CHAPTER IV

REMOVAL OF TRACE CONTAMINANTS FROM WASTEWATER BY USING POLYBENZOXAZINE-BASED AEROGEL

4.1 Abstract

The removal of trace contaminants from wastewater by polybenzoxazine-based aerogel, a novel type of phenolic resin, was studied in batch experiments. The adsorption behavior of polybenzoxazine towards metals was also investigated by varying amount of adsorbent and type of metals. The results indicated that polybenzoxazine-based aerogel showed more than 80% removal of Cu(II), Fe(II), Pb(II) and Sn(IV) following order: Sn(IV) > Cu(II) > Fe(II) > Pb(II). It was found that the metal adsorption onto polybenzoxazine-based aerogel reached equilibrium in 12 hours. Furthermore, the adsorption behavior in mixed metals system, the adsorption isotherms and the feasibility of using polybenzoxazine-based aerogel as a polymeric ligand exchanger (PLE) were investigated.

Keywords: Heavy metals; Wastewater; Polybenzoxazine-based aerogel; Polymeric ligand exchanger

4.2 Introduction

Increasing in environmental concern causes many industries to have more awareness in their waste. Waste from industrial composes of many components, both organic and inorganic compounds. They can cause harm effects in environment and human health. For this reason, some trace contaminants in waste water have to be removed before being discarded into water resources.

Many methods have been used for the wastewater treatment such as chemical precipitation, physical methods and biological treatment. However, these methods have some limitations. Chemical precipitation generates a large volume of sludge for disposal. The operation and maintenance costs are high for physical methods as in case of electro dialysis and reverse osmosis. Among these methods, the adsorption offers the greatest advantages of contaminants removal and the flexibility design and operation. Moreover, it is an efficient and economic method [1].

The adsorbents that have been used for water treatment include plant wastes, activated carbon, clay, etc. Although plant wastes and clays are known as low-cost materials; they have low adsorption capacity. Polymeric ligand exchangers (PLEs) are another group of adsorbent that have shown great potential for wastewater treatment [2], due to their triple functions of ion exchange, chelate formation and physical adsorption. Generally, the PLEs are composed of supporting polymer with chelating functional groups and a transition metal immobilized on it.

The series of polybenzoxazine, a novel type of phenolic resins, can be prepared from phenols, amine, and formaldehyde. They have become attractive materials because of the flexibility in the molecular design. Furthermore, no strong acid catalyst is required in polymerization process and the reaction does not release any by-product [3].

The purpose of this work is to study the effect of types of metals, weight of adsorbent and contact time. The maximum capacity of metals removed was also studied by using adsorption isotherms. Then, the feasibility of using polybenzoxazine-based aerogel as a PLE was determined.

4.3 Experimental

4.3.1 Materials

Bisphenol-A ($C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde (CH_2O) was purchased from Merck, Germany. Tetraethylenepetamine (TEPA, $C_8H_{23}N_5$) was purchased from Fluka, Switzerland. 1,4- Dioxane ($C_4H_8O_2$) was purchased from Labscan, Ireland. All chemicals were used without further purification to synthesize polybenzoxazine aerogel. The model trace contaminants were chromium(II), cadmium(II), copper(II), iron(II), manganese(II), nickel(II), lead(II), tin(IV), zinc(II) and phosphate. Solutions containing metal salts in the form of nitrate: chromium(II), copper(II), iron(II), manganese(II), nickel(II), lead(II) and zinc(II) were of analytical grade and purchased from Merck, Germany; except cadmium(II) nitrate was purchased from Fluka, Switzerland. Tin(IV) in the form of chloride was purchased from Merck, Germany. Sodium phosphate was purchased from Carlo Erba Reagent, Italy. Concentrated hydrochloric acid and sodium hydroxide (J.T. Baker, USA and Carlo Erba, Italy, respectively) were used to adjust pH. Phosphate was analyzed following the ascorbic acid method described in the standard methods for the examination of water and wastewater. Reagents which were used for determine amount of phosphate are potassium antimonyl tartrate ($K(SbO)C_4H_4O_6 \cdot {}^1/_2H_2O$) purchased from Riedel-de Haen, Germany, amonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot H_2O$) purchased from Lab-Scan, Thailand, ascobic acid ($C_6H_8O_6$) purchased from POCH, Poland. All solutions were prepared by using deionized water.

4.3.2 Measurements

A Fourier Transform Infrared Spectroscope (FT-IR), Nicolet 670, was used to identify structural characteristics of polybenzoxazine-based aerogel. Potassium bromide (KBr) pellet technique was applied in the preparation of powder samples. The thermal behavior of partially-cured and fully-cured polybenzoxazine was studied by differential scanning calorimeter (DSC), Perkin-Elmer DSC 7. The samples were heated from 30 °C to 280 °C at a heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 10 ml/min. Surface morphology of polybanzoxazine-based aerogel was investigated by using a scanning electron microscope, Hitachi S-

4800, surface morphology of polybanzoxazine-based aerogel with an accelerating voltage of 15-40 kV. Samples were coated with platinum under vacuum before observation. Inductive Coupled Plasma Spectrometer, Perkin Elmer Optima 4300V, was used for the quantitative analysis of metal ions in the model wastewater. The calibration method was applied in analysis.

4.3.3 Methodology

4.3.3.1 Preparation of Polybenzoxazine-based Aerogel

The polybenzoxazine-based aerogel was synthesized by dissolving bisphenol-A in dioxane, followed by adding formaldehyde solution and TE-PA. The mixture was stirred continuously while the reaction was cooled with an ice bath until the homogeneous yellow viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde:diamine was 1:4:1. The precursor was left at room temperature until the gel was formed. After that it was placed in an oven at 80°C before solvent being removed by supercritical drying. The obtained polybenzoxazine-based aerogel was then fully cured in an oven.

4.3.3.2 Characterization of Polybenzoxazine-based Aerogel

The structural characteristics of polybenzoxazine-based aerogel were identified by using FTIR. The morphology was observed by SEM. Furthermore, the thermal property was measure using DSC.

4.3.3.3 Adsorption Experiments for Heavy Metals

Batch adsorption experiments were performed to determine the heavy metals adsorption. Different heavy metal solutions with different amounts of polybenzoxazine-based aerogel in a range of 50-80 mg were mixed in glass bottles. The mixtures were stirred continuously for 4-48 hours at room temperature and constant rate of stirring. The pH of the mixtures were maintained in a range from 4-5.The mixture were then filtered through Whatman No.42 filter paper. The filtrates were then quantified by using ICP. The adsorption of metals onto the polybenzoxazine-based aerogel was calculated from the difference between initial and final concentration of heavy metals in solution. The adsorption isotherms for each metal were obtained by varying the initial concentration of the metal solutions while the amount of the adsorbent was kept constant.

4.3.3.4 Adsorption Experiments for Phosphate

Metal-loaded polybenzoxazine was used as a polymeric ligand exchanger for phosphate removal. The adsorption of phosphate on metal-loaded polybenzoxazine was studied by batch experiments. The known weight of metal-loaded polybenzoxazine was equilibrated with known concentration of phosphate solution in a glass bottle. The solution pH was adjusted and maintained at 8-9 during the test. After the equilibrium was attained, the suspension of adsorbent was separated from the solution by flitration using Whatman No.42 filter paper. The remaining concentration of phosphate was analyzed by applying the ascorbic acid method described in the standard methods for the examination of water and wastewater.

4.4 Results and Discussion

4.4.1 Preparation of Polybenzoxazine-based Aerogel

In our previous work, we used triethylenetetramine (TETA) as a precursor to synthesize polybenzoxazine-based aerogel. The aerogel then was used to remove mateals from model wastewate. The results showed that Sn(IV) was removed completely while the other metals was not complete. According to Wade *et al.* [2], chelating resins with nitrogen donor atoms can serve as excellent metal hosting polymers in which the higher numbers of the nitrogen donor, the stronger the binding between the polymers. Thus, in this study, tetraethylenepetamine (TEPA) was chosen as an amine to synthesized polybenzoxazine-based aerogel due to its high nitrogen donor atoms content.

The benzoxazine precursor was synthesized from bisphenol-A, TEPA and formaldehyde via quai-solventless method. The mole ratio of bisphenol-A: formaldehyde: diamine was 1:4:1. 1,4-dioxane was used to facilitate the mixing of reactants to accelerate the synthesis reaction. Then, the mixture was left at room temperature to form a gel before drying by CO_2 supercritical drying in order to maintain the pore structure. The CO_2 supercritical drying was conducted at 45 °C and 7.4 MPa which is above the critical point of CO_2 as shown in figure 4.1[4]. The organic aerogel was then fully cured in an oven yielding polybenzoxazine-based aerogel. The synthesis reaction of polybenzoxazine is shown in figure 4.2.

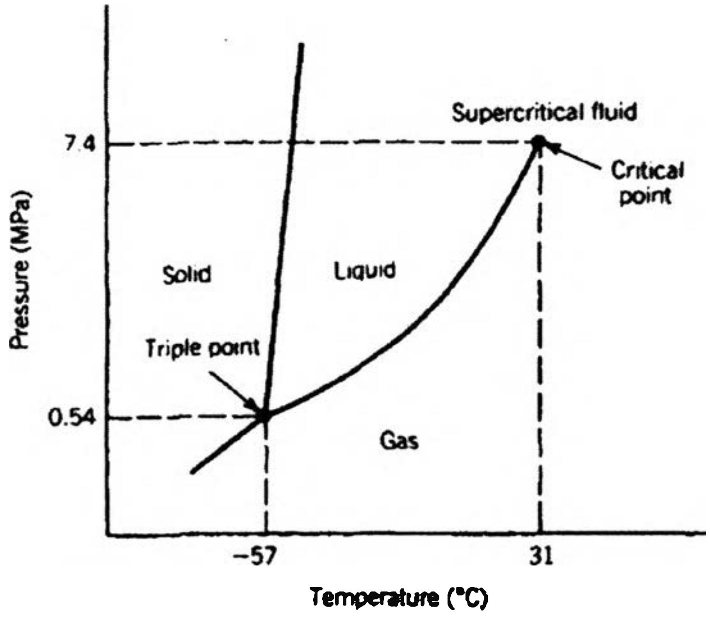

Figure 4.1 Phase diagram of carbon dioxide [4].

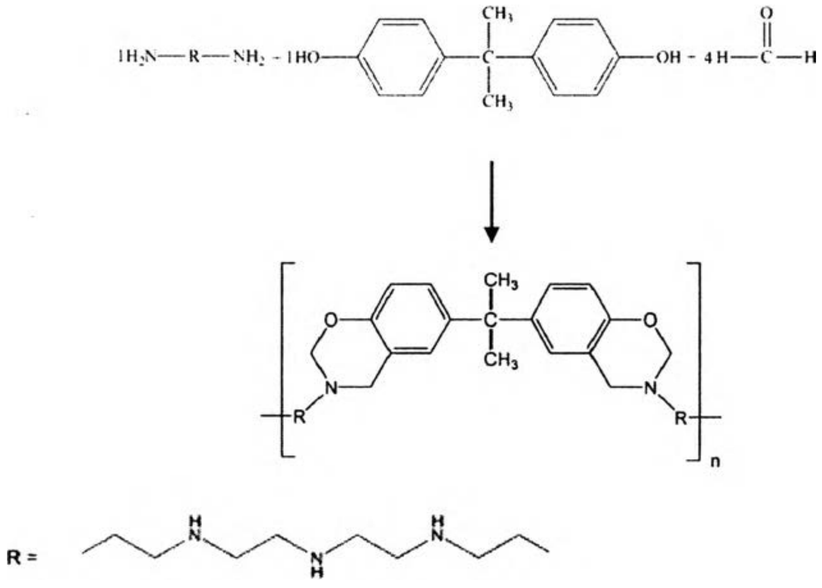

Figure 4.2 Chemical reaction of polybenzoxazine-based aerogel.

4.4.2 Characterizations of Polybenzoxazine-based Aerogel

The benzoxazine precursor and polybenzoxazine were characterized by using FT-IR to examine the functional groups.

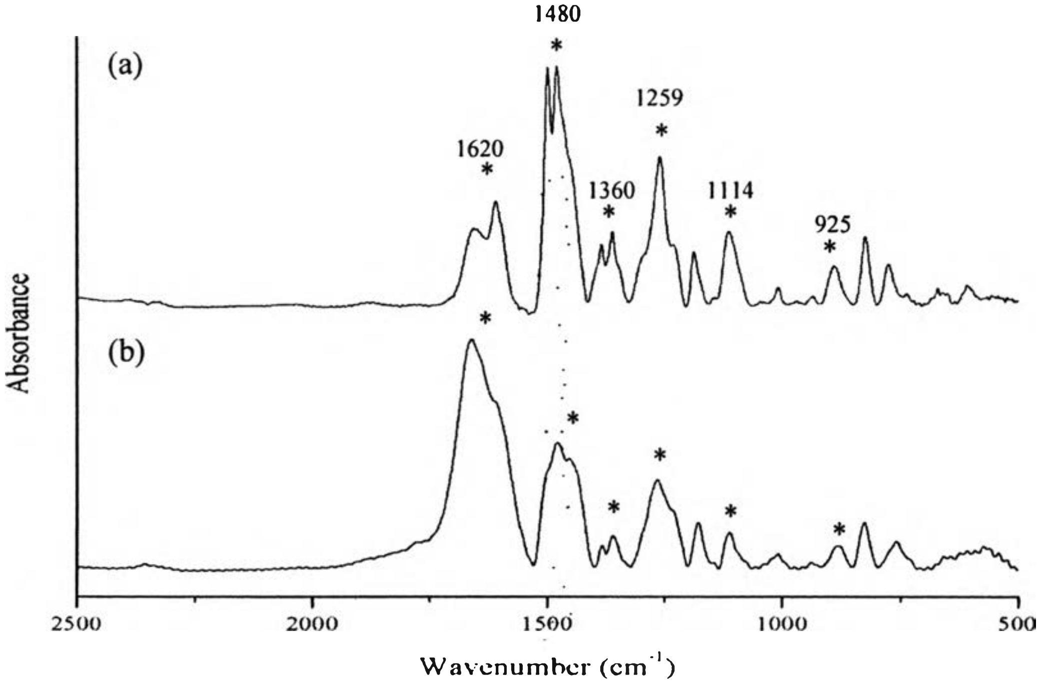

Figure 4.3 FTIR spectrum of benzoxazine precursor (a) and polybanzoxazine (b).

The FTIR spectrum of benzoxazine precursor (figure 4.3 (a)) shows the asymmetric stretching band of C–N–C at 1114 cm^{-1}. The absorption band at 1259 cm^{-1} and 1360-1380 cm^{-1} indicate the asymmetric stretching of C–O–C of oxazine and CH_2 wagging of oxazine, respectively. The peaks at 1480 cm^{-1} assigned to stretching tri-substituted benzene ring and the out-of-plane bending vibrations of C–H were observed at 925 cm^{-1}. According to Dunkers *et al.* [5], these adsorption bands confirmed that benzoxazine precursor and polybenzoxazine were obtained. The polymerization of benzoxazine precursor was studied by FTIR and DSC. The FTIR spectrum in figure 4.3 (b) shows the significant decreasing of characteristic absorption peaks when the benzoxazine precursor was cured. Moreover, the intensity of the adsorption band at 1620 cm^{-1} referring to tetra-substituted benzene ring after polymerization was increased. In addition, the thermal behavior of polybenzoxazine and benzoxazine precursor confirmed that the polymerization of benzoxazine occurred. Figure 4.4 (a) shows the exothermic peak from 200-270 °C of benzoxazine precursor while the exothermic peak of polybenzoxazine disappeared as shown in figure 4.4 (b). These obviously show that the polymerization of benzoxazine precursor by ring-opening of oxazine was taken place [3].

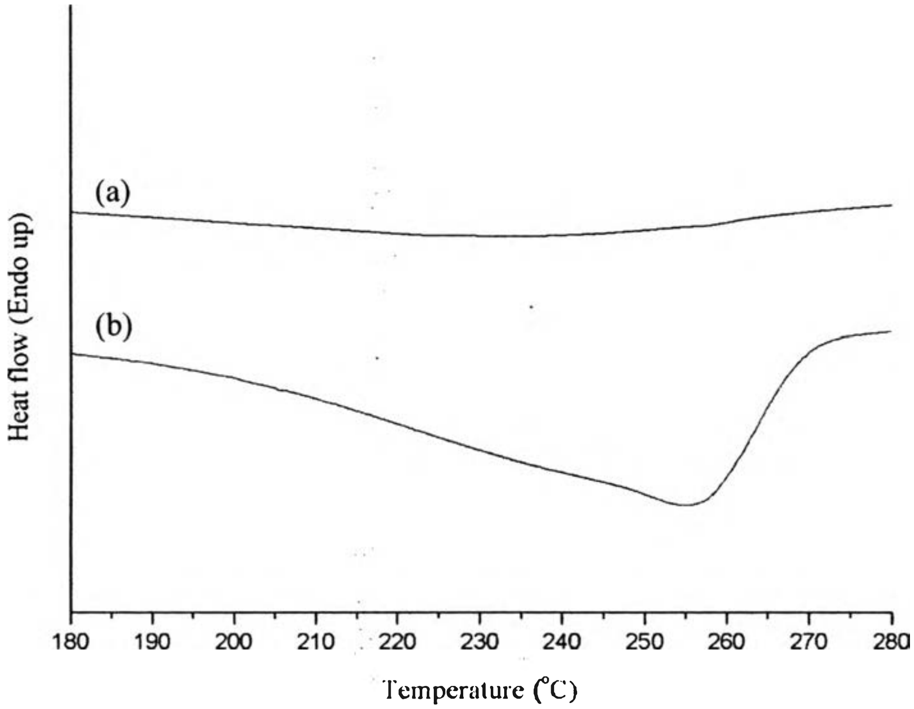

Figure 4.4 DSC thermograms of polybenzoxazine (a) and benzoxazine precursor (b).

In order to study the morphology of polybenzoxazine-based aerogel, SEM was used, as shown in figure 4.5 (a) with a magnification of 20.0k and figure 4.5 (b) with a magnification of 60.0k.

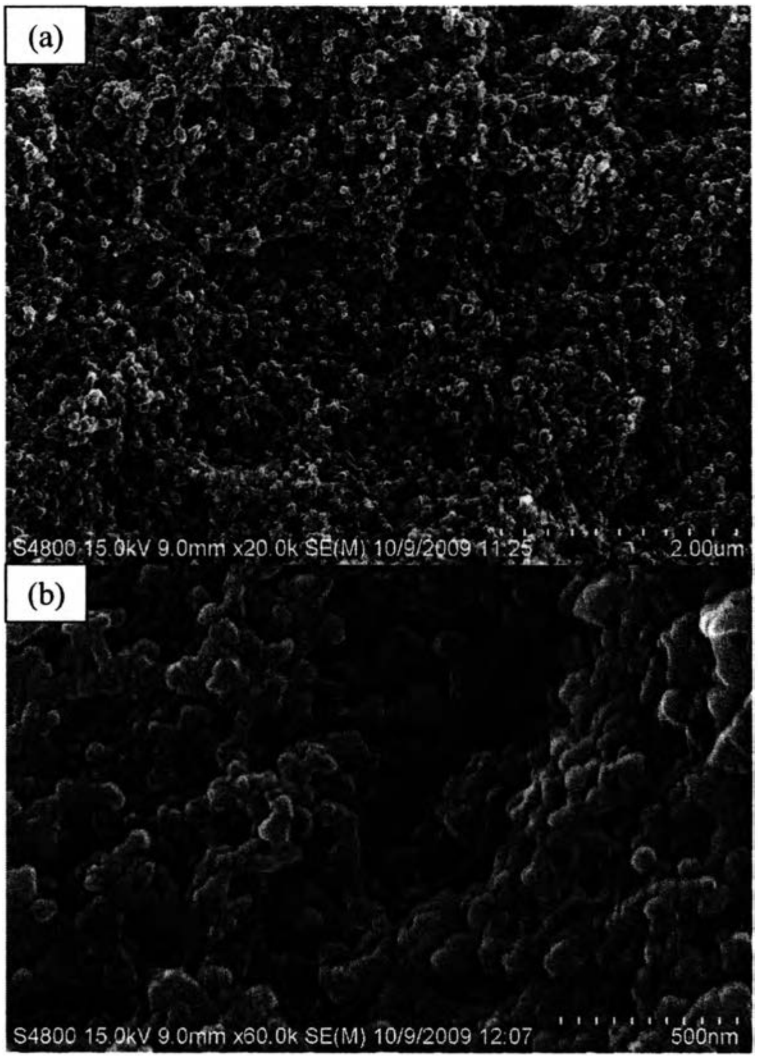

Figure 4.5 SEM micrographs of polybenzoxzazine-based aerogel with a magnification of (a) 20.0 k and (b) 80.0 k.

The microstructure of polybenzoxazine-based aerogel composed of agglomerated polybenzoxazine particles in three-dimension network with continuous open macrospores. This result agrees with the study of Parkpoom *et al.* [6] which studied the porous structure of polybenzoxazine-based organic aerogel.

4.4.3 Adsorption Experiments for Heavy Metals

The adsorption of metal onto polybenzoxazine-based aerogel was conducted by batch experiments. The pH of the solutions was kept in the range of 4-5 to avoid precipitation of metal hydroxide. The adsorption of metal onto the wall of a glass bottle, determined by running the blank experiments, was found to be negligible. The percentage of heavy metal removal was calculated by the following equation:

$$\text{Metal ion removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

Where C_0 is the initial metal ion concentration of test solution (ppm), C_e is the final concentration of test solution (ppm).

4.4.3.1 Metal Affinity

The metal affinity was investigated by using polybenzoxazine-based aerogel as an adsorbent in the metal solution. The experiments were done separately for each metal and the results are shown in figure 4.6. The result indicated that removal of metal ions using polybenzoxazine-based aerogel as an adsorbent was in the following order: Sn(IV), Pb(II) > Fe(II) > Cu(II) > Ni(II) > Cr(II) > Cd(II) > Zn(II).

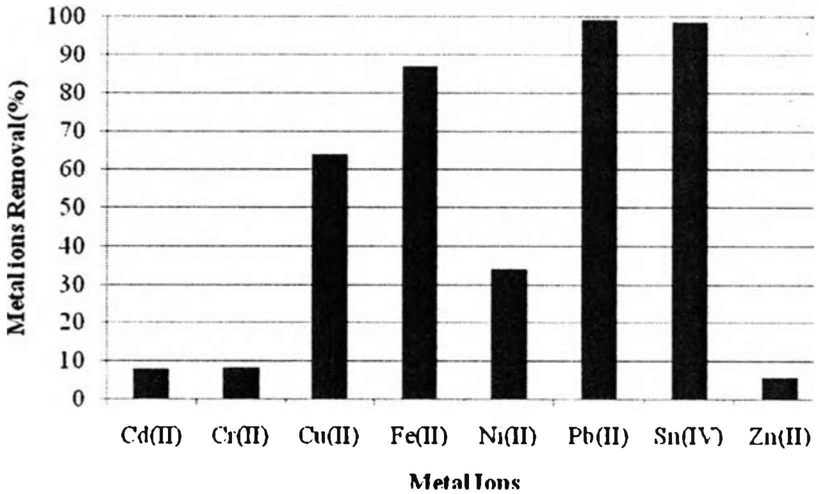

Figure 4.6 The adsorption of metal ions onto polybenzoxazine-based aerogel in single metal system

The adsorption of metal ions to a neutral chelating resin can be explained as a surface complexation process. Therefore, our knowledge on solution coordination chemistry is applicable to this process. To describe the results of metal–ligand complexes in homogeneous systems, the the ionic properties of the metal ions, electronegativity ionic charge and ionic radius, are strongly related. From this result, polybenzoxazine-based aerogel showed high Cu(II), Fe(II), Pb(II) and Sn(IV) removal from wastewater model giving more than 80% of removal. Then, Cu(II), Fe(II), Pb(II) and Sn(IV) were chosen for further study.

4.4.3.2 Effect of Contact Time

The effect of the contact of time was investigated and the result is shown in figure 4.7. Since polybenzoxazine-based aerogel showed great adsorption towards Sn(IV), Fe(II), Cu(II) and Pb(II), these metals were chosen for this experiment. A sharp increase of removal in the 4 hrs was followed by slow increase. The time for reaching the equilibrium is not the same for each metal. The metal adsorption onto polybenzoxazine-based aerogel with initial concentration of metal solution 1 ppm can reach equilibrium in 12 hours which is faster than our previous work [7], except for Cu. Usually, the rate for adsorption by a porous adsorbent is controlled by the rate of transport of the adsorbate within the pores of the adsorbent [8]. The less time means the advantageous when water treatment systems are designed.

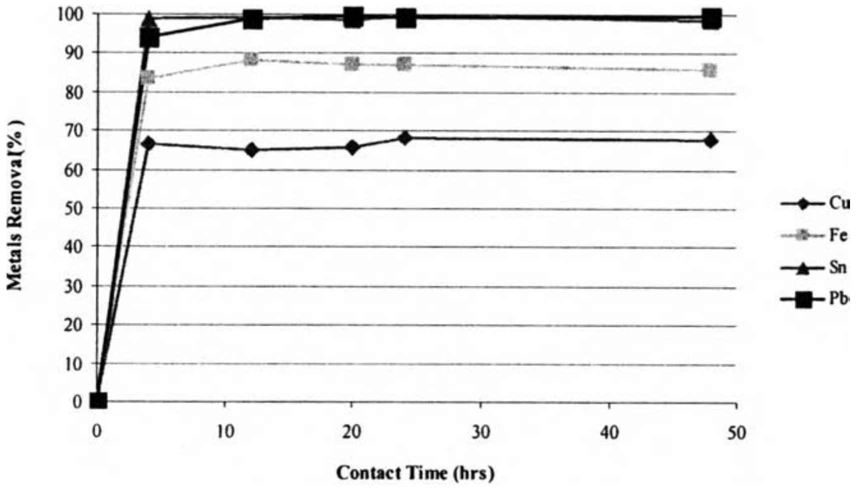

Figure 4.7 The adsorption of metal ions onto polybenzoxazine-based aerogel in single metal system at different contact time.

Furthermore, it was found that the amount of metal removal agreed with the results from the effect of weight of adsorbent. That is, the polybenzoxazine-based aerogel show the complete removal of Sn(II) and Pb(II)

4.4.3.3 Adsorption in Mixed-Metal Solution

The effect of the presence other ions in the system was studied. In the mixed-metal solution, the amount of each metal was decreased as show in figure 4.8. Competition among four heavy metals reduced the amount of adsorbed Sn from 100% to 68% while the other metals were also decreased. This result showed that the adsorption of heavy metals was affected by the competition of other metals. Corami et al.,[9] suggested that in the single-metal adsorption only internal competition which is between the same metals and competition with H^+ for adsorption sites affected heavy metal adsorption, while in the mixed-metal system competition among each heavy metal for precipitation and for adsorption sites has to be considered since four metals compete for the same binding site. The adsorption follows the order: Sn(IV) > Cu(II) > Fe(II) > Pb(II) which is quite different from the result in figure 4.6. In adsorption process, the condition where more highly retained ion can displace the previously adsorbed can occur [10].This condition can be used to explain the change in adsorption order in mixed-metal system.

The adsorption of metal ions to neutral chelating resin can be explained by a coordination complexation process. Metal ions in aqueous solution exist as aqua ions, where water molecules act as ligands, and coordinate to the metal ion via the oxygen donor atoms. The coordination complexes are formed by the interaction of metal ion (M^{m+}) acting as a Lewis acid with a ligand (L) acting as a Lewis base. The formation of a complex in aqueous solution can be represented symbolically by the reaction below.

$$[M(H_2O)_n]^{m+} + LH \rightleftharpoons [M(H_2O)_n{}^{-1}L]^{(m-1)+} + H_3O^+$$

To understanding the formation of coordination complexes, knowledge of acid dissociation constant (pK_a) of hydrated metal ions is important. Table 4.1 shows pK_a of metal ions.

Table 4.1 Some characteristic properties of metals[11].

Metal Ions	Electronegativity	Hydrated radius (pm)	pK_a
Cu(II)	1.90	4.19	7.5
Fe(II)	1.83	4.28	9.5
Pb(II)	2.33	4.01	7.7
Sn(IV)	1.96	N/A	-0.6

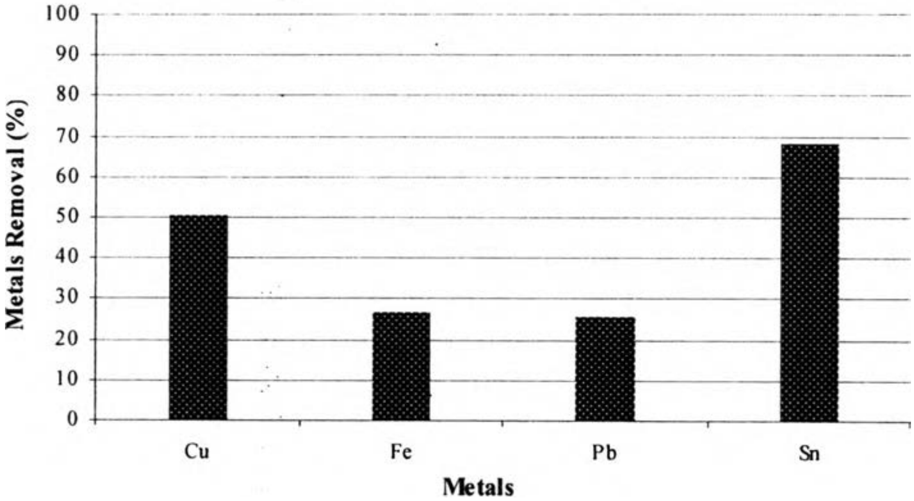

Figure 4.8 The adsorption of metal ions onto polybenzoxazine-based aerogel in mixed metal system.

In this study, Sn(IV) showed the highest amount of removal due to the highest acidity. So, it can form a complex with nitrogen atom which act as Lewis base easily. Comparing the pK_a value of Pb(II) and Fe(II), Pb(II) has higher value than Fe(II). Thus, Pb(II) should form complex easier than Fe(II). However, the result was opposite. The stability of the coordination complex cannot be explained by only electronegativity or pK_a but hydrated size of ions also has been considered. Pb(II) has smaller hydrated size compared to Fe(II). In this case, the hydrated might play more important role the acidity of metal ions. The small size of Pb(II) might be too small to contact all of nitrogen atom of polybenzoxazine.

4.4.3.4 Effect of Nitrogen Donor Atoms

The results from polybenzoxazine-based aerogel synthesized from tetraethylenepetamine (TEPA) were compared with polybenzoxazine-based aerogel synthesized from triethylenetetramine (TETA) from our previous study [7]. Both results were obtained from the same weight of adsorbent, contact time and initial concentration of metals. The compared results are shown in figure 4.9. It was observed that the higher metal removal when polybenzoxazine-based aerogel synthesized from TEPA was used result from different nitrogen content in polybenzoxazine. This result can be correlated with the study of Haratake et al., [12]. They synthesized macroporous chelating polymer which were different in nitrogen content in which the adsorption capacity for Cu increased when the nitrogen content in chelating polymer was increased.

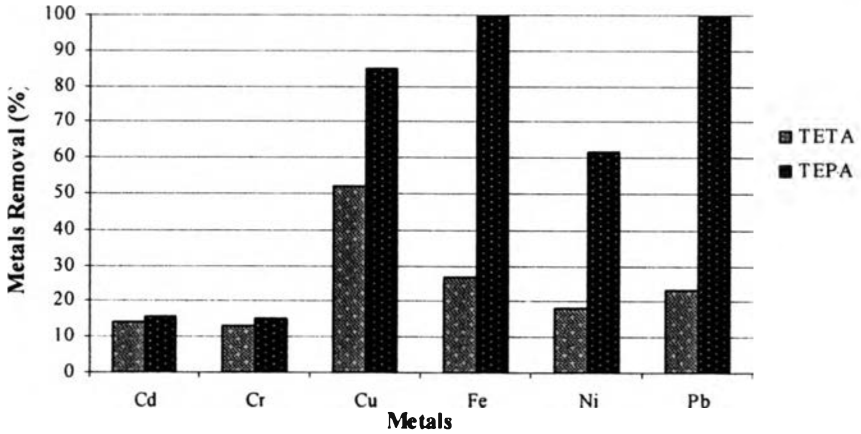

Figure 4.9 The adsorption of metal ions onto polybenzoxazine-based aerogel with different amine.

4.4.3.5 Adsorption Isotherms

The analysis of the isotherms is useful to describe the adsorption capacity to facilitate evaluation of the process for a given application, for selection of the appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements [13]. The adsorption isotherms were constructed by plotting the amount of heavy metal adsorbed on polybenzoxazine-based aerogel (q_e) versus the equilibrium concentration of heavy metals in solution (C_e). The amount of adsorbed metals per unit mass of adsorbent (q_e) was calculated by

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where C_0 : the initial concentration of heavy metals
C_e : the concentration of heavy metals at equilibrium
m : the amount of adsorbent
V : the volume of solution

The adsorption isotherms were determined with respect to each metal ion, i.e. Cu(II), Fe(II), Pb(II) and Sn(IV) in a single metal system. Figure 4.10 shows the isotherms determined for single metal system. In order to classify the type of the adsorption isotherm, the two most commonly used models are the Langmuir and the Freundlich isotherms.

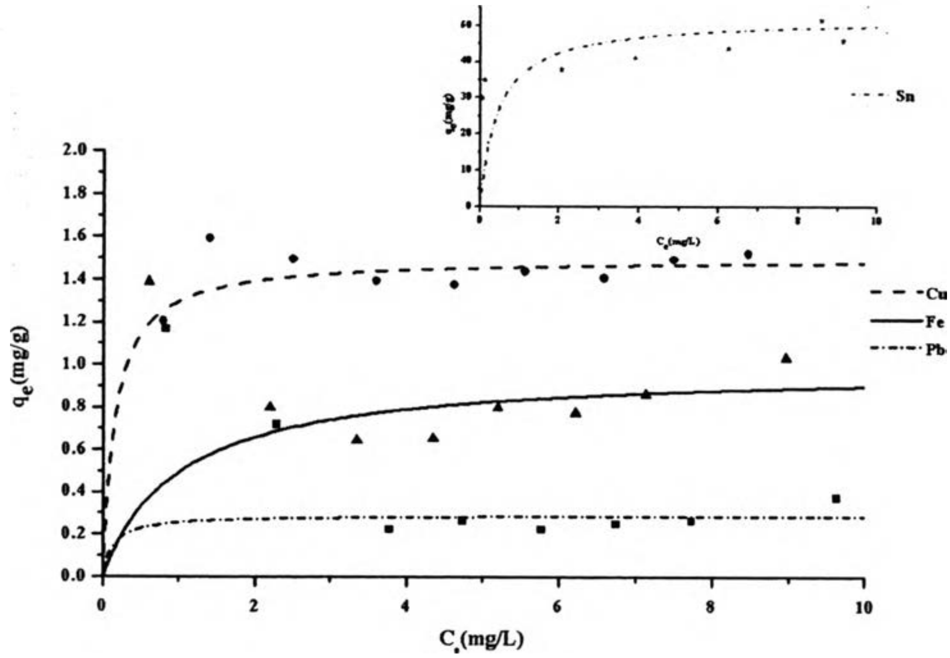

Figure 4.10 Adsorption isotherms of the selected metal ions onto polybenzoxazine-based aerogel.

The Langmuir model is described by the equation as described below:

$$q_e = \frac{Q_{\max} K_L}{1 + K_L C_e} \quad (3)$$

Where Q_{max} : the maximum amount of metal ion to form a complete monolayer on the surface

K_L : the Langmuir constant

Then, the Langmuir parameters, Q_{max} and K_L, can be determined from a linearized form of equation (2) as follows:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{Q_{\max}}\right) + \frac{1}{Q_{\max} K_L} \quad (4)$$

The Langmuir constant can be used to determine the suitability of the adsorbent to the adsorbate by using a dimensionless constant called separation factor (R_L), which is defined as

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

The separation factor (R_L) indicates the possibility of the adsorption process as follows:

$R_L > 1.0$	: unfavorable
$0 < R_L < 1$	: favorable
$R_L = 0$	: irreversible

On the other hand, the Freundlich isotherm is used for model the adsorption onto heterogeneous surface and the multilayer adsorption. The Freundlich equation is shown as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

Where K_f : the adsorption capacity

n : the constant that indicate the favorability of metals onto the adsorbent

The linearized Freundlich model isotherm is represented by the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{7}$$

The plots of log q_e versus log C_e can be used to determine the value of K_f and 1/n which are the Freundlich parameters.

The adsorption data from the adsorption isotherms of the selected metal ions (Cu, Fe, Pb and Sn) using polybenzoxazine aerogel as an adsorbent were analyzed by using Langmuir and Freundlich equations. The values of Langmuir and Freundlich correlation coefficients (R^2) and Langmuir parameters are given in table 4.2

Table 4.2 The values of Langmuir and Freundlich correlation coefficients (R^2) and Langmuir parameters.

Metal Ions	Langmuir Equation			Freundlich Equation
	Q_{max}(mg/g)	K_L	R^2	R^2
Cu	1.501	6.296	0.9942	0.1711
Fe	0.890	1.694	0.9492	0.3765
Pb	0.258	7.384	0.9520	0.8634
Sn	51.8	2.244	0.9718	0.9977

From table 4.2, the linear plots of metals were better fit with Langmuir equation due to the R^2 values close to unity while Sn seem to be more consistence with Freundlich equation. It suggests the formation of monolayer adsorption of metal ions on the surface of polybenzoxazine aerogel in the studied concentrations

[14]. On the other hand, Sn showed better fit with Freundlich which indicates that the formation of multilayer adsorption on the surface of polybenzoxazine [15].

By using the Langmuir equation the maximum adsorption capacity (Q_{max}) and the Langmuir constant can be deduced. The maximum adsorption capacity sequence is Sn(IV) > Cu(II) > Fe(II) > Pb(II). K_L is the Langmuir adsorption equilibrium constant which is a measure of the energy adsorption. A greater K_L value indicates a steep initial slope of an isotherm implying a high affinity of the adsorbent towards the metal ions under the dilute conditions [16]. Furthermore, it was found that the R_L values for metals onto polybenzoxazine aerogel were between 0 and 1 indicating that the adsorption processes are highly favorable.

4.4.4 Adsorption Experiments for Phosphate

Metal-loaded polybenzoxazine was used as a polymeric ligand exchanger for phosphate removal. The results is shown in figure 4.11. Sn-loaded polybenzoxazine gave the highest amount of phosphate removal due to the highest adorption capacity of Sn onto polybenzoxazine. However, the phosphate removal by metal-loaded polybenzoxazine seems to be low. Although, the polybenzoxazine offers a great metal removal at very low concentration, it has low maximum metal uptake which might be due to the inter- and intra-molecular H-bonding in the polybenzoxazine molecules, resulting in fewer numbers of nitrogen donor atoms being available to form a complex with the metal ions [17]. The low maximum capacity can have an effect to the ability for polymeric ligand exchanger. Another reason is unstable pH during batch experiments. Zhao et al. [18] stated that it is difficult to maintain a constant aqueous-phase pH during the batch experiment test. Therefore, minicolumn technique which is the aqueous solution of fixed composition and pH (predetermined) were pass through short glass column containing adsorbent was used.

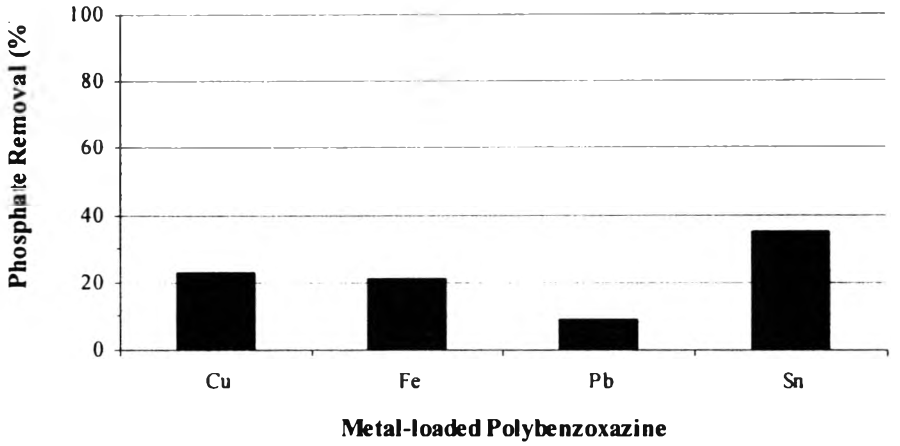

Figure 4.11 The phosphate removal by using metal-loaded polybenzoxazine.

4.5 Conclusion

Polybenzoxazine-based aerogel was successfully synthesized from bisphenol-A, formaldehyde and diamine, tetraethylenepentamine (TEPA). Polybenzoxazine-based aerogel showed high Cu(II), Fe(II), Pb(II) and Sn(IV) removal from wastewater model following order: Sn(IV) > Cu(II) > Fe(II) > Pb(II). Morover, the results indicated that the amount of metal ions removed from the solutions depended on the adsorption time. For the isotherm experiment, the results showed that adsorption of Cu(II), Fe(II) and Pb(II) fit with Langmuir isotherm while Sn(IV) gave better fit with Freundlich isotherm. In addition, the metal loaded polybenzoxazine-based aerogel can serve as polymeric ligand exchanger (PLE) to remove phosphate from the model wastewater.

4.6 Acknowledgements

The authors would like to thanks the National Center of Excellence for Petroleum, Petrochemical and Advance Materials, Chulalongkorn University and the Asahi Glass Foundation, Japan for financial support of this research.

4.7 References

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