

CHAPTER 6

DISCUSSION

6.1. Trichloroacetic acid imprinted polymer and piezoelectric quartz crystal microbalance transducer

Parameters concerning both the sensing technology and the polymer composition, such as mole ratio of monomer and template or cross-linker and functional monomer, polymer layer height, type of solution background, concentration of template, template analogs, and supplementary with current density in case of polypyrrole, were found to affect the recognition of the imprinted polymer.

The QCM sensor modified with imprinted poly(EDMA-*co*-VPD) and polypyrrole give a plateau of signal response at about 20 KHz layer height while the QCM sensor modified with the latter material showed the remarkable higher saturation frequency shift. The signal responses of these two imprinted polymers at optimum mole ratio of functional monomer and template were different. For the poly(EDMA-*co*-VPD), the highest difference of frequency shift of imprinted and control polymer was obtained at 4:1 functional monomer and template mole ratio. In contrast, the imprinted polypyrrole manifested the greatest frequency shift at 1:1 monomer and template mole ratio.

According to the effect of polymer layer height, the imprinted polypyrrole can uptake the higher monomer amount to the layer than those of imprinted poly(EDMA-*co*-VPD). The highest binding site population (B_{\max}) of imprinted polypyrrole was observed to be higher than the other. The former sensor revealed the higher saturation frequency shift response than that of latter sensor at the similar template concentration. This was presumably due to the stronger ionic interaction of imprinted polypyrrole led to the higher signal translation efficiency of the sensing system.

The QCM sensors integrated with TCAA-imprinted poly(EDMA-*co*-VPD) and polypyrrole showed high specificity to the template and analogs. In comparison, the QCM sensor integrated with poly((EDMA-*co*-VPD) give reasonable group specific to HAAs rather than the

QCM sensor integrated with polypyrrole, which this make the former sensor useful for the screening of the group of HAA usually present in chlorinated water in complex mixtures.

When integrate TCAA-imprinted poly(EDMA-*co*-VPD) or TCAA-imprinted polypyrrole as a recognition material in the QCM sensor, higher layer stability and durability is obtained for rigid poly(EDMA-*co*-VPD). However, the more easily fabrication is achieved for polypyrrole due to the electrochemical polymerization technique during the preparation.

6.2. Trichloroacetic acid imprinted polymer and inter-digitated conductometric transducer

Two different inter-digitated conductometric (IDC) sensors integrated with TCAA-imprinted poly(EDMA-*co*-VPD) and polypyrrole as a sensing element demonstrated similar optimal composition of functional monomer and template. The imprinted poly(EDMA-*co*-VPD) coated IDC sensor showed the highest resistance shift response when using 1:1 functional monomer and template mole ratio. But the polymer composing with this composition gave a low robustness of the film onto electrode. On the contrary, the polymer with 2:1 functional monomer and template mole ratio showed high specific sensitivity with a good physical stability of the film. In case of TCAA-imprinted polypyrrole, the greatest resistance shift response of the sensor was also found at 1:1 functional monomer mole ratio. The produced polymer layer showed an enough rigid structure on the transducer surface, this mole ratio was therefore chosen as initial composition in the preparation of the polymer layer in further experiments.

Normally, the ambient temperature is one important parameter determining the entropy of polymer. The polymer chain conformation altered as a result of entropy changed. This directly implies that temperature can affect the conformation of polymer chain and subsequently, the porosity of polymer layer (Schwartz *et al.*, 2005). The resistance shift response of two imprinted polymers differed as surrounding temperature changed. The TCAA-imprinted poly(EDMA-*co*-VPD) manifested greater resistance shift TCAA response with an increase in temperature. This could be explained by the charge-transfer complex of TCAA with the MIP film. The Arrhenius plot could be applied to the results obtained. Similarly to TCAA-imprinted poly(EDMA-*co*-VPD), TCAA-imprinted polypyrrole demonstrated the reduction in resistance shift of the TCAA response with increased temperature. This suggested that the electrochemically conducting

polypyrrole has pi-conjugated. This finding agreed with that of the previous report (Kim *et al.*, 1995).

TCAA-imprinted poly(EDMA-*co*-VPD) coated sensor revealed the resistance shift response comparable with control sensor showed high specific sensitivity to the template and stable and reasonable signal response in solution containing inorganic anions. Whereas the signal response of sensor coated with both the imprinted and non-imprinted polypyrrole can not be observed when an experiment was carried out in solution containing inorganic salts (such as NaCl). In addition, the resistance shift response of both sensors was found remarkably reduced with increased electrolyte concentration. This was presumably due to such sensor being sensitive to Na⁺ and the use of this sensor was limited. The further experiments were therefore recommended to carry out in solution containing low amount of Na⁺ to avoid such intervening effects.

The assay with the sensor contains TCAA-imprinted poly(EDMA-*co*-VPD) as recognition element showed wide dynamic working range (0-500 $\mu\text{g l}^{-1}$) for TCAA and 5 analogs. In contrast, the assay using IDC sensor integrated with TCAA-imprinted polypyrrole coated sensor manifested specificity to TCAA, with much narrower dynamic working range (0-130 $\mu\text{g l}^{-1}$). The results demonstrated the difference in sensitivity and specificity of the TCAA-imprinted poly(EDMA-*co*-VPD) and TCAA imprinted polypyrrole integrated into the IDC sensor.

The IDC sensors fabricated with TCAA-imprinted poly(EDMA-*co*-VPD) and polypyrrole were used to detect haloacetic acid determination in real-life samples. The analytical application for determination of TCAA and mixed HAAs in domestic and commercial drinking water was readily achieved with the IDC sensor containing TCAA-imprinted poly(EDMA-*co*-VPD) as recognition element. The results revealed high sensitivity and selectivity of the method. In addition, the study demonstrated feasibility of using TCAA-imprinted polypyrrole sensing element incorporated with the IDC analysis system in quantifying TCAA in both domestic and commercial bottled drinking water.

6.3. Trichloroacetic acid imprinted polypyrrole and voltammetric transducer

The molecularly imprinted polypyrrole coated onto voltammetric transducer can be easily and conveniently prepared by the electrochemical polymerization method. The immobilization process of this polymer on electrode required only a few minutes. TCAA was utilized as counter ion and a template molecule. After removing the template by washing, the memory cavity was left in the polymer which showed complementary shape and size with TCAA. This imprinted polymer was able to recognize the template molecule through ionic interaction between negatively ionized form of a template molecule and the positively charged chain of polypyrrole. The positive charges in polypyrrole were determined by the oxidation level. The overall charge of polypyrrole gradually became negative as the over-oxidized state of polymer chain increased. It was therefore necessary to control the polymer synthesis process to avoid the over-oxidized state of polymer.

The current peak height obtained from the voltammetric measurement indicated the electron percolation from the recognition events to the electrode surface. The imprinted polypyrrole film with good recognition prepared at pH 4 while tested the sensor at pH 7. At the other pH in synthesis and testing non-specific binding was presumed responsible for the current peak height for both imprinted and non-imprinted polymer.

Current density required in synthesis process was also examined. The current peak height remarkably declined with increasing current density. The over-oxidation of polypyrrole could be responsible for such low recognition ability of the film. The recognition ability of imprinted polypyrrole was completely diminished when 1.0 mA cm^{-2} of current density was applied.

It was observed that the polymer film completely coated on the electrode surface after 1.5 hrs. The longer the deposition time, the significantly improved signal response of the constructed sensor was obtained. This suggested saturation of the binding site in the imprinted polymer.

The mole ratio between functional monomer and template was another important factor reflecting the recognition property of the imprinted polymer. The signal response of the sensor reached optimum at the 1:1 for functional monomer to template mole ratio.

This voltammetric sensor using TCAA-imprinted polypyrrole as recognition element also showed specific current change to TCAA and its analogs. The assay with this sensor showed

800 $\mu\text{g ml}^{-1}$), similar to that

The sensor gave high cre

broad dynamic working range ($0.1-800 \mu\text{g ml}^{-1}$), similar to that with the QCM sensor integrated with TCAA-imprinted polypyrrole. The sensor gave high cross-selectivity to the structurally related compounds as well. The analogs can bind to the TCAA binding site with different degrees of freedom correspondingly with the number and type of halogen atom substituted in the structure. However, the detection limit of this sensor was not low enough to detect the HAAs concentration in the actual drinking water. The recovery data was therefore obtained from the extrapolation analysis with commercial drinking water spiked with various concentrations of template and mixed HAAs. Interestingly, the recovery percentage obtained from this voltammetric sensor was lower than that obtained from the other sensors (QCM and IDC) using the same polymer material.

6.4. Trichloroacetic acid imprinted polypyrrole modified microfiltration regenerated cellulose (RC) membrane

The TCAA-imprinted polypyrrole particulate had been successfully prepared by the electrochemical polymerization method using ammonium persulfate as redox initiator. It was found that the oxidation state of polymer was governed by the initiator concentration and synthesis pH. The higher ammonium persulfate and pH in synthesis caused the lower template absorptivity of polymer. This suggested that the polypyrrole structure was altered to the over-oxidized state as ammonium persulfate and pH during synthesis increased. The negative charge of the over-oxidized polypyrrole might prevent the rebinding of template to the polymer. The imprinted polypyrrole showed the highest imprinting factor (bound amount of MIP/NIP) at synthesis pH 4 and 0.1 M ammonium persulfate. This condition may provide polypyrrole with strong imprint structure and with optimum positive charge on the polymer backbone.

Distilled water was shown to have high potency in template removal over ethanol and acetonitrile. The modification of a regenerated cellulose membrane with molecular imprinting process was revealed by the change of the membrane color from white to black. It was due to the conjugated double bond of polymer formed, which this can absorb light in visible-wavelength region. The properties of regenerated cellulose membrane (thickness, mean pore size and

porosity) were changed after such modification. Such change was expected to reflect by swelling of membrane with the initiator in solution.

The increased concentration of ammonium persulfate in the modification process brought to the amount of polypyrrole and swelling of the membrane base increased. This suggests that the electrochemical deposition of polypyrrole can be enhanced by increasing concentration of ammonium persulfate. It was found that the initiator has softened the membrane. It was also observed to swell in aqueous solvent greater than the original membrane.

The result from the diffusion measurements with dead-end filtration showed that flux of the imprinted and non-imprinted membranes was lower than that of the original one. At higher pH (in synthesis), the imprinted membranes displayed lower flux than the non-imprinted membranes. This was assumed that the template in solution may promote the deposition of polypyrrole on the cellulose membrane. However, the flux of modified membranes increased with increasing concentrations of ammonium persulfate. It is suggested that the membranes swelled in the presence of the initiator, which this allows higher flux of the permeate.

The imprinted membrane showed good recognition property at higher pH of measurement. This was explained that the template can be negatively ionized in great extent at this pH and greatly interacted to the positive charge of quaternary amine anchor in the imprint cavity.

The selectivity of the imprinted membrane to the template and other five structurally related analogs (DCAA, MCAA, TBAA, DBAA and MBAA) was examined. The imprinted membrane prepared at different condition manifested different specificity characteristics. Using a lower synthesis pH and lower concentration of ammonium persulfate, the membrane showed template specific rather than group specific. This suggested that pH and initiator concentration affect the structure of imprinted cavity in non-crosslink polypyrrole, hence change specificity of TCAA-imprinted polypyrrole on membrane.

Finally, the membrane properties *i.e.*, permeate flux, mechanical strength and molecular adsorption were compared between the freshly prepared membrane and the aged membrane (stored for 3 months). The results indicated the applicability and durability of the imprinted membrane even the membrane that was stored for several months.