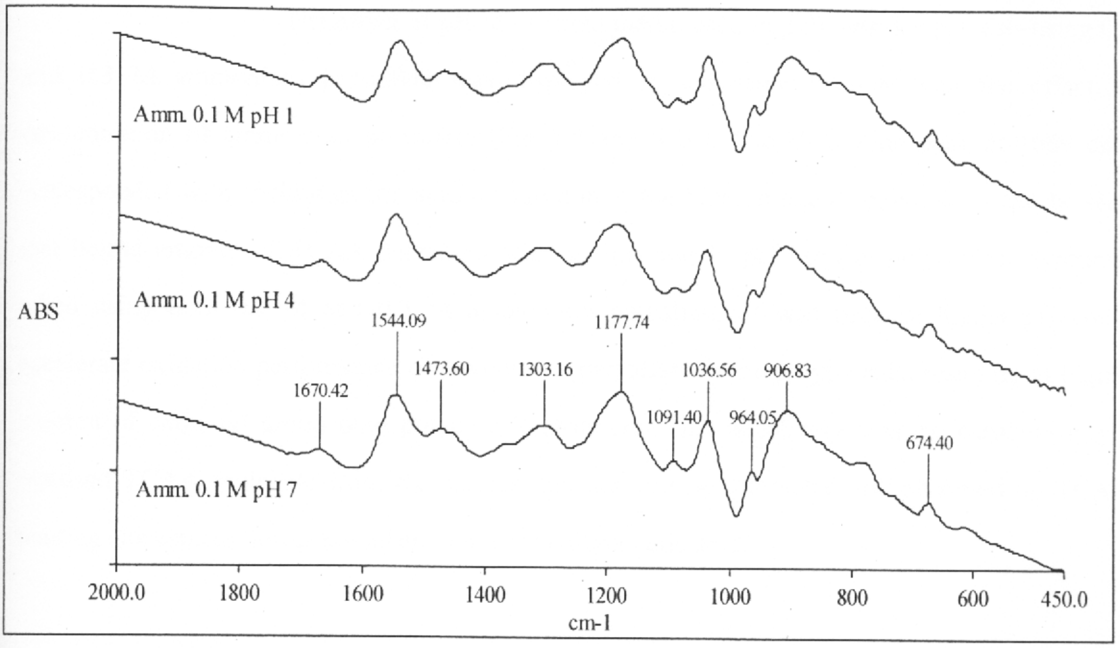


Fig. 5.7. IR spectrum of polypyrrole synthesized using pH1, 4 and 7 and using 0.1 M ammonium persulfate.

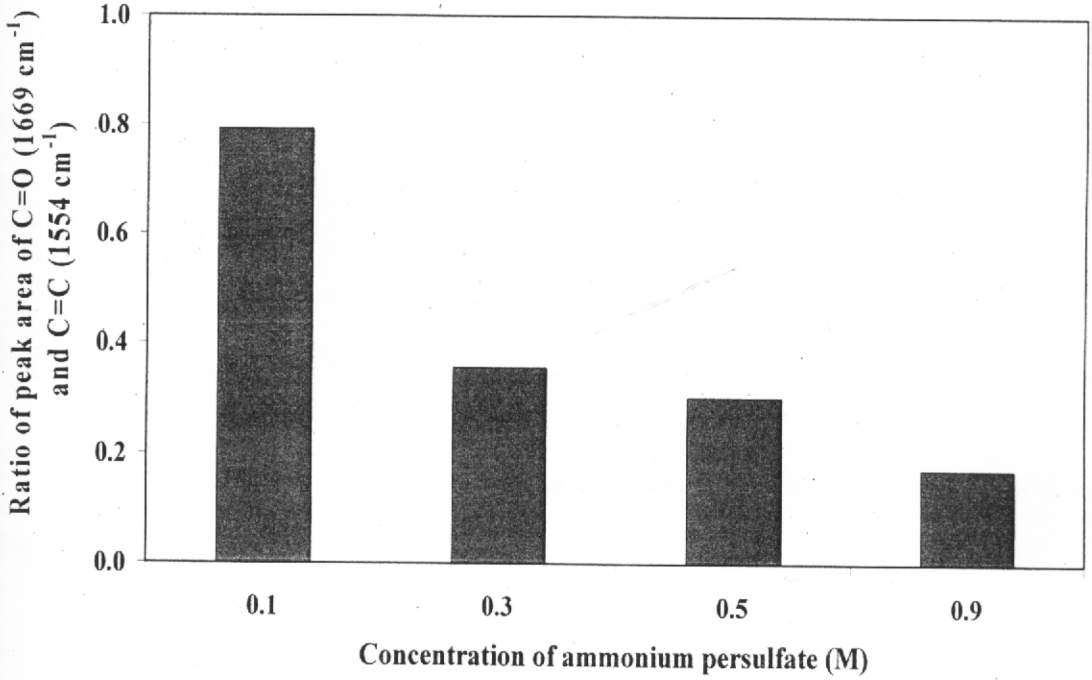


Fig. 5.8. The Effect of concentration of ammonium persulfate used in polypyrrole synthesis on peak area at wavenumber 1669 cm^{-1} corresponded with IR absorption of trichloroacetic acid carbonyl group. And the buffer pH1 was used as a medium solution in the synthesis.

The effect of pH of reaction media used in polypyrrole synthesis using 0.1 and 0.3 M ammonium persulfate was displayed in the same manner with the effect of concentration of ammonium persulfate (Fig 5.9 and 5.10). The absorption peak at 1669 cm^{-1} corresponded with trichloroacetic acid recognition at the binding site of polymer. It can be seen that bound amount of TCAA decreased with an increase in pH used in polypyrrole synthesis when using both 0.1 M and 0.3 M ammonium persulfate. It was because higher pH could accelerate oxidation performance of ammonium persulfate to the polypyrrole, resulting in higher amount of carbonyl group onto polypyrrole structure. This negatively charged carbonyl group repulsed TCAA molecule from the surface and can not be interacted and absorbed on TCAA binding site causing lower bound amount of trichloroacetic acid.

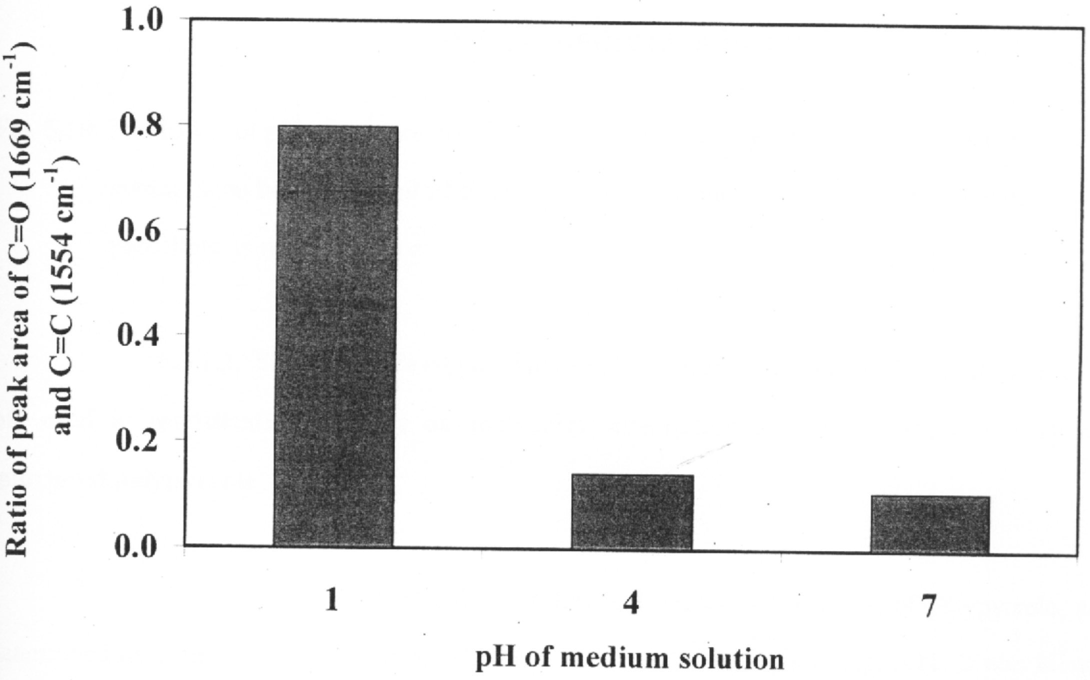


Fig 5.9. The Effect of pH of solution medium used in the molecularly imprinted polypyrrole synthesis on amount of trichloroacetic acid absorption and using 0.1 M ammonium persulfate as redox initiator.

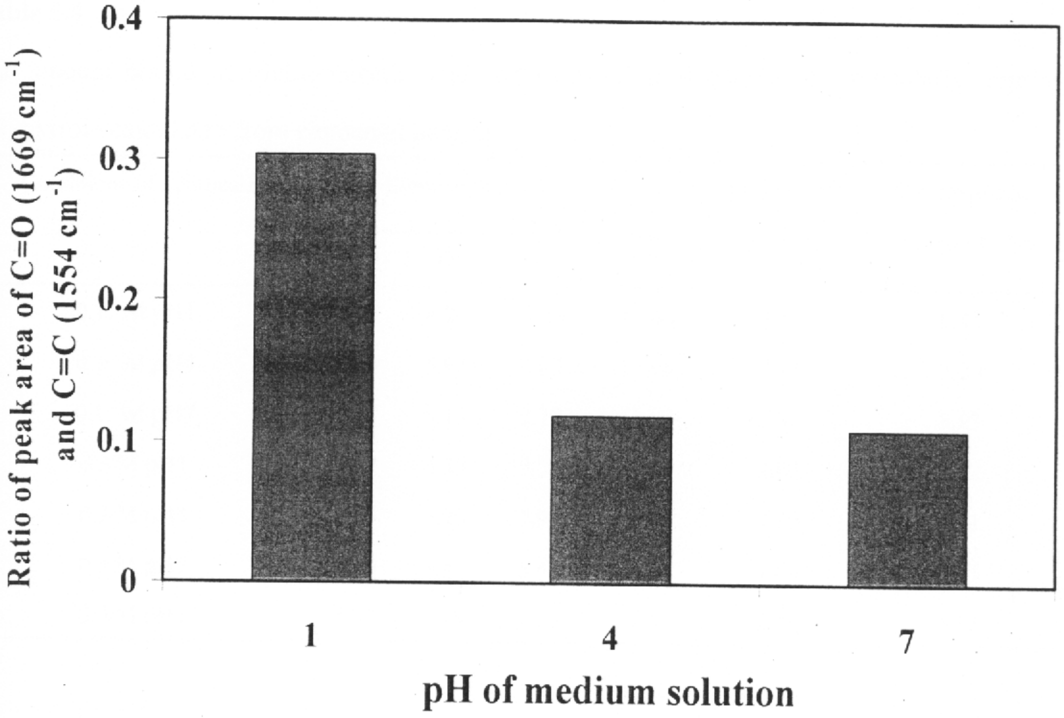


Fig. 5.10. The Effect of pH of solution medium used in molecularly imprinted polypyrrole synthesis on bound amount of trichloroacetic acid when using 0.3 M ammonium persulfate as redox initiator.

5.5.1.2. The influence of concentration of ammonium persulfate and synthesis pH used in modification process on molecular adsorption and overoxidized degree of imprinted polypyrrole

The amount bound of TCAA and degree of oxidation of polypyrrole, as determined by elemental analysis using SEM, are shown in Table 5.4 and Fig. 5.11. It was found that the amount bound of TCAA to the polymer decreased, while degree of oxidation of polypyrrole increased with an increase in concentration of ammonium persulfate and pH used in polymer synthesis. It can be explained by interaction between carbonyl functional group of the template and the polymer. The distribution of TCAA before template removal, as examined by elemental analysis using SEM, in the polypyrrole is illustrated in Fig. 5.12.

Table 5.4

The amount bound of trichloroacetic acid and over-oxidized degree of molecularly imprinted polypyrrole calculated from elemental analysis

Conditions of synthesis	Element (%)			TCAA (%)	Oxygen of TCAA	Overoxidized oxygen of Ppy
	C	O	Cl			
0.1 M pH1	82.57	4.24	12.67	19.46	3.81	0.43
0.1 M pH4	83.89	5.93	9.09	13.96	2.73	3.20
0.1 M pH7	85.23	6.15	7.70	11.83	2.32	3.83
0.3 M pH1	84.37	4.58	9.51	14.61	2.86	1.72
0.3 M pH4	84.59	5.90	7.93	12.18	2.39	3.51
0.3 M pH7	84.36	8.47	5.45	8.37	1.64	6.83
0.5 M pH1	84.07	6.19	7.86	12.07	2.36	3.83

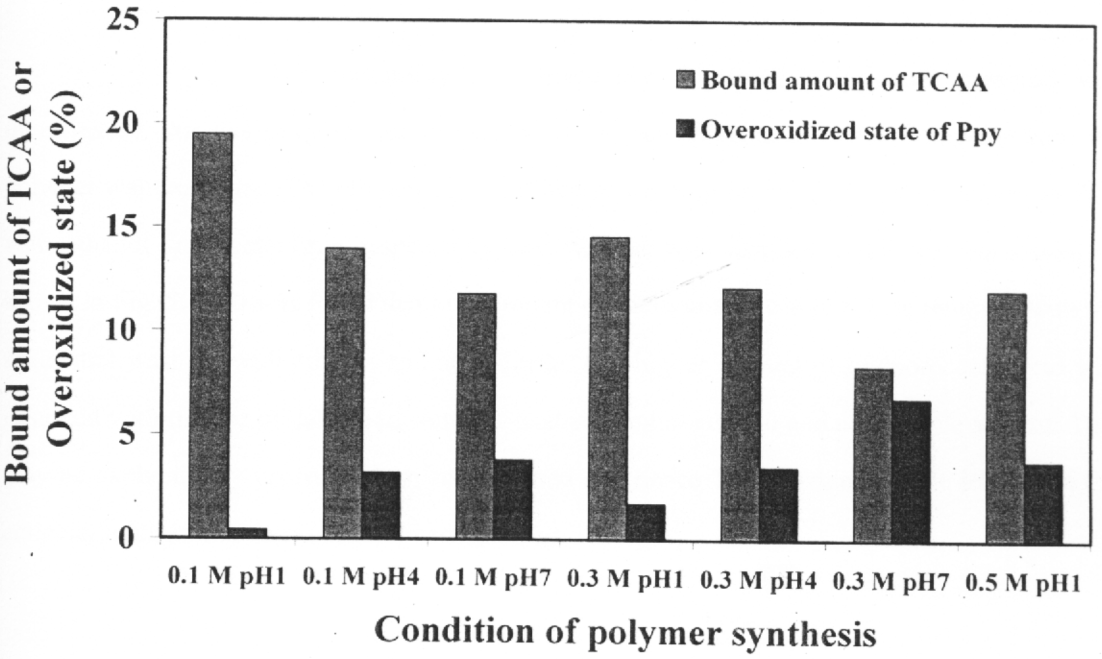


Fig. 5.11. The Effect of pH of rebinding media and concentration of ammonium persulfate on bound amount of trichloroacetic acid in polypyrrole.

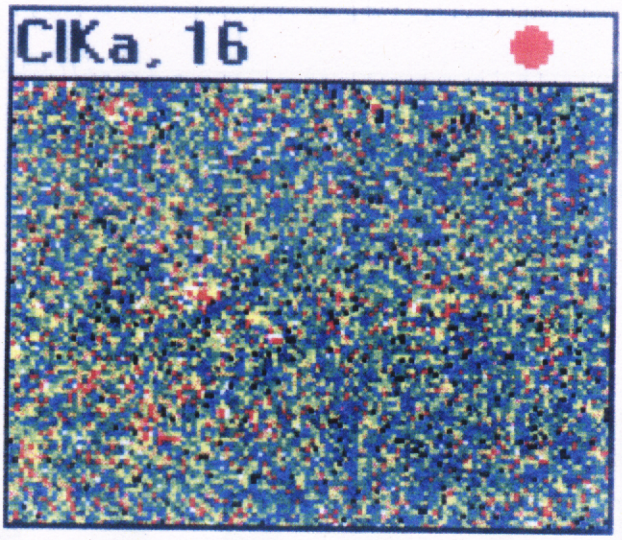


Fig. 5.12. Distribution of TCAA in polypyrrole particles; white spot indicated lower density of TCAA and vice versa.

5.5.1.3. The effect of washing solvent used in template removal process on bound amount of imprinted polypyrrole

The reusability of molecularly imprinted polypyrrole prepared was investigated. For this purpose, the efficiency of various solvents to extract template from the polymer was examined. The efficacy of two different washing processes *i.e.*, sequentially washed with ethanol and acetonitrile respectively and washed with distilled water was compared, as shown in Fig. 5.13. It was found that high amount of trichloroacetic acid can be removed with the sequential washing with ethanol and acetonitrile. But higher amount of trichloroacetic acid was removed with the use of deionized water instead sequential ethanol and acetonitrile solvent. This may be explained by polarity of the solvent used and hence TCAA which can be ionized in the aqueous solution can be easily removed by water.

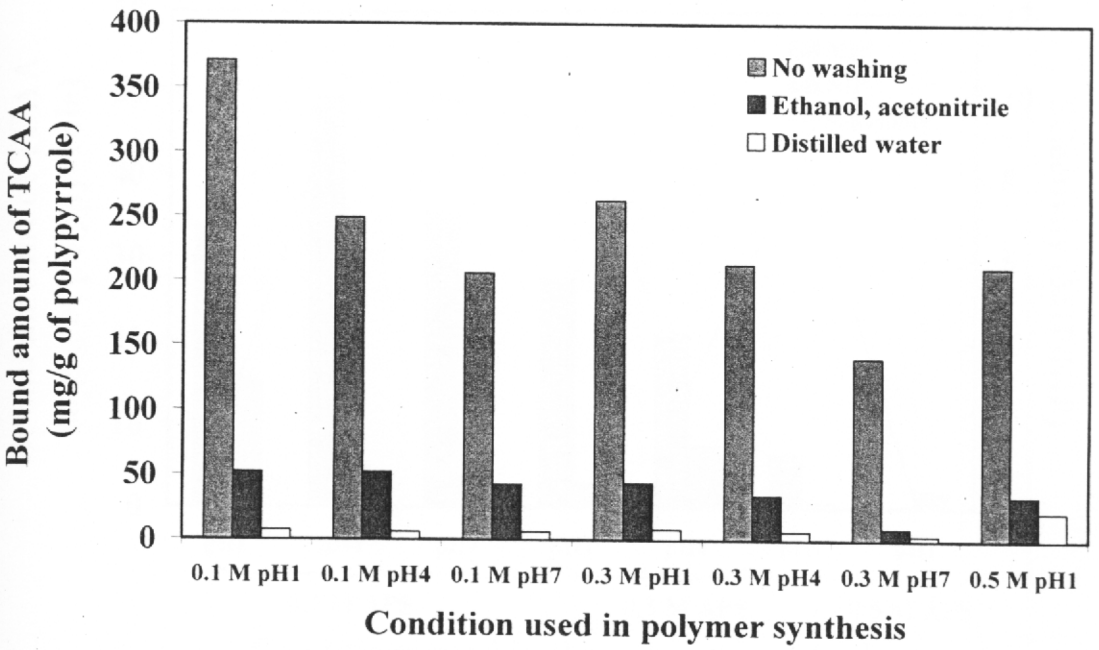


Fig. 5.13. The effect of solvent type on trichloroacetic acid removal performance from molecularly imprinted polypyrrole.

5.5.1.4. The selectivity of the imprinted polymer synthesized at various synthesis pHs and concentrations of ammonium persulfate

In this study, the selectivity of the imprinted polymer synthesized at various synthesis pHs and concentration of ammonium persulfate was examined by determining the amount bound of TCAA on the polymer, using elemental analysis. This result showed in the Fig. 5.14, it was found that synthesis condition used 0.1 M of ammonium persulfate and pH 4 of reaction solution had highest reversible bound amount of TCAA when compared with the other condition. It may be because this condition can create the imprinted site in a network structure, which is strong enough and suitable for rebinding process. In addition, the polypyrrole generated under this condition probably had highly positive charge on the backbone structure and TCAA can therefore be attracted to interact and absorbed with. When compared with non-imprinted polypyrrole, imprinted polypyrrole had much higher bound amount of TCAA. This indicated that the binding sites were produced in the polypyrrole when TCAA was added in polymerization process.

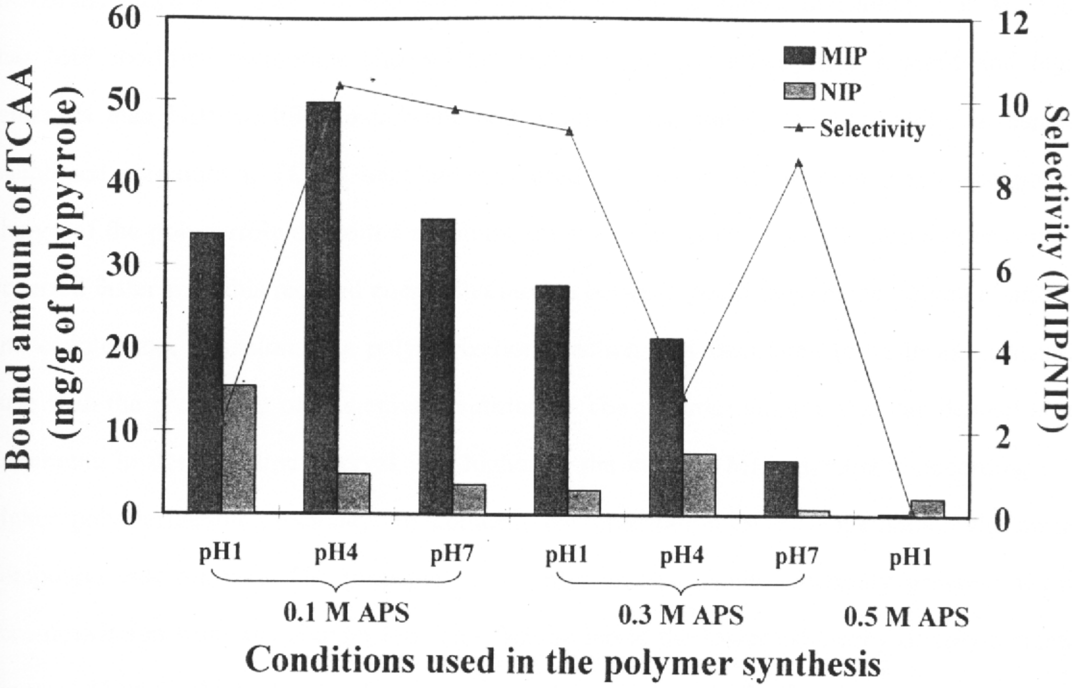
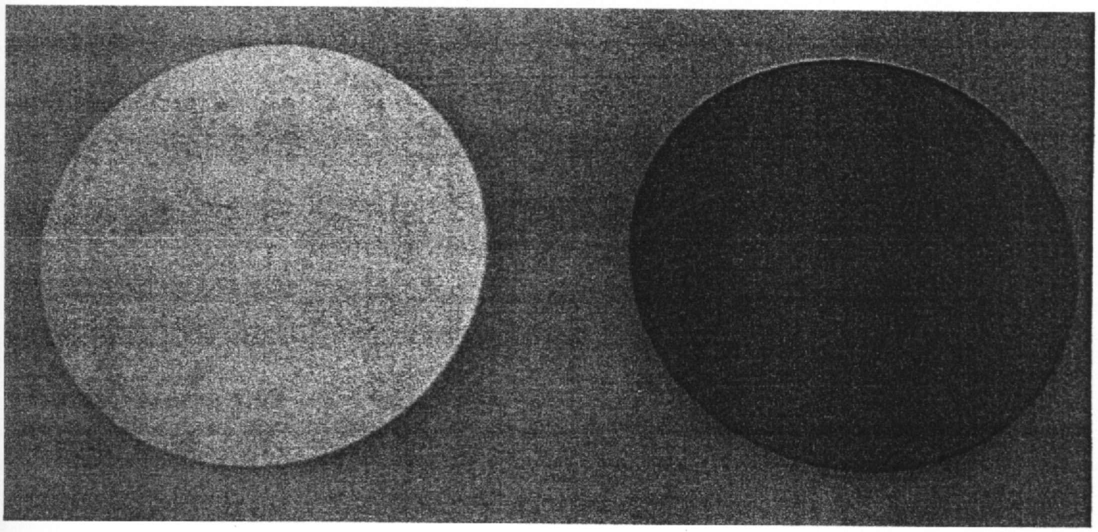


Fig. 5.14. The Effect of ammonium persulfate concentration and pH used in polypyrrole synthesis on bound amount of trichloroacetic acid, oxidized degree and absorption selectivity of polypyrrole.

5.5.2. The effect of electrochemical modification process with imprinted polpyrrole on RC membrane characteristics

For evaluating the use of polypyrrole as recognition material to TCAA and analogs in microfiltration composite membrane, the parameters concerning electrochemical polymerization (pH used in the reaction and initiator concentration) were investigated. The specificity of the prepared membrane was examined by comparing between the MIP-based membrane and non-imprinted polymer based membrane.

As can be seen in the Fig. 5.15, the whole membrane turned to black color after electrochemical deposition of polypyrrole in the oxidizing agent. This changed color is an evident for the previous mentioned deposition process concerning with several phenomena. Polypyrrole is inherently black from many exited conjugated double bonds in molecular structure. As it known that these type of structure usually absorb all of the visible light waverange. Not only the color of membrane changed by the modification process, but also the other characteristics of the membrane (thickness, pore size and porosity) were altered, as shown in Table 5.5. It was found that MIP modified membrane showed the higher deposited polypyrrole amount and higher thickness than NIP modified membrane and original membrane did. Assumedly, in the MIP membrane preparation, TCAA template was used as counter ion to compensate the positive charge of the polypyrrole deposited at the membrane. The stable chain of the polymer could be occurred faster with this reduced energy interaction between positively charge polymer backbone and counter ion. Therefore, the polymerization reaction was facilitated to be in an accelerated state with the promoting of this anionic substance. The polymer amount that can deposit on the membrane in defined time interval was higher in the case of MIP membrane according to its higher polymerization efficiency. In contrast, the preparation of NIP membrane the anionic compound was omitted. The propagation of polymer chain may inherently progress without accommodation from any counter ion. This fashion led to the lower efficiency of polymerization process. The adsorbed amount of polymer as well as thickness of NIP membrane was therefore lower than MIP membrane (see Table 5.5).



(a) (b)

Fig. 5.15. Micro-filtration RC membrane before (a) and after (b) modifying with imprinted polypyrrole

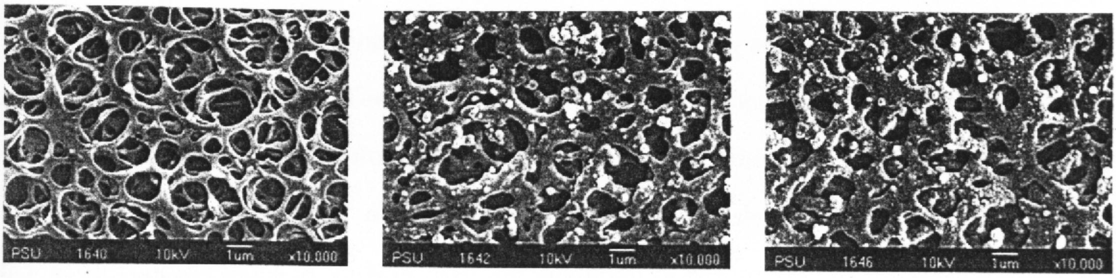
When comparing pore size and porosity of MIP, NIP and original membrane (see Table 5.5), it was found that both MIP and NIP membrane had the same pore size, but both membrane had slightly different pore size from the original membrane. While the modified membrane showed the higher porosity than the original membrane. It was possibly due to this type of membrane, regenerated cellulose, can swell in the ammonium persulfate redox intiator used in the experiment. Its pore structure *i.e.*, grain and pore size, may be altered from original. Actually, the deposition process should decrease the membrane pore size, but the membrane swelling may cause the incremental membrane pore size. When making consideration in porosity of those three membranes, the MIP and NIP membrane had lower porosity than original membrane. It was presumably due to the opposite two events occurred during deposition process. Although the deposition process can increase the pore size of the membrane by swelling process, but the smaller pores in the membrane were covered with polymer layer. This can be confirmed by scanning electron micrograph of the membrane as shown in Fig. 5.16.

Table 5.5

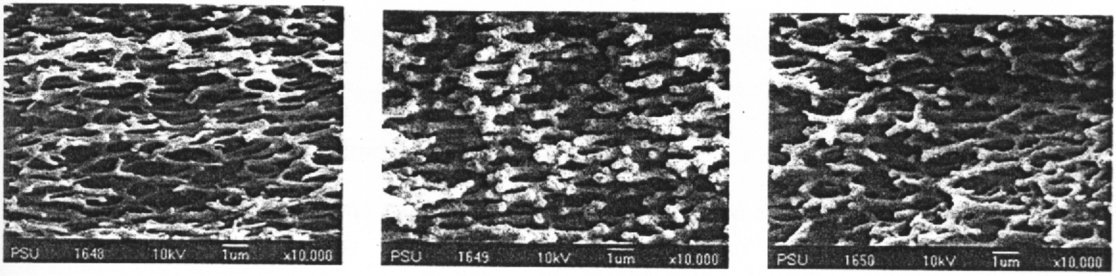
Comparison of the membrane characteristics before and after modifying with imprinted polypyrrole utilizing electrodeposition process at pH 0.7

Membrane type	Polymer content	Thickness (μm)	Mean pore size (μm)	Porosity (%)
RC*	-	112	0.21	11.03
MIP	33.6	200	0.24	8.14
NIP	20.1	120	0.24	8.99

*RC is regenerated cellulose



(a) RC-surface (b) MIP-surface (c) NIP-surface



(d) RC-inside (e) MIP-inside (f) NIP-inside

Fig. 5.16. SEM pictures of surface and inside structure of RC, MIP and NIP membrane using 10,000 X resolution

As can be seen in Fig. 5.16, the MIP and NIP modified membrane have the thick grain deposited in both surface and inside of the membrane comparing with the original membrane. While the grain appeared in case MIP and NIP membrane can not be distinguished with SEM picture for the surface position. But there is some difference of the grain shown in MIP and NIP membrane at inside. MIP membrane showed thicker grain than that of NIP membrane. These SEM pictures also proved that the several membrane characteristics can be altered with electrochemical modification process using polypyrrole as deposition material.

5.5.3. The effect of immersion time of RC membrane in ammonium persulfate solution on weight change of the membrane

The amount of polymer deposited on the membrane was absolutely controlled by the amount of initiator molecule adsorbed at the membrane structure. Hence, the parameters determined the adsorption process of initiator molecule on the membrane grain can affect to the amount of polymer deposited onto the membrane structure. In this part of study, the effect of immersion time of RC membrane in aqueous solution containing ammonium persulfate at various concentrations was explored. These were ordinarily known as factors having the direct influence on adsorption process of initiator onto the supporting membrane. The study started with three negligible different weight RC membranes, and the result was shown in Fig. 5.17. It was found that at all concentrations of initiator used the saturation of adsorption process was observed and this saturation phenomenon was fastest in case of the highest concentration of initiator (1.5 M). After making calculation of weight change percent of saturation process for all membrane studied, the interested values were exposed. The weight change of 0.33, 0.49 and 0.60% was responsible for the membrane immersed in 0.5, 1.0 and 1.5 M ammonium persulfate, respectively. This expected behaviour of the saturation process of membrane in various concentrations of ammonium persulfate solution may be due to the higher concentration of initiator composed of higher amount of initiator molecule. The high abundance of initiator molecule in solution led the adsorption process of initiator molecule into the accelerated fashion to the membrane grain. The saturation phenomenon of membrane with initiator molecule can therefore come quicker. When making consideration to the weight of membrane after saturation point, all membranes sharply lost their weight and gained to level off state. Although, the initiator used in this work can help to begin polymerization process but the other side of its property which can be used to categorize this chemical as oxidizing agent caused the serious effect with the membrane. RC membrane commenced to degrade after a certain time period in ammonium persulfate solution and this behaviour can be observed explicitly with the use of highest concentration of initiator. The membrane immersed in 0.5, 1.0 and 1.5 M ammonium persulfate showed the weight decline about 1.25, 1.60 and 1.84%, respectively. This was probably due to the higher concentration of redox initiator molecule caused the higher efficiency redox reaction at the membrane structure. At the time exceeded the saturation the resulted membrane was fragile and can not be handled to the next process anymore. This is very important thing that should be kept in mind when preparing the modified membrane through soaking process in redox initiator. The immersion time should not to be longer than the saturation time of the membrane otherwise the damage of membrane was obtained.

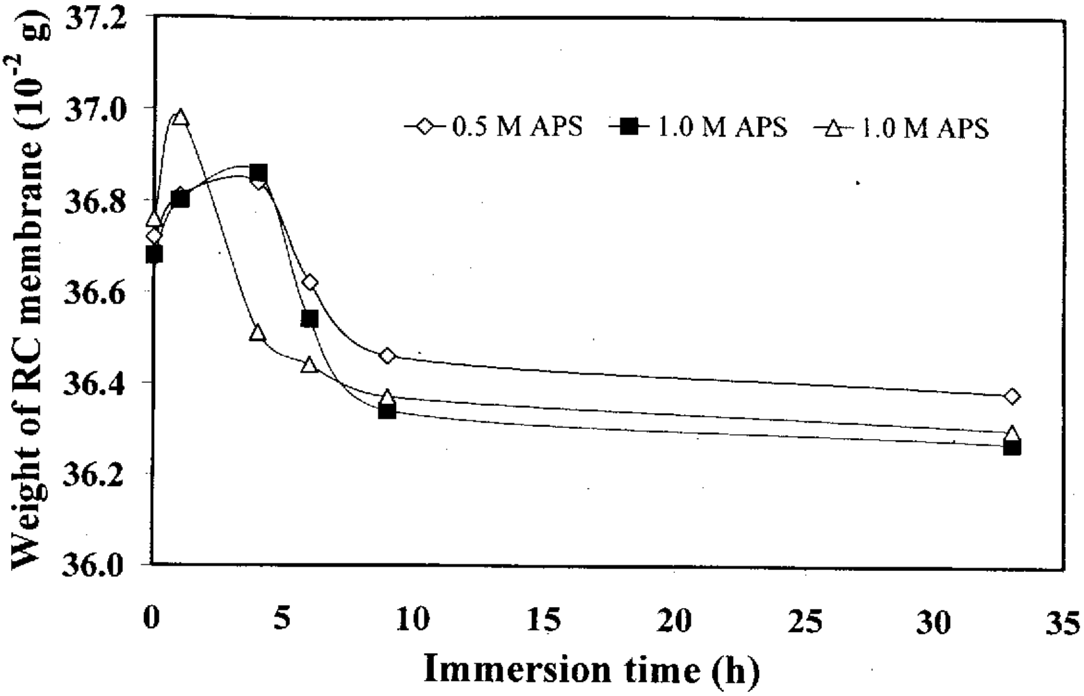


Fig. 5.17. The influence of immersion time in ammonium persulate redox initiator of RC membrane on the weight change of the membrane using various concentrations of ammonium persulfate

5.5.4. The effect of NaCl concentration in binding solution on the recognition ability of modified membrane to the template

In IDC sensor, the electrode modified with imprinted polypyrrole shows low sensitivity to the template when exposed in NaCl solution. The bound amount of the template can be influenced by the competitive interaction of the added salt and charged surface of polymer. In order to know how big this kind of electrolyte interfere to the rebinding process in case of imprinted polpyrrole modified membrane the effect of NaCl concentration is therefore investigated. The influence of NaCl concentration on the recognition ability of the imprinted polypyrrole modified membrane was shown in Fig. 5.18. It was found that the bound amount of template of MIP modified membrane negligibly decreased with an increase of NaCl concentration in initial range. At high concentration of NaCl the bound amount of MIP modified membrane sharply declined compare to the bound amount of NIP modified membrane. Whereas NIP modified membrane provided a less bound amount constantly throughout NaCl concentration range studied. It was probably due to that the electrolyte completely decomposed as charged species in solution. These ion species preferably encountered with the opposite charged surface or functional group wherever they can come closely. The negatively charged ion of this salt may compete with the template by solvating around the positively charged functional group of the polymer and hence protection of inclusion of template molecule. The bound amount of template by MIP modified membrane was therefore remarkably reduced. In case of NIP modified membrane, the bound amount of template was virtually low. Since the competitive interfering from electrolyte was impossible and bound amount of the NIP membrane was similar for all the concentrations of electrolyte.

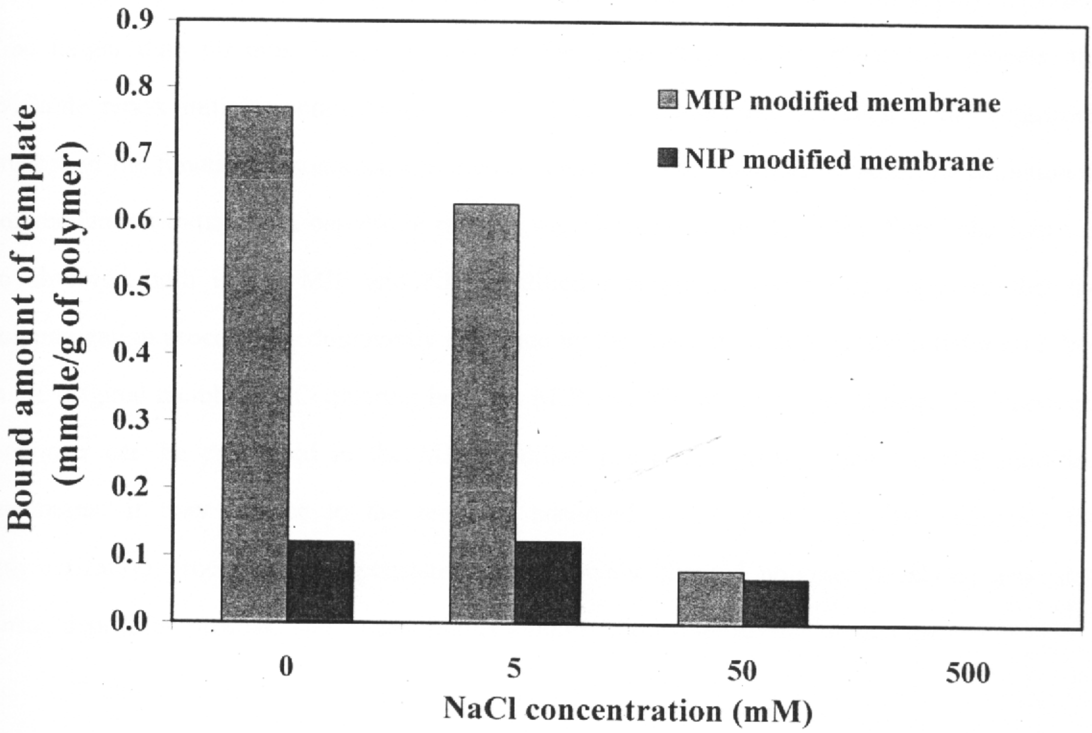


Fig. 5.18. The effect of NaCl concentration in binding solution on the recognition ability of polypyrrole modified membrane

5.5.5. The effect of polymerization time on the amount of polypyrrole deposited into membrane and recognition ability of modified membrane to the template

The other parameter determined the amount of conducting polymer deposited in modified membrane is polymerization time. For this, the original membrane saturated with redox initiator was allowed to expose with functional monomer solution for a certain period of time to complete the polymerization process. The different recognition properties of modified membrane can be designed according to the amount of polymer deposited in the membrane. In order to find the suitable time for completing polymerization of a modified membrane, the effect of time intervals used in deposition step was determined and the results were shown in Fig. 5.19. It was revealed that the polymer amount in the modified membrane proportionally increased with an increase in polymerization time in the range of 0-60 min, and began to level off at polymerization time longer than 60 min. It was because in the initial stage of polymerization process, the available redox initiator concentration adsorbed in the membrane was higher, the deposition process of the functional monomer was then accelerated to the membrane. After the depletion of polymerization initiator the deposition process was slower and finally faded. This behaviour can be observed both in the MIP and NIP modified membrane. The result suggested that the polymerization process was dominantly governed by the concentration of redox initiator absorbed in the original membrane. Comparing between MIP and NIP modified membrane, the functional monomer can be embedded in the MIP modified membrane greater than the NIP modified membrane. It may be due to the template adsorbed in the membrane that facilitated the polymerization process by compensating the positively charged polymer backbone generated during deposition process. This caused higher amount of polymer in MIP membrane.

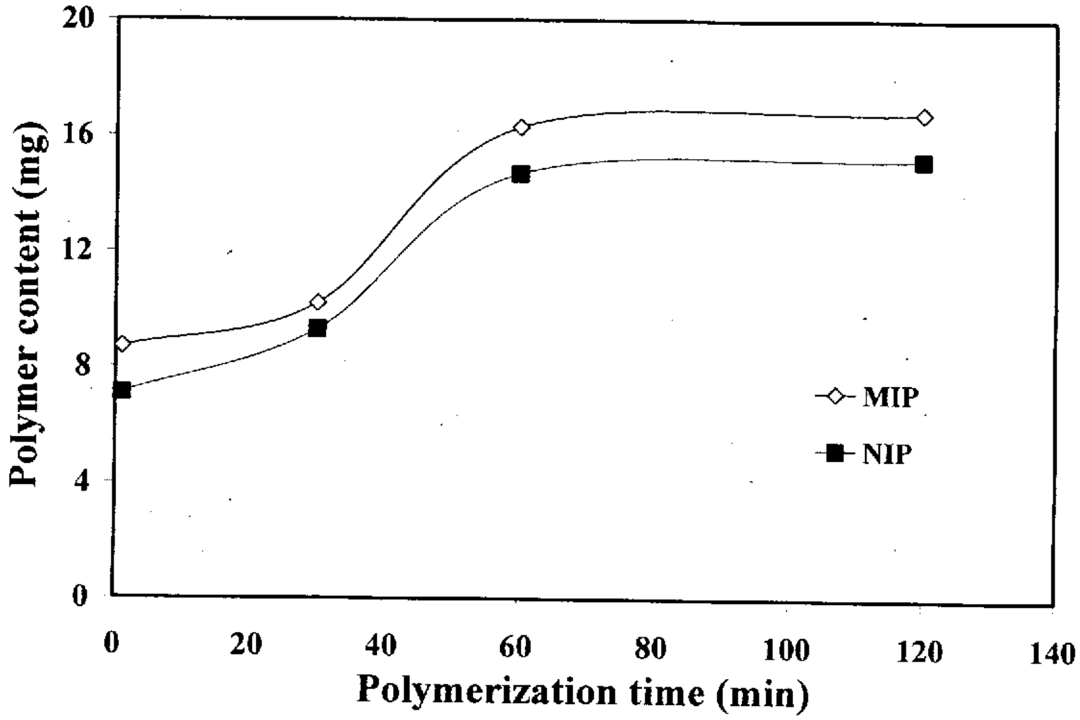


Fig. 5.19. The effect of polymerization time on amount of polymer deposited in polypyrrole modified membrane ($n = 3$).

The influence of polymerization time on the recognition ability to the template of the modified membrane was shown in the Fig. 5.20. It was found that the amount bound of either MIP or NIP modified membrane remarkably increased in an initial period of polymerization time and start to meet the constant value when using the polymerization time higher than 60 min. This behaviour of amount bound of the polymer on membrane expectedly corresponded with polymer amount deposited in the membrane. It was possibly from the concentration of polymerization initiator was very high at the initial stage of deposition process. The rate of polymerization enhanced amount of polymer deposited in the membrane. There was difference in amount of template adsorbed on MIP and NIP in all cases of polymerization time, which referred to imprinting effect.

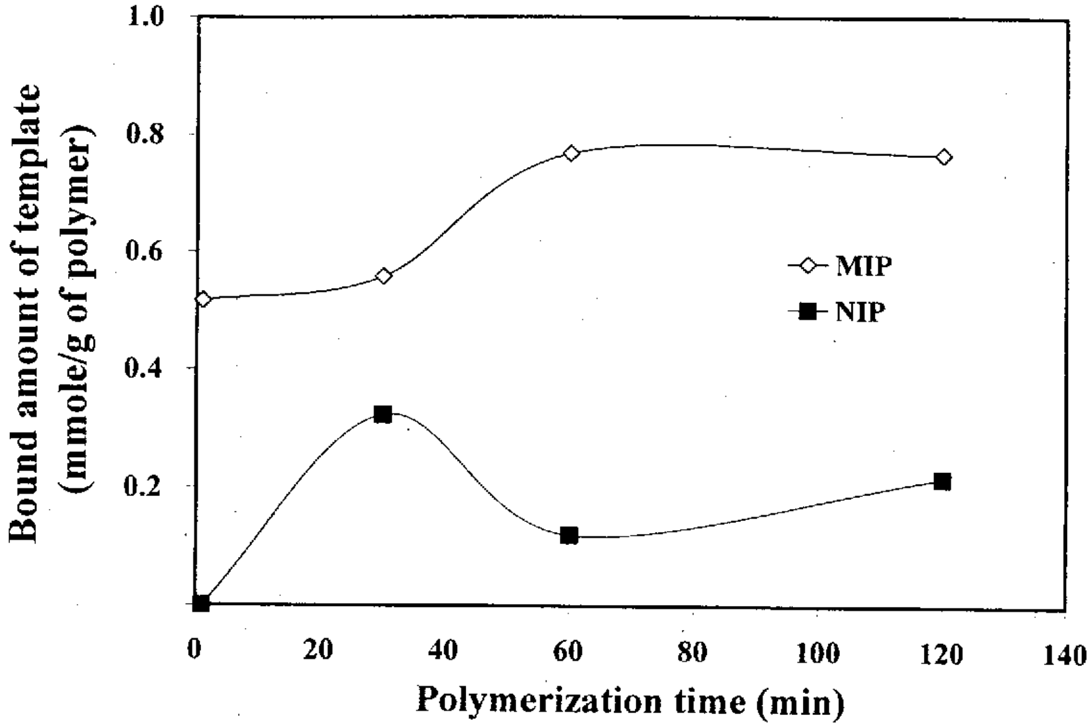


Fig. 5.20. The influence of polymerization time on template bound amount of modified membrane ($n = 3$).

5.5.6. The influence of pH of modification process and concentration of ammonium persulfate on the amount of polypyrrole deposited into membrane

As shown in Fig. 5.21, the amount of polymer deposited in the cellulose membrane increased with decreasing in pH. This may be because at lower pH the ammonium persulfate initiator decomposed more easily than at higher pH. The polymerization process is performed faster as higher level of the free radical species generated. Hence, the higher amount of polymer deposited in the membrane.

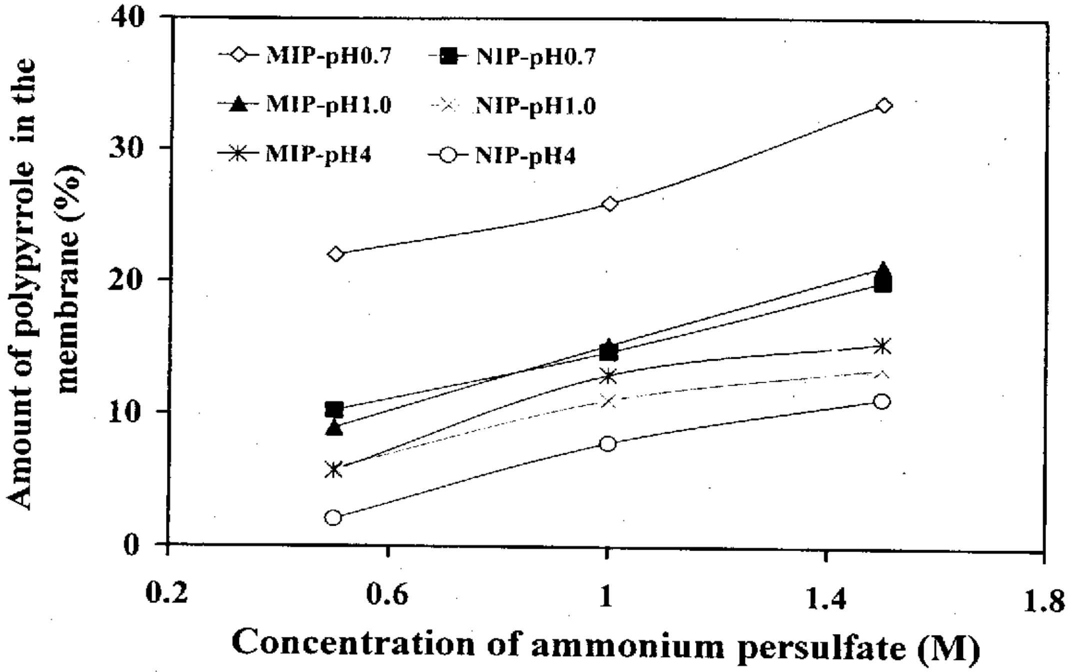


Fig. 5.21. Influence of ammonium persulfate concentration on the amount of polymer deposited in RC membrane at various pH used in modification process

At the same pH of the modification process, MIP membrane had higher deposited polymer amount than that of NIP membrane. It could be explained in the same fashion as studying pH effect of the polymer. It might be due to the insertion of anionic moiety of template molecule absorbed at the membrane surface to the positively charged polymer backbone occurred during polymerization. Therefore, the polymerization process of this conductive polymer can be enhanced with the dominantly existed anionic species in the solution.

5.5.7. The effect of concentration of ammonium persulfate on the swelling of the modified membrane preparing at various pH on modification process

The effect of concentration of ammonium persulfate initiator on the swelling of MIP and NIP modified membrane was shown in Table 5.6 and Fig. 5.22. It can be seen that the MIP and NIP modified membranes had higher swelling with an increase in concentration of ammonium persulfate. It was due to initiator molecule can penetrate into regenerated cellulose membrane and may cause dimension change of the membrane. Additionally, initiator molecule may allow the membrane grain softer through the oxidizing reaction. The initiator used in the process is a good oxidizing agent. It can withdraw electrons from the membrane structure by which the membrane structure can be altered and the robustness of the membrane could be reduced from those unstable structures (Farooque, 1999). This phenomenon can be observed when leaving the membrane in a solution of ammonium persulfate for a few days. The membrane became paste solid and some part was destroyed until it can not be handled. This observation showed that the initiator used can cause problem to the membrane even immersing it for a few hours. It suggested that the long time soaking of the membrane in initiator solution should avoid.

Table 5.6

Effect of concentration of ammonium persulfate on swelling of modified membrane prepared at various pH of modification medium

Ammonium persulfate concentration (M)	Swelling (%)					
	pH 0.69		pH 1		pH 4	
	MIP	NIP	MIP	NIP	MIP	NIP
0.5	330.6	346.6	346.9	327.0	350.0	350.0
1	330.2	352.0	357.4	330.9	359.5	362.8
1.5	351.0	378.8	362.7	349.6	377.0	379.1

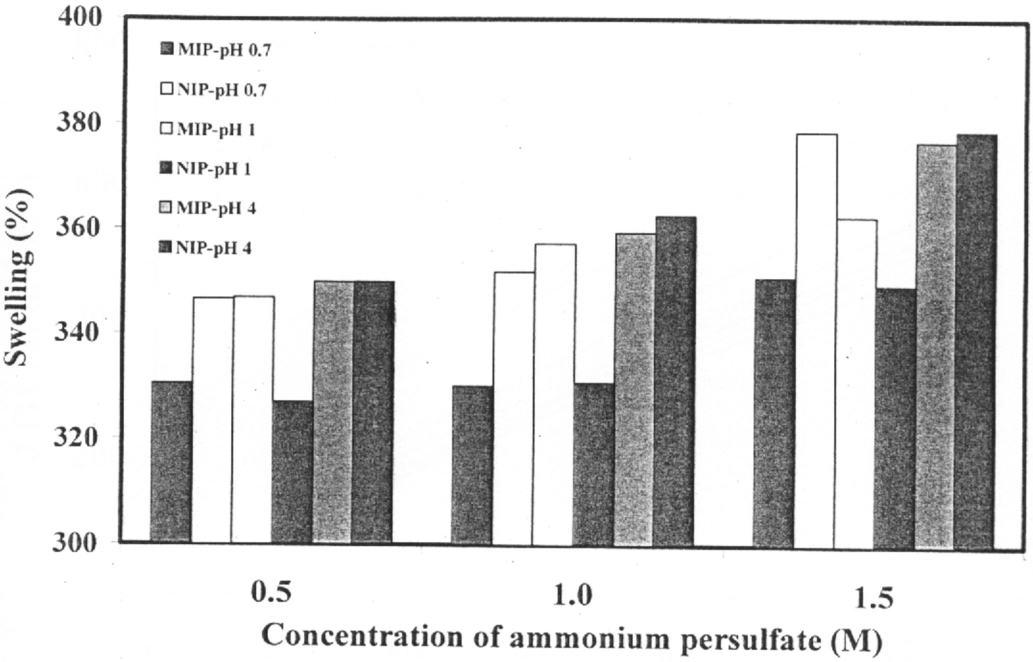


Fig. 5.22. Effect of concentration of ammonium persulfate initiator on swelling index of MIP and NIP preparing with various pH used in modification process.

According to the SEM micrographs in Fig. 5.16, the pore size of the modified membranes was bigger when compared with the original membrane. When making consideration between different pHs of modification process, the higher swelling was observed with increasing in pH. This may be because the efficiency of oxidizing agent to react with the membrane was enhanced when the pH of modification process was increased. It then resulted in higher swelling of the modified membranes.

5.5.8. The influence of pH used in preparation process and concentration of ammonium persulfate redox initiator on permeate flux of modified membrane

The effect of pH used in preparation process of the modified membrane, when 0.5, 1.0 and 1.5 M of ammonium persulfate was used, was shown in the Fig 5.23, 5.24 and 5.25, respectively.

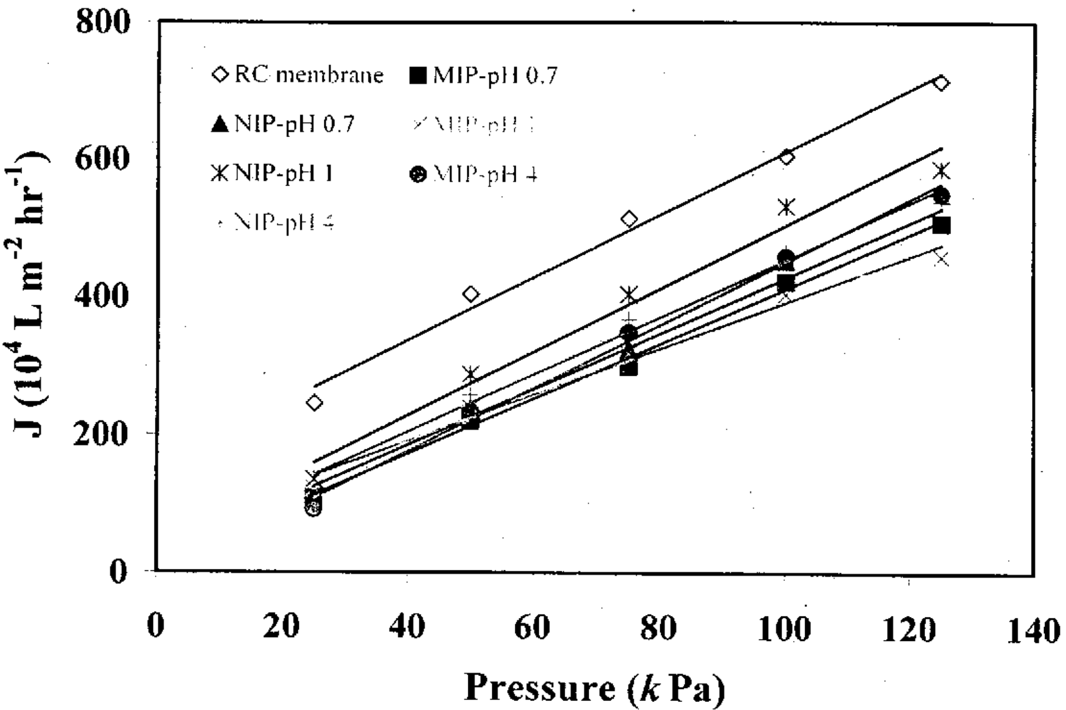


Fig. 5.23. Effect of pH used in modification process of TCAA-MIPpy membrane on permeate flux when 8.17 mg l^{-1} (0.05 mM) TCAA solution and 0.5 M ammonium persulfate was used in polymerization process.

Generally, the modified membranes showed the lower permeate flux than that of the original membrane. According to the morphology of the membrane investigated with SEM (see Fig. 5.16), the porosity of MIP and NIP membrane was reduced with modification process. The porosity that referred to availability of channel for transport of target molecule was also decreased. Therefore, the flux, which is the flow rate of permeate filters pass through the constant surface area and defined time was, decreased. Comparing between flux of MIP and NIP modified membrane, MIP membrane had lower flux than those of NIP membrane when pH 0.7 and 1.0 of modification medium were used. This may be because in the preparation of the MIP membrane anionic template was utilized to compensate the positively charge surface of polypyrrole backbone. Such characteristic facilitated the deposition process and the template deposited to the membrane more easily with its lower ionization state. Hydrophobic interaction between membrane material and TCAA template was promoted when medium pH reduces. The ionization of the acid was reduced, which allowed the adsorption of the acid on membrane faster. Hence, the polymerization process of MIP membrane is enhanced. The lower porosity of MIP membrane than that of NIP membrane could support this assumption.

The observations as above-mentioned were occurred with the filtration in case of modified membrane prepared with 1.0 and 1.5 M of ammonium persulfate. Higher concentration of ammonium persulfate employed the lesser difference in flux of MIP and NIP membrane at pH 1 and 4 was observed. As can be seen in Fig. 5.24 and Fig. 5.25, MIP and NIP membrane showed the similar flux at pH 1 and 4. It may be explained as that at high concentration of ammonium persulfate the MIP and NIP membranes swelled and hence the membrane pore sizes were expanded. This leads to fast filtration of TCAA, thereby the low selective separation.

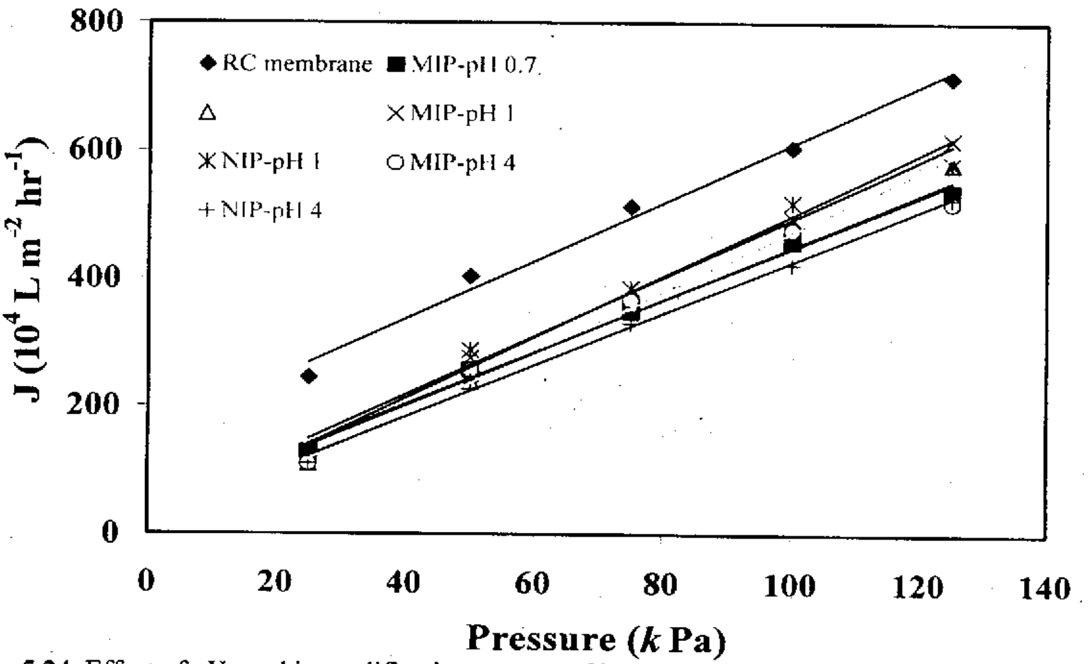


Fig. 5.24. Effect of pH used in modification process of TCAA-MIPpy membrane on permeate flux when 8.17 mg l^{-1} (0.05 mM) TCAA solution and 1.0 M ammonium persulfate was used in polymerization process.

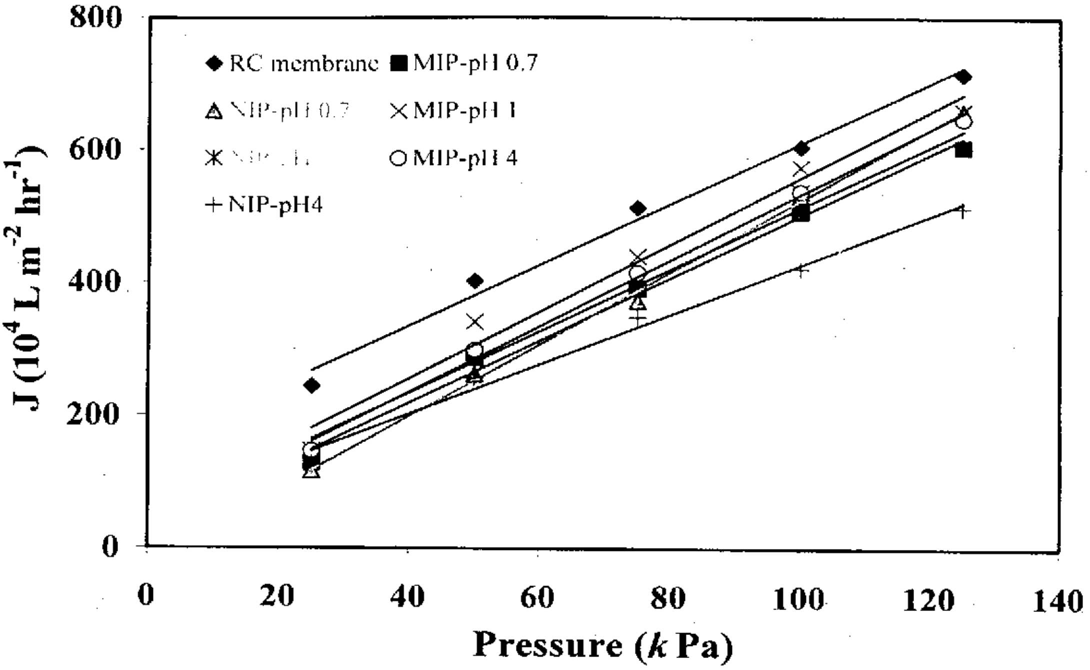


Fig. 5.25. Effect of pH used in modification process of TCAA-MIPpy membrane on permeate flux when 8.17 mg l^{-1} (0.05 mM) TCAA solution and 1.5 M ammonium persulfate was used in polymerization process.

In this part, the effect of pH used in deposition process and concentration of ammonium persulfate, redox initiator, on the membrane characteristics in terms of permeate flux was investigated.

After modification with the polypyrrole polymer, the permeate flux of the cellulose membrane reduced significantly as shown in Fig. 5.26. This is because the pore size of the membrane is reduced with modification. The deposition of electrochemically polypyrrole at the surface and at the pore of cellulose membrane causes size and shape of the pores in membrane change. The results showed that the increasing of concentration of ammonium persulfate enhanced permeate flux of the modified membrane. This may be because the RC membrane used in this study can swell in a solution of ammonium persulfate. This could change membrane characteristics, especially pore size of the membrane. As can be seen in Fig. 5.26, MIP membranes had a little lower permeate flux of TCAA than NIP membranes. This indicates that the template molecule is specifically adsorbed on MIP membrane, presumably at imprint site.

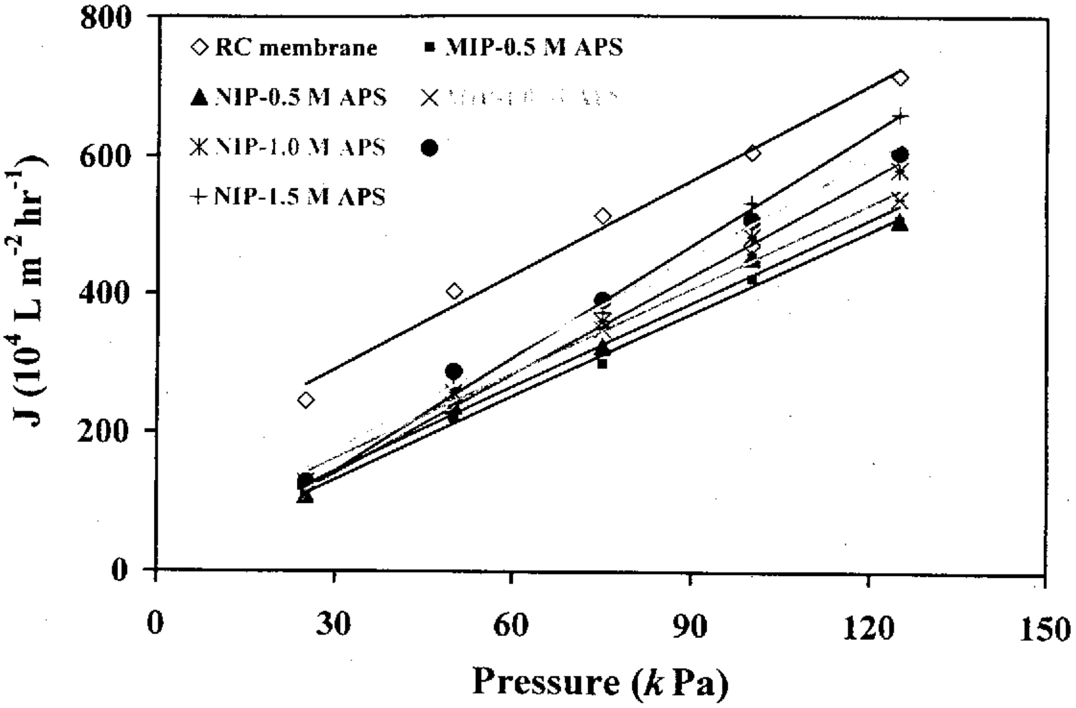


Fig. 5.26. Influence of ammonium persulfate concentration on permeate flux of modified membrane in the pressure range of 25-125 kPa when the membrane used was prepared at pH 0.7

5.5.9. The influence of filtration pH on selectivity of the modified membrane

The calibration curve was obtained from the plot between known TCAA concentration versus ratio of peak area of TCAA and internal standard which was analyzed by GC-ECD as shown in Fig. 5.27. There was linearity in the TCAA concentration range of 0.8-13 mg l^{-1}, with a correlation coefficient (R^2) of 0.988. The effect of filtration pH on recognition ability of the modified membrane was studied when the membrane was prepared with different pH and concentration of ammonium persulfate. The data was depicted in Table 5.7 and the results present as histograms was shown in Fig. 5.28. Selectivity which is defined as ratio of amount about of TCAA or analogs of MIP membrane to that of NIP membrane was considered.

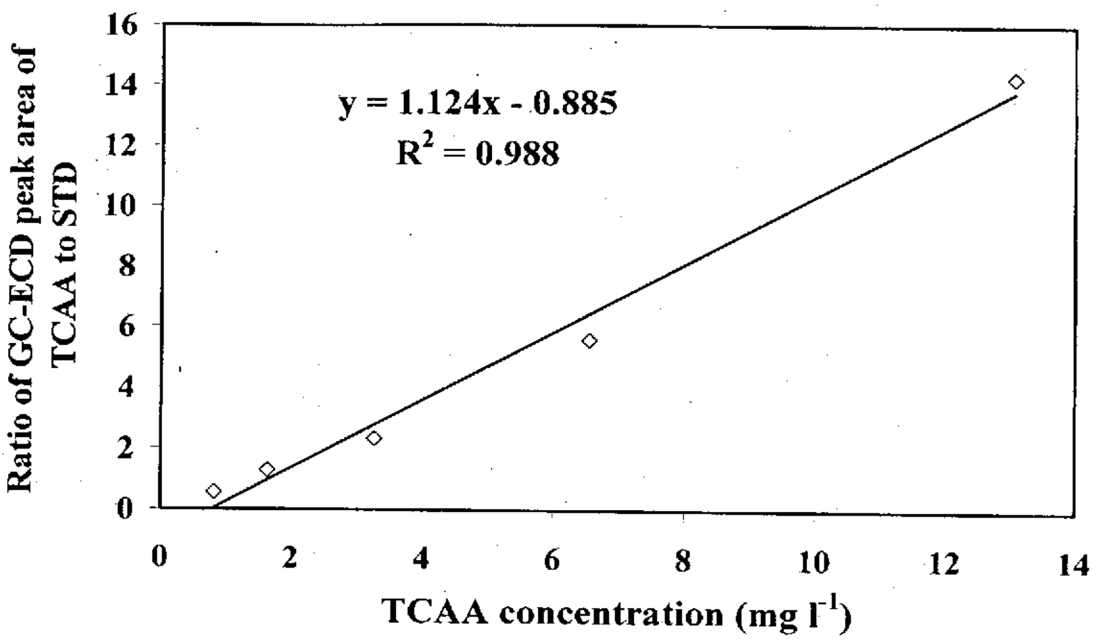


Fig. 5.27. Calibration curve of TCAA-imprinted polypyrrole modified RC membrane responded with various concentrations of TCAA

Table 5.7

The influence of filtration pH on selectivity of the modified membranes prepared at different pH and concentration of ammonium persulfate

Synthesis conditions	Selectivity (bound amount by MIP/NIP)			
	pH 0.7	pH 1	pH 4	pH7
0.5 M APS pH 0.69	0.47	0.79	1.09	8.64
1.0 M APS pH 0.69	0.65	1.08	5.08	1.97
1.5 M APS pH 0.69	0.61	1.03	1.69	1.33
0.5 M APS pH 1.6	0.68	1.34	6.35	5.70
1.0 M APS pH 1.6	0.87	3.26	6.39	8.44
1.5 M APS pH 1.6	0.73	2.32	5.74	3.02
0.5 M APS pH 4	0.44	0.98	2.65	3.36
1.0 M APS pH 4	0.61	1.25	9.71	1.53
1.5 M APS pH 4	0.54	1.67	5.72	1.36

The results showed that the optimum synthesis condition (1.0 M APS, pH 4) gives the greatest selectivity to the modified membrane, which no selectivity dependency of pH and concentration of ammonium persulfate used in preparation process, was revealed. Thus the selectivity shown for the modified membranes depended on the pH of the filtration. The high selectivity of the modified membrane was obtained at pH 4 and 7 of filtration. This may be due to that at these pHs TCAA (pKa 0.69) can be ionized. The negatively ionized form of TCAA can interact with positively charged surface of the polymer within imprint cavity. Therefore, TCAA is greatly retained by MIP membranes. The selectivity of the modified membranes preparing with various conditions that had a value below dashed red line was considered to be a non-selective condition because their selectivity was not higher than 1. This suggests that the MIP membranes have higher retained amount of TCAA than NIP membranes. Several synthesis and filtration conditions allow the MIP membrane with a good selectivity for filtration. In order to verify the optimum condition, the application of the modified membrane in terms of selectivity, mechanical stability and filtration performance of the membrane stored for several months was determined.

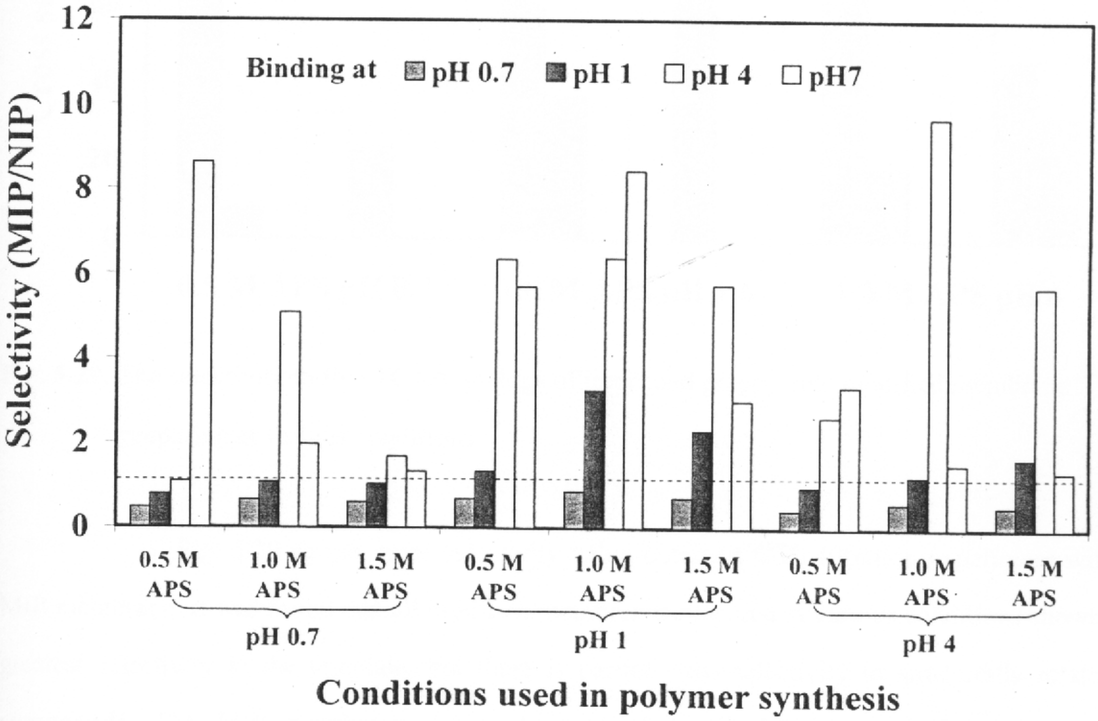


Fig. 5.28. Selectivity of TCAA imprinted polypyrrole modified RC membrane at various synthesis and binding conditions

5.5.10. The cross-selectivity of the modified membrane toward TCAA analogs

The selectivity range of TCAA-imprinted polypyrrole modified cellulose membrane to the haloacetic acid group was examined using five structurally related analogs (DCAA, MCAA, TBAA, DBAA and MBAA) as substrate. The collected filtrates from the dead-end filtration system were analysed for TCAA by GC-ECD analysis method. The cross-selectivity as calculated from ratio of amount bound of TCAA absorbed by MIP membrane to that of NIP membrane was recorded.

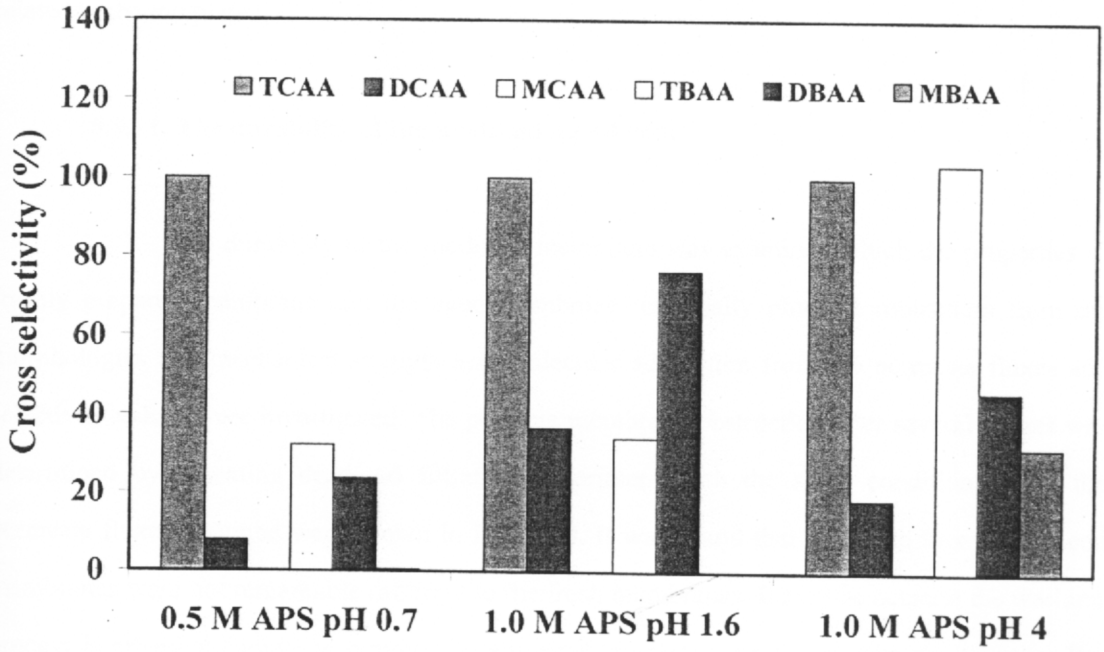


Fig. 5.29. The selectivity to five TCAA analogs of imprinted polypyrrole modified membrane preparing at various conditions

Fig. 5.29 shows cross-selectivity value obtained from filtration experiment with MIP membrane. It was found that all modified membranes prepared at various conditions showed greatest selectivity to the template, but there is partial cross-selectivity to structurally related compounds. The MIP membrane prepared at pH 0.7 and 0.5 M ammonium persulfate demonstrated highest specificity for template. At low pH and initiator concentration, the structure of imprinted polymer was in oxidized state and persisted in this state for a longer period of time, which the recognition sites were produced complementary mostly with template. On the other hand, high pH and concentration of ammonium persulfate affected to structure of imprint cavities generated during modification process. This leads to the change of imprint cavities in respect of size, shape or charged species that is specific not only to template but also with analogs. It was also observed that the selectivity to MCAA by the MIP membrane was not exhibited at all conditions. It was probably due to that MCAA molecule has only one chlorine atom can not fit properly into TCAA-imprint cavities. In comparison, the selectivity of MIP membrane to tri-substituted haloacetic acid was higher than di- and mono-substituted haloacetic acid, respectively. This indicates the specificity of MIP modified membrane to the compound that was closely related to the template.

5.5.11. The durability of the modified membrane

The durability of the modified membrane was examined which the properties of freshly prepared membrane and the aged membrane, especially physical robustness from the morphologies and mechanical strength and molecular adsorption from the permeate fluxes and selectivity values were investigated. The possible membrane obstruction after several usages was determined by repeating dead-end filtration experiment with the same condition which the permeate fluxes obtained were shown in Fig. 5.30. It was found that permeate flux of the aged membranes were not remarkable different to the fresh membranes. It may be because the washing process is effective enough to remove the adsorbed template from the membrane. Additionally, the tensile strength of the membranes was not changed (see Fig. 5.31). This result suggests that the storage time did not affect to mechanical strength of membrane. This mechanical stability of the membrane is likely related to the membrane base. Although the membrane structure was partly destroyed during immersion step, which causes a decrease in the robustness of membrane, the modified membranes can retain their strength similarly as the original membrane do.

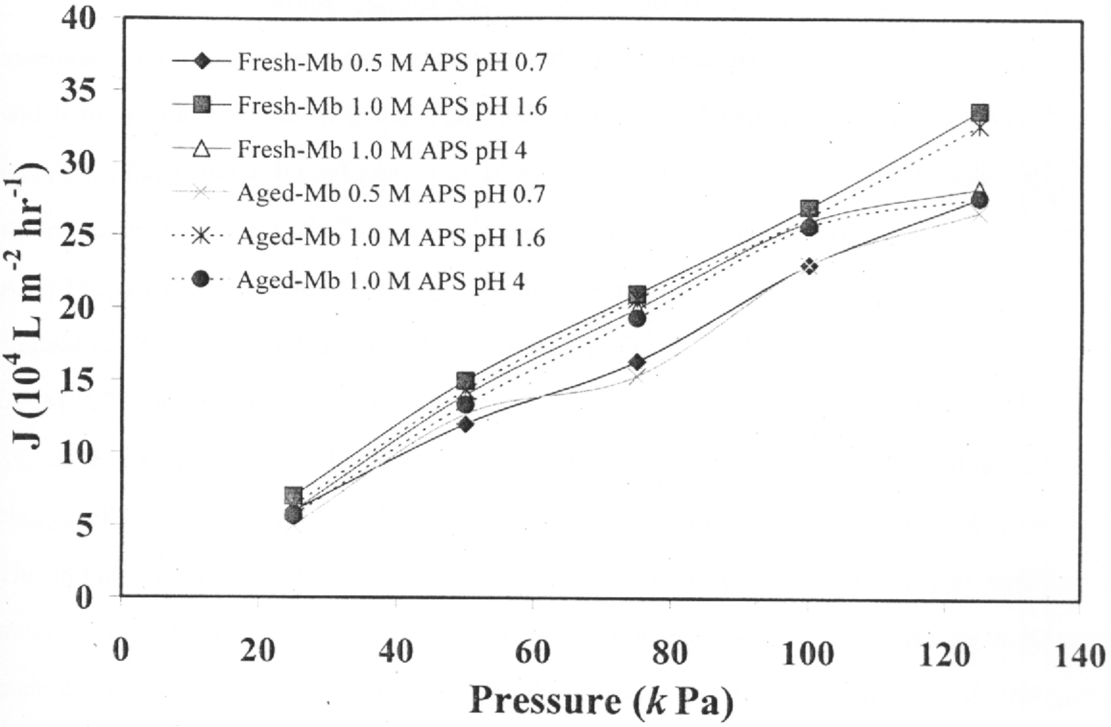


Fig. 5.30. The influence of membrane storage on permeate flux of fresh and aged membrane

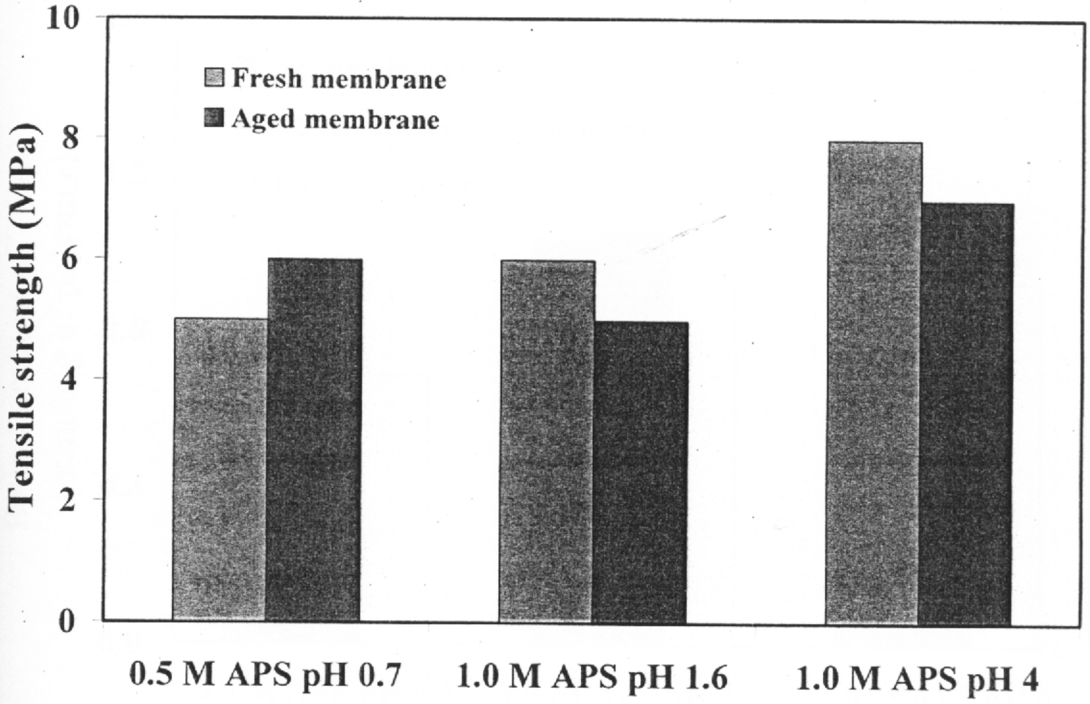


Fig. 5.31. The effect of increased storage time on the tensile strength of fresh and aged membrane

To determine the repeatability of the preparation method for a MIP modified membrane, the membranes were reproduced and applied into the dead-end filtration experiment which the result was shown in the Fig. 5.32. It was found that both lots of freshly prepared membrane have similar bound amount of TCAA closely with relative standard deviation (R.S.D.) values less than 0.03 (n = 3). This indicated the consistency in modification process of membrane. After keeping the membrane for several months, the membranes showed a little change in bound amount of TCAA as showed in Fig. 5.32. As seen in Fig. 5.33, the aged membranes produced at 0.5 M APS and pH 0.7 and at 1.0 M and pH 1.6 showed positive change of bound amount of TCAA than that of the membrane prepared at 1.0 M APS and pH 4 which showed the negative change of bound amount (-8.9%). This may be accounted by the effect of preparing condition. The initiator concentration and pH used during preparation process can affect to stability of modified membrane. With the use of higher initiator concentration the higher degree of polymer main chain oxidation may be obtained, which the structure and polarity of the binding sites in the membrane upon storage may be altered, hence lower binding of template molecule.

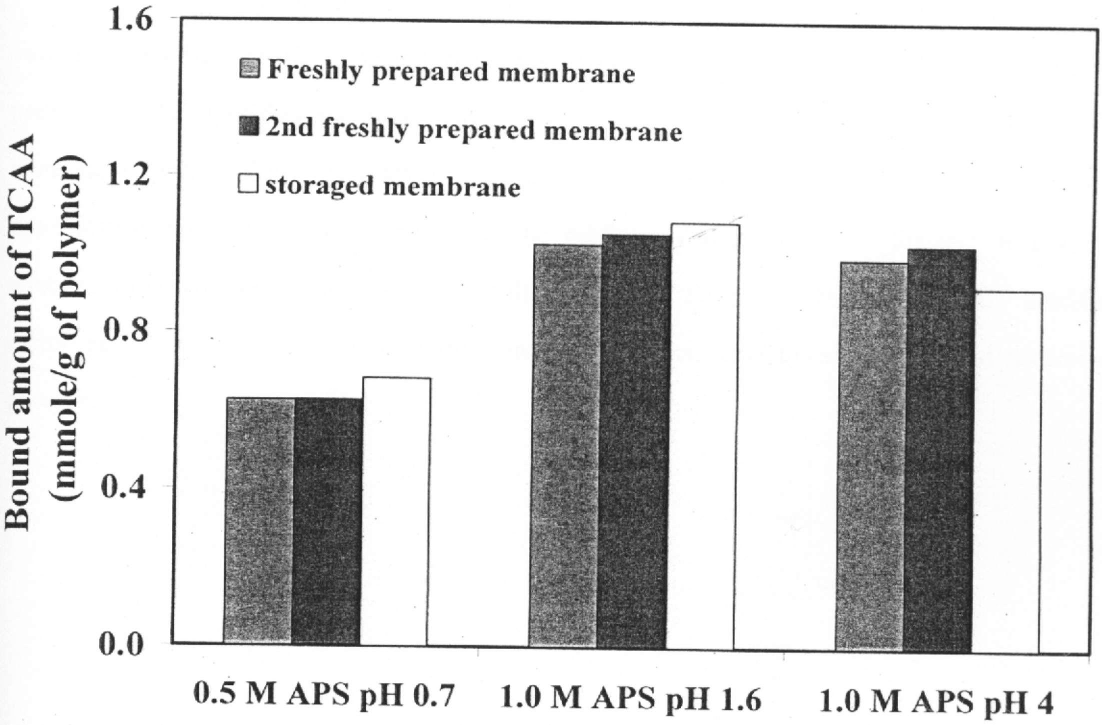


Fig. 5.32. The effect of membrane storage on amount bound of TCAA

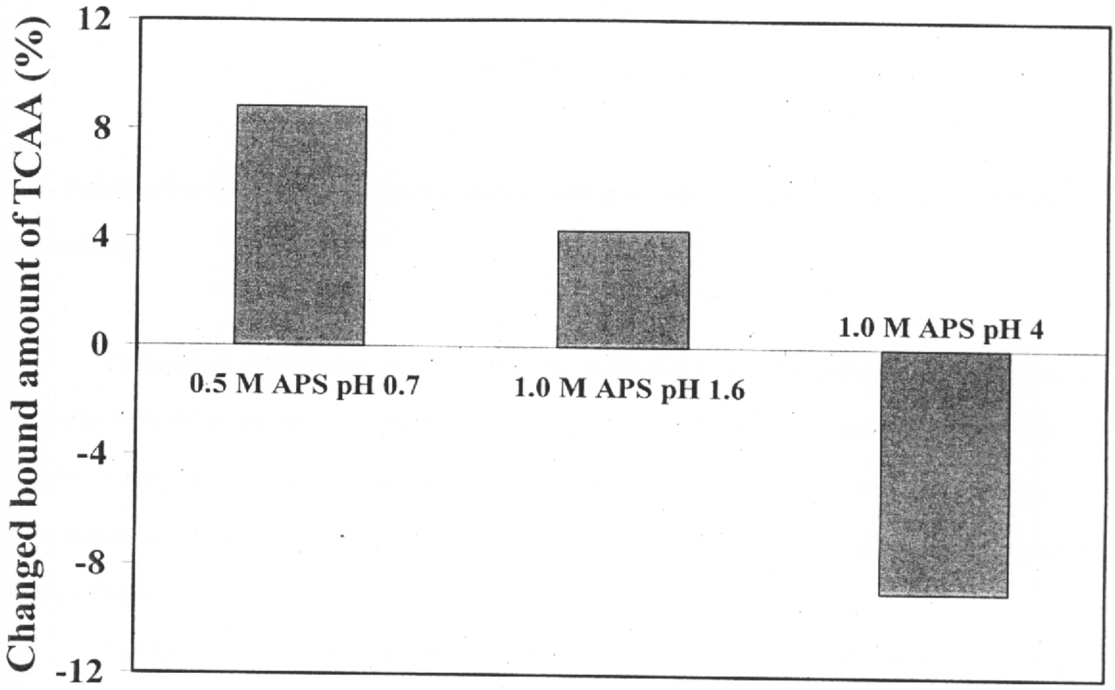


Fig. 5.33. The effect of preparing condition on change of bound amount of TCAA on membrane

After making consideration to the repeatability of modified membrane through various properties of the selected preparing conditions, the most promising condition for preparing MIP modified membrane was revealed. In order to modify regenerated cellulose membrane with TCAA imprinted conducting polypyrrole as recognition material, the modification process of membrane should be performed at pH 0.7 with the use of a 0.5 M ammonium persulfate as initiator. The results suggested the good persistency of MIP modified membrane in terms of membrane performance, robustness, mechanical stability and reusability process.