

CHAPTER IV
HUMIC ACID COATED ON POLYBENZOXAZINE XEROGEL
FOR COPPER ROMOVAL

4.1 Abstract

A polybenzoxazine xerogel was synthesized from bisphenol-A, formaldehyde, and aromatic diamine. FTIR, DSC, TGA, measurements were used to characterize the properties of the polybenzoxazine xerogel. SEM micrograph showed the interconnected structure of the organic xerogel derived from 25 wt% of polybenzoxazine. Humic acid 0.1 w% was coated on polybenzoxazine xerogel at room temperature via the layer-by-layer polyelectrolyte multilayer (PEM) surface modification method using poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) as primer coating for 4 layers. The PEM layers were investigated using UV-VIS measurements. The results showed that the absorbance of the prepared samples increased when the number of PEM layers increased. Finally, copper(II)acetate at pH7, was added to the coated xerogel to study the ability of humic acid to remove copper. The UV-VIS results indicated that copper was adsorbed on the humic surface. When the injection time of copper was increased, the absorbance of copper after the adsorption was decreased.

Keywords: Humic, Copper, Polybenzoxazine, Heavy metal removal.

4.2 Introduction

Copper has been known as one of the most common toxic metals, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes (Hayrunnisa *et al.*, 2010). The excessive intake of copper by men leads to severe headaches, hair loss, hypoglycemia, increased heart rate, nausea, damage of kidney, and liver. It may also cause psychological problems, such as brain dysfunction, depression, and schizophrenia. The world health organization (WHO) recommended a maximum acceptable concentration of Cu (II) in drinking water of 1.5 mg l^{-1} . It is essential that potable waters be given some treatment to remove copper before domestic supply (Aman *et al.*, 2008). Nowadays, numerous methods have been proposed for efficient heavy metals removal from water, including but not limited to chemical precipitation, ion exchange, adsorption, membrane filtration, reverse osmosis and electrochemical technologies (Hua *et al.*, 2012). Humic acid, which is involved in many chemical and physicochemical interactions in aqueous systems, acts as an ion exchange resin (Saied *et al.*, 2005). Humic acid can chelate heavy metal effectively and has potential to be used in wastewater treatment for heavy metal removal by binding of metal-humic acid interactions.

Polybenzoxazine is a new type of phenolic resin that has been used as precursors for organic xerogels. Polybenzoxazine has great properties such as good mechanical properties, low shrinkage, low water absorption, high thermal stability, high molecular design flexibility and flame retardance. Benzoxazine monomers can be synthesized from phenols, amines, and formaldehyde. In this study, a coating of humic on polybenzoxazine xerogel was prepared via the layer-by-layer surface modification method. Effects of number of layers on a thin film were investigated. First of all, a polybenzoxazine xerogel was synthesized from bisphenol-A, formaldehyde, and aromatic diamine reactants. FTIR, DSC, TGA, and SEM measurements were used to

characterize the properties of polybenzoxazine xerogel. Later, a thin film was prepared at room temperature with the humic concentration of 0.1 %w. UV-VIS measurement was used to study the absorbance of humic substance at each humic layer after coating. Afterwards, the ability of synthesized material for removing copper was examined.

4.3 Experimental

4.3.1 Materials

All chemicals were used without further purification. Bisphenol-A was purchased from Aldrich, Germany. 4,4'-Methylenedianiline (MDA) , was purchased from Aldrich, Thailand. Formaldehyde solution (37% by weight) was purchased from Merck, Germany. *N,N*-Dimethylformamide (DMF) was purchased from Labscan Asia Co., Ltd., Thailand and Silver Nitrate (AgNO₃) was purchased from Fisher Scientific, UK.

4.3.2 Measurement

4.3.2.1 *Fourier Transform Infrared Spectroscopy (FT-IR)*

A Fourier Transform Infrared Spectroscopy (FT-IR), Nicolet Nexus 670, was used to identify structural characteristics of polybenzoxazine, polybenzoxazine coated PDADMAC, PSS, humic acid and heavy metal in adsorption mode. They were mixed with potassium bromide (KBr) to prepare powder samples.

4.3.2.2 *Ultraviolet-visible spectroscopy (UV-VIS)*

The absorbance of polybenzoxazine coated PDADMAC, PSS, humic acid was investigated by using Ultraviolet-visible spectroscopy.

4.3.2.3 *Scanning Electron Microscopy (SEM-EDX)*

The morphology of polybenzoxazine xerogel was investigated by using scanning electron microscope, Hitachi S-4800, with an accelerating voltage of 2 kV. Samples were coated with Platinum under vacuum before observation. Samples

were coated with platinum under vacuum before observation. In addition, the amount of metal ion on the surface can be determined by EDX mode.

4.3.2.4 Surface Area Analyzer (SAA)

The surface area, average pore size, total pore volume and micropore volume of polybenzoxazine xerogel was investigated by using Surface area Analyzer; Quantachrome, with outgas time 12 hours.

4.3.2.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC), METTLER, was used to study the thermal behavior of partially-cured and fully-cured polybenzoxazine. The samples were heated from 30 °C to 200 °C at a heating rate of 10 °C/min under N₂ atmosphere with a flow rate of 20 ml/min.

4.3.2.6 Thermogravimetric/Differential Thermal Analyzer (TG-DTA)

The thermal property of polybenzoxazine xerogel was investigated by using Thermo gravimetric Analyzer; Perkin Elmer, with heating rate 20°C/min. Platinum pan was used as a reference pan and heated from 30° to 300°C.

4.3.3 Methodology

4.3.3.1 Preparation of Benzoxazine Precursor

Bisphenol-A and MDA were dissolved into DMF in glass bottles. Formaldehyde was then added into the bisphenol-A solution and stirred continuously for one hour until homogeneous yellow viscous liquid was obtained. The temperature is kept under 10°C using an ice bath. After that MDA solution was added into the mixture. The ratio of bisphenol-A, formaldehyde and MDA is 1:4:1. The benzoxazine precursor was identified structural characteristic by using FTIR measurement.

4.3.3.2 Preparation of Polybenzoxazine Xerogel

The benzoxazine precursor was transferred into vials and sealed then heated in the oil bath at 80 °C for 48 h in a closed system, followed by evaporating the solvent at ambient condition for one day.

4.3.3.3 Preparation of Polymer Solutions (PDADMAC, PSS) and Humic Acid

The solutions were prepared by dissolving 1 mM PDADMAC, 1 mM PSS and 0.1 % Humic acid in distilled water, followed by adding 1.0 M NaCl to PDADMAC and PSS, 0.3 M NaCl to PDADMAC and Humic acid and adjust pH to 9-10 by adding of 0.1 M NaOH solution.

4.3.3.4 Preparation of Glass Slide Coated with Polymer Solutions (PDADMAC, PSS) and Humic Acid (Layer-by-Layer Method)

A glass slide was rinsed by distilled water before use and then achieved with a primary coating formed by 4 layers of PDADMAC with 1.0 M NaCl and PSS followed by a secondary coating of PDAD-Humic with 0.3 M NaCl respectively for 2, 4, 6, and 8 layers. Rinsed a glass slide by distilled water for each layer and then a glass slide was dried for 4 days at room temperature in the box. The coating of polymer solutions was confirmed by using reflectance UV-VIS Spectroscopy.

4.3.3.5 Surface Modification of Polybenzoxazine Xerogel Coated with Polymer Solutions (PDADMAC, PSS) and Humic Acid (Layer-by-Layer Method)

After the polybenzoxazine xerogel was evaporated over night, it was cut with the thickness of 3 mm. A polybenzoxazine precursor was passed through by distilled water before use. It was coated with a primary coating formed by 4 layers of PDADMAC with 1.0 M NaCl and PSS, followed by a secondary coating of PDADMAC-Humic with 0.3 M NaCl for 2, 4, 6, and 8 layers, respectively. After

finishing coating each layer, the precursor was rinsed with distilled water. The coating of polymer solutions was confirmed by using UV-VIS Spectroscopy.

4.3.3.6 Preparation of Layer-by-Layered Polybenzoxazine Xerogel for Copper Removal

The obtained polybenzoxazine xerogel was then fully cured by curing step in an oven. The synthetic reaction is shown in Figure 3.1

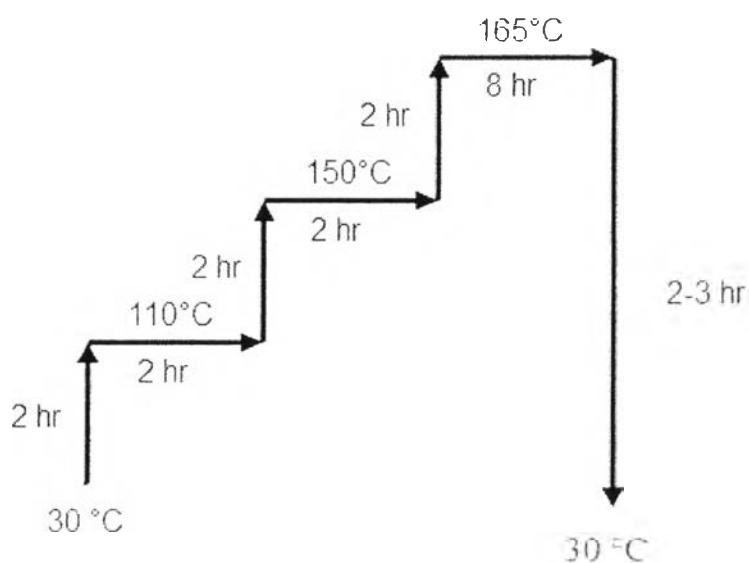


Figure 4.1 Schematic of a step of curing.

4.3.3.7 Copper Removal

To study the interaction between copper and humic acid, the injection time was valid from 1 to 120 min. Copper (II) acetate solution with 250, 500, 1000 ppm concentration was slowly injected through the surface of polybenzoxazine xerogel coated with layer-by-layer method.

4.4 Results and Discussion

4.4.1 *The Chemical Structure of Polybenzoxazine Precursors*

The chemical structure of benzoxazine precursor was examined by FTIR spectra as shown in Figure 4.2. For the benzoxazine precursor; the asymmetric stretching of C–O–C (1222 cm^{-1}), the asymmetric stretching of C–N–C (1120 cm^{-1}), CH_2 wagging of oxazine (1333 cm^{-1}) were observed. Additionally, the characteristic adsorptions assigned to tri-substituted benzene ring at 1611 cm^{-1} and out of plane bending vibrations of C–H at 934 cm^{-1} were observed, indicating that precursor containing benzoxazine structure in the backbone was obtained.

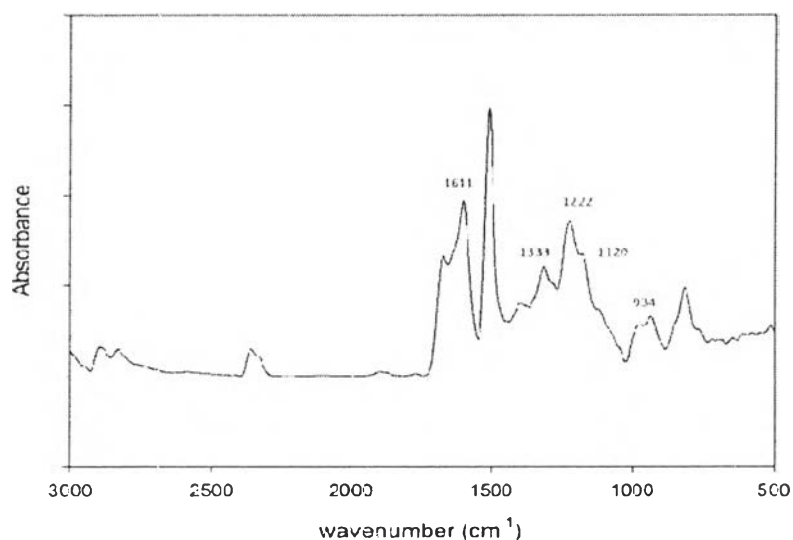


Figure 4.2 FTIR spectra of fully-cured polybenzoxazine.

In additions, the FTIR spectra of the layer-by-layer polybenzoxazine xerogel coated with PDAD, PSS and Humic Acid are shown in Figure 4.3. It confirmed that each layer can coat on PBZ xerogel, FTIR spectra of the layer-by-layered polybenzoxazine xerogel was found C–H stretching of PDAD at 2800–3000, SO_3^{2-} of PSS at peak 1180–1250 cm^{-1} , COO^{-1} of humic acid at 1650 cm^{-1} . The FTIR of the layer-by-layered polybenzoxazine xerogel which added copper was found position of the bands changed during complex formation. The shifting of the band from 1616 to 1658 cm^{-1} was

observed. The absorption band at 1400 cm^{-1} shows a stronger intensity because of the deprotonation of COOH to COO^- then bound with copper ion, this result supported the study of Lu et al., 1997.

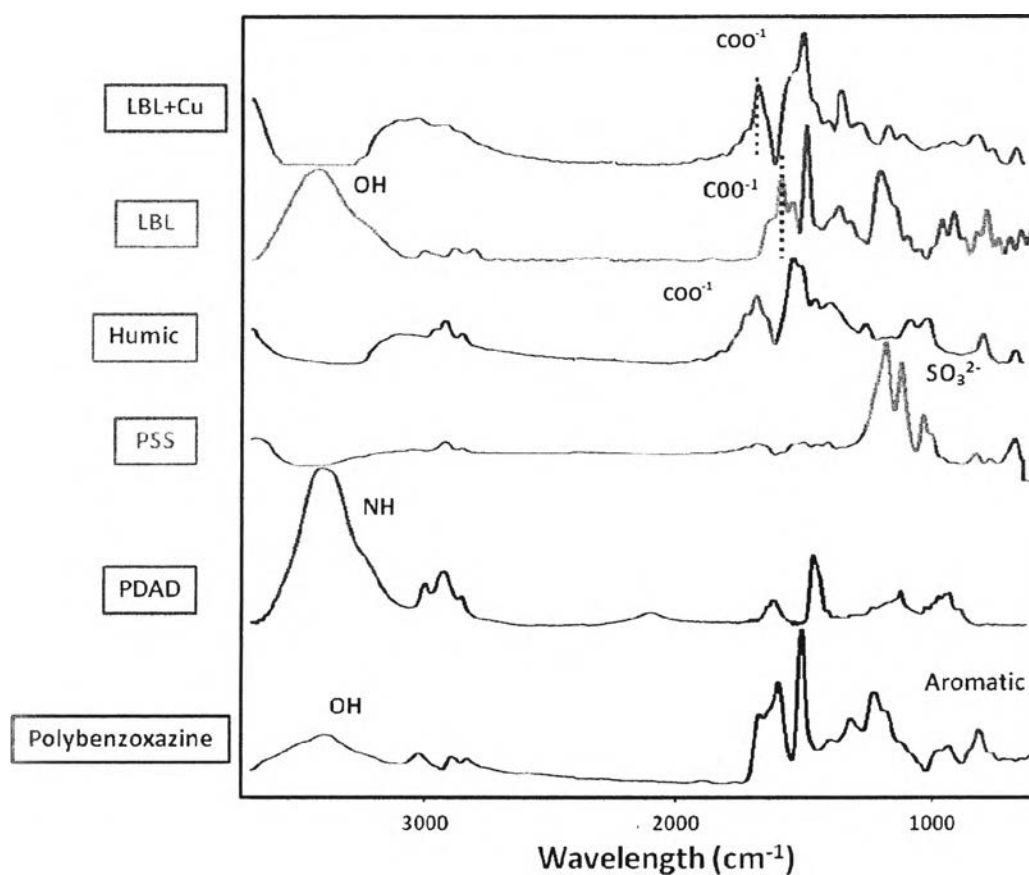


Figure 4.3 FTIR spectra of fully-cured polybenzoxazine, PDAD, PSS, Humic acid, the layer-by-layered polybenzoxazine xerogel, the layer-by-layer polybenzoxazine xerogel which added copper (II) acetate.

4.4.2 Morphology of Polybenzoxazine Xerogels and Carbon Xerogels

Figure 4.4 shows SEM micrographs of the organic xerogel and carbon xerogel which exhibit the 3D interconnected particles into a network with continuous open macropores. This result agrees with the study of Parkpoom *et al*, [23] which studied the porous structure of polybenzoxazine-based organic aerogel.

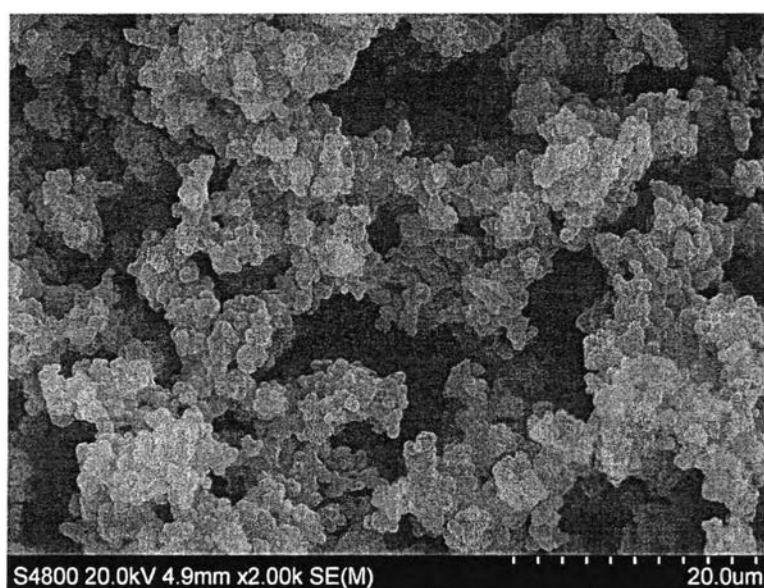


Figure 4.4 SEM micrograph showed the interconnected structure of the organic xerogel derived from 25 wt% of polybenzoxazine.

4.4.3 Thermal Behaviors of Polybenzoxazine Precursors

The DSC thermograms of polybenzoxazine and benzoxazine precursor confirmed that the polymerization of benzoxazine occurred. Figure 4.5(a) shows the exothermic peak from 140-180 °C of benzoxazine precursor while the exothermic peak of polybenzoxazine disappeared as shown in Figure 4.5(b). These obviously show that

the polymerization of benzoxazine precursor by ring-opening of oxazine was taken place.

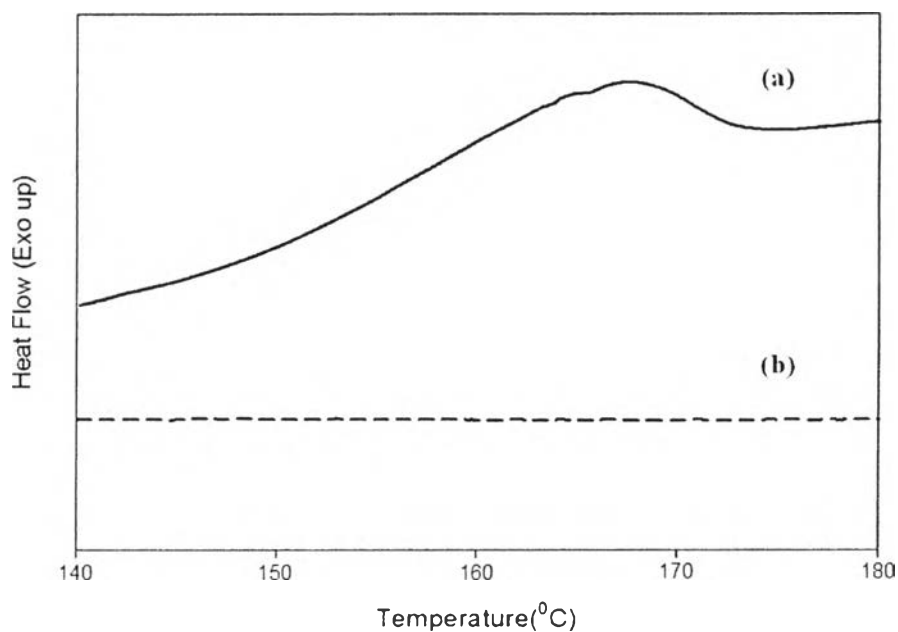


Figure 4.5 DSC thermograms of (a) the polybenzoxazine precursor after drying at 80°C (pre-cured) and (b) after heat treatment at 165 °C (fully-cured).

The TGA thermograms (Figure 4.6a and b) the decomposition temperature begins at 260°C with the maximum mass loss rate in the temperature range of 260-600°C. The thermal decomposition temperature was enhanced for the PBZ xerogel added with copper. In addition, the char yield of the PBZ xerogel added with copper was increased.

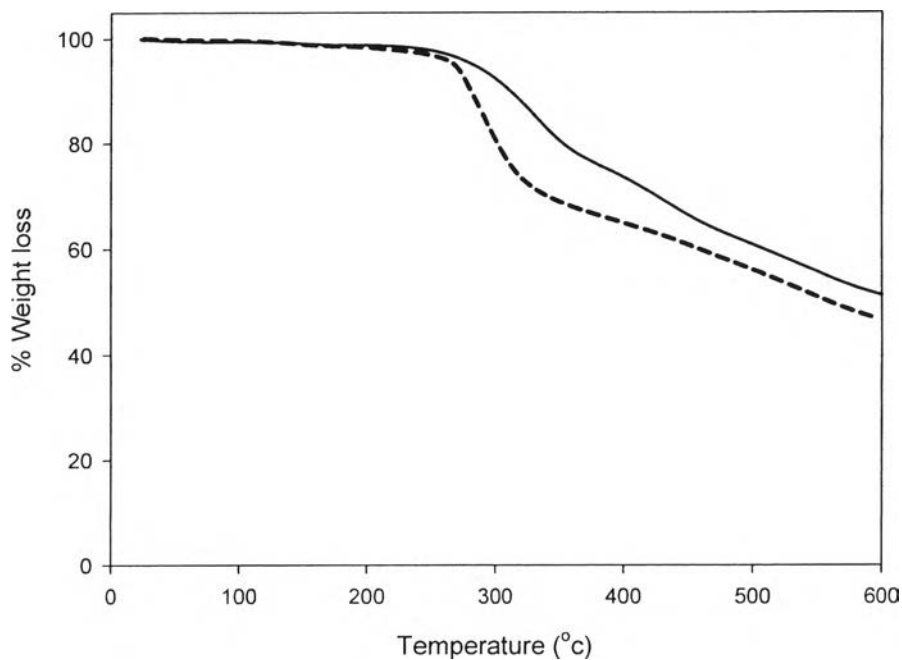


Figure 4.6 TGA thermogram of polybenzoxazine xerogel with coated by PDADMAC, PSS and Humic acid (a) and added copper (II) acetate (b).

4.4.4 *Optical Properties of Polymer Solutions and Humic Acid Layer by-Layered on the Glass Slide and Polybenzoxazine xerogel*

4.4.4.1 *Glass Slide*

UV-VIS was used to measure the absorbance of glass slide coated with Polymer solutions and humic acid in the range between 300 and 1000 nm. The spectrum is shown in Figure 4.7. The highest absorbance is appeared at the wavelength of 770 nm. Coating of the polyelectrolyte multilayer on glass slide was used to confirm the coating ability of PDADMAC, PSS and humic acid.

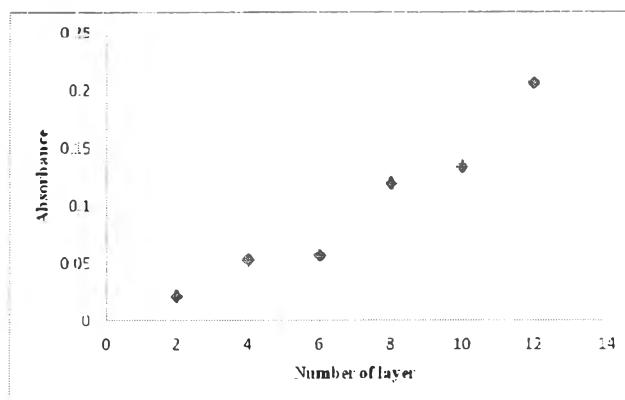


Figure 4.7 Absorbance as a function of the number of layer for glass slide.

4.4.4.2 Polybenzoxazine Xerogel

UV-VIS was used to measure the absorbance of Polymer solutions and humic acid coated polybenzoxazine xerogel in the range between 300 and 1000 nm. The spectrum is shown in Figure 4.8 The highest absorbance is appeared at the wavelength of 770 nm. Coating polyelectrolyte multilayer on polybenzoxazine xerogel which used to confirm the coating of PDADMAC, PSS and humic acid on the polybenzoxazine xerogel.

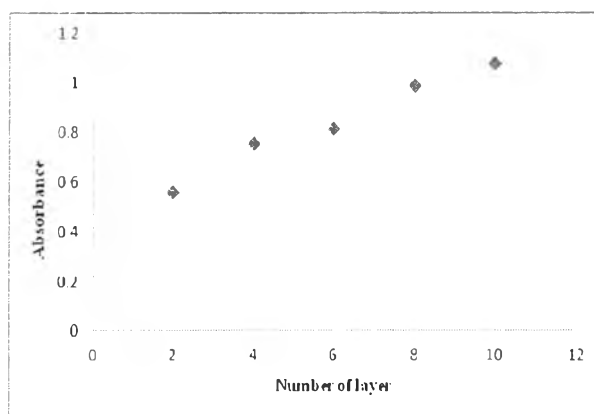


Figure 4.8 Absorbance as a function of the number of layer for polybenzoxazine xerogel.

4.4.5 Copper Removal

Regarding copper (II) acetate adsorption capacity. It shows that a reasonably linear relationship exists between concentration and copper (II) acetate absorbance. From figure 4.9, the highest absorbance was observed at 1000 ppm concentration of copper (II) acetate.

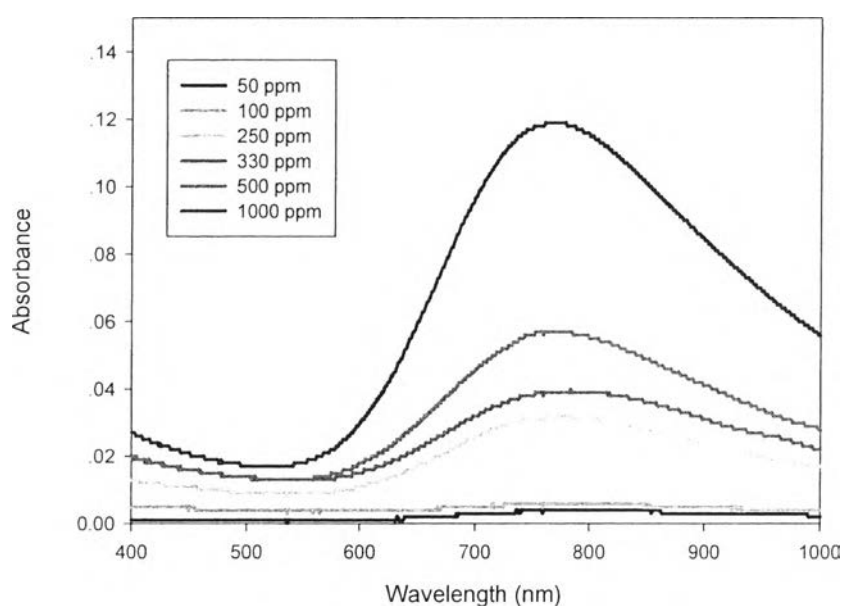


Figure 4.9 Calibration curve of $\text{Cu}(\text{OAc})_2$ solutions from the UV–VIS absorption spectrum with the concentration of 50, 100, 250, 330, 500, 1000 ppm $\text{Cu}(\text{OAc})_2$ at room temperature.

From the UV-Vis adsorption measurement, the polybenzoxazine xerogel was not bind with copper ions because the absorbance of the copper(II)acetate solution was similar to the residual copper solution after passing through the polybenzoxazine xerogel.

In contrast with the absorbance of residue copper after passing through polybenzoxazine xerogel coated with polymer solutions (PDAD, PSS) and humic acid. It

was found to decrease due to copper ions were bound on the humic-coated precursor, as shown in figure 4.10.

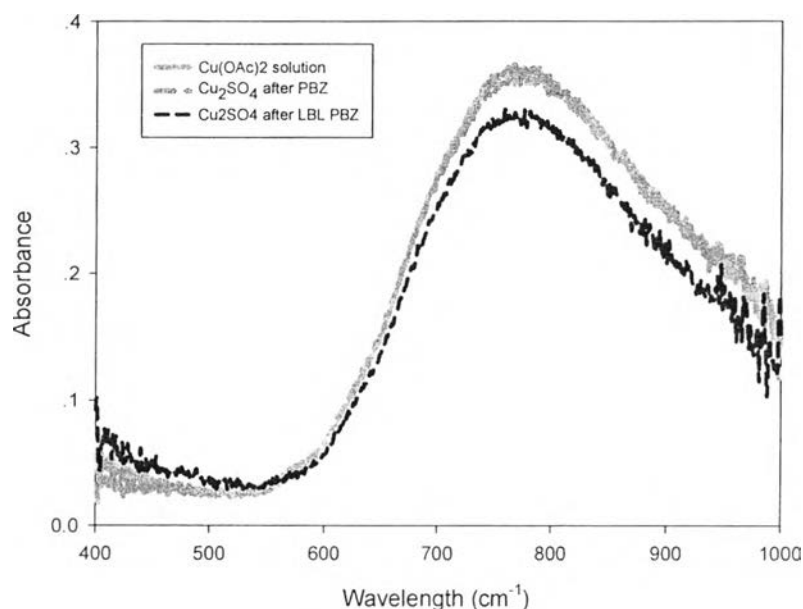


Figure 4.10 The UV-Vis adsorption of copper acetate solution, residual copper(II)acetate after passing through polybenzoxazine xerogel, and residual copper acetate after passing through polybenzoxazine xerogel with layer-by-layer method.

From figures 4.11 and 4.12 the change in the copper concentration from 250 to 1000 ppm affect the adsorption of copper on humic-coated precursor. It was seen that polybenzoxazine coated with primer gives higher copper adsorption compare to polybenzoxazine without primer. When the injection time was increased, the absorbance of residual copper solution was decreased, implying that more copper ions were bound on the humic-coated precursor.

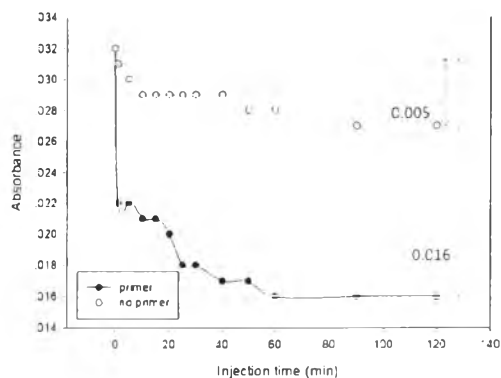
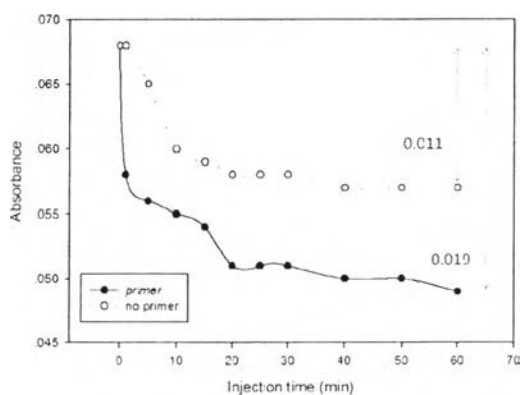
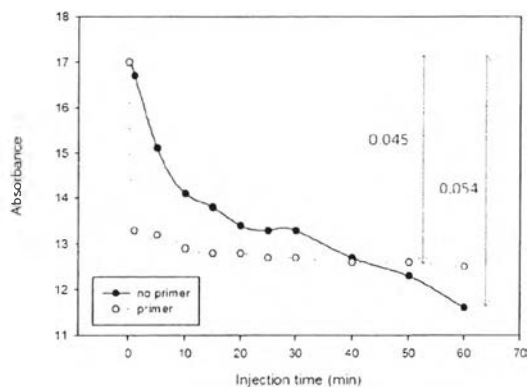
(a) $\text{Cu}(\text{OAc})_2$ 250 ppm(b) $\text{Cu}(\text{OAc})_2$ 500 ppm(c) $\text{Cu}(\text{OAc})_2$ 1000 ppm

Figure 4.10 Absorbance of residue copper solution as a function of the injection time of layer-by-layered polybenzoxazine xerogel with and without primer at (a) $\text{Cu}(\text{OAc})_2$ 250 ppm, (b) 500 ppm, (c) 1000 ppm.

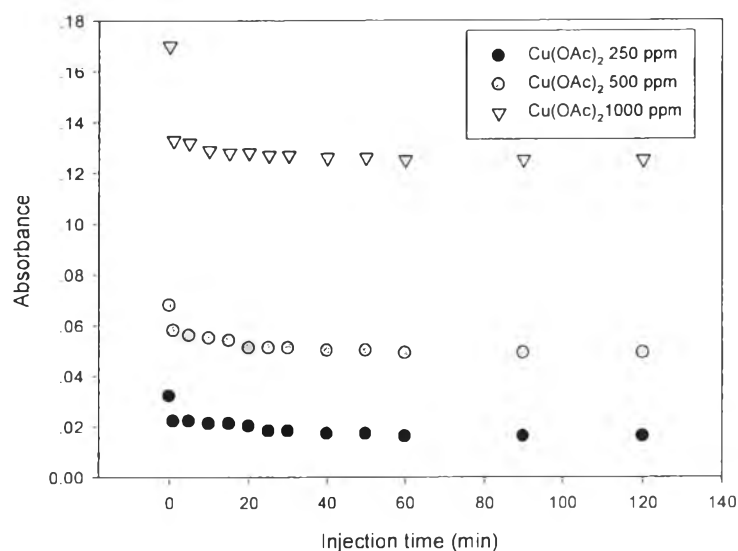


Figure 4.11 Absorbance of residual copper solution with primer coating from 250 to 1000 ppm as a function of the injection time of layer-by-layered polybenzoxazine xerogel.

Conclusion

PBZ xerogel was successfully synthesized from bisphenol-A, formaldehyde and MDA via sol-gel process by using polybenzoxazine as a precursor. Polybenzoxazine xerogel coated with polymer solutions (PDADMAC, PSS) and humic acid (Layer-by-Layer method) was used to evaluate the binding of humic acid and copper. UV-VIS Spectroscopy was used to confirm the coating of PDADMAC, PSS and humic acid on precursor. It can be seen that more copper ions were bound on the humic-coated precursor. The structure of polybenzoxazine precursor, polybenzoxazine xerogel coated with polymer solutions and humic acid were confirmed by FTIR spectroscopy. The thermal behaviors of polybenzoxazine precursor was determined by TGA and DSC.

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