



## CHAPTER IV

### REMOVAL OF HEAVY METALS FROM WASTEWATER MODEL BY USING POLYBENZOXAZINE-BASED AEROGEL AS A POLYMERIC LIGAND EXCHANGER

#### 4.1 Abstract

Heavy metals are commonly associated with water pollution. Thus, the removal of heavy metals from wastewater has become mandatory. The purpose of this work is investigation of polymeric ligand exchanger (PLE) prepared for metal ions removal. Our study made use of polybenzoxazine aerogel as PLE. The results indicate that removal of metal ions using polybenzoxazine is in the following order:  $\text{Sn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{2+}$ , which is in accordance with the Irving-Williams rule. Moreover, the amount of metal ions removed depends on the amount of absorbent polybenzoxazine and sorption time. As expected, the maximum adsorption capacity of mixed metal solutions is lower than that of single metal solutions for all types of metal at the same conditions. Additionally, desorption process is shown to be a function of pH, type of solutions, and temperature.

Keywords: Heavy metals; Wastewater; Polymeric ligand exchanger; Building block; Binding unit; Polybenzoxazine-based aerogel; Metal-ligand complexes

## 4.2 Introduction

Heavy metals are commonly associated with water pollution. These metals are very toxic and their discharge into water affects human health and the environment. Thus, the removal of heavy metals from wastewater has become mandatory. The method most employed for heavy metal removal is chemical precipitation which is simple and inexpensive. However, it has the disadvantage of generating a large volume of sludge for disposal [1].

Alternative recovery method is ligand-exchange-based separation. Polymeric ligand exchangers (PLE) are a class of promising sorbents that sorbs chemicals based primarily on their ligand characteristics rather than ionic charges [2]. PLE offers an easy route to the preparation of organic/inorganic hybrid materials and has become a most interest research theme [3-5]. Generally, polymeric ligand exchangers (PLE) are composed of: a cross-linked hosting resin that can firmly bind with a transition metal such as lead, nickel, copper, and manganese and metal ions that are immobilized to the functional groups of the hosting resin [6].

The series of polybenzoxazine obtained by the ring-opening polymerization of cyclic monomer has been developed as a novel type of phenolic resin. The monomer can be prepared from phenols, amines and formaldehyde. The extensive variation of phenols and amines allows great molecular design flexibility. Polymerization proceeds through the ring-opening of the cyclic monomers only by heat treatment without the need of catalyst. Furthermore, the reaction does not give out any by-product or volatile; thus products with excellent dimensional stability can be achieved [7].

The purpose of this study is to investigate the performance of polybenzoxazine-based aerogel as the polymeric ligand exchanger. The optimal condition for metal ions removal will be determined as a function of pH, time, types of solutions and temperature [8-10].

### 4.3 Experimental

#### 4.3.1 Materials

Bisphenol-A (BPA,  $C_{15}H_{16}O_2$ ) was purchased from Aldrich, Germany. Formaldehyde ( $CH_2O$ , analytical grade) was purchased from Merck, Germany. Triethylenetetramine (TETA,  $C_6H_{18}N_4$ ) was purchased from Fluka, Switzerland. 1,4-Dioxane ( $C_4H_8O_2$ , analytical grade) was purchased from Labscan, Ireland. All chemicals were used without further purification. Solutions containing metal salts in the form of nitrate: Chromium(II), Copper(II), Iron(II), Manganese(II), Nickel(II), Lead(II), and Tin(II) were of analytical grade and purchased from Merck, Germany; except Cadmium(II) nitrate was purchased from Fluka, Switzerland. Concentrated hydrochloric acid and sodium hydroxide (J.T. Baker, USA and Carlo Erba, Italy, respectively) were used for the adjustment of pH. Sodium chloride (AJAX Chemicals, Australia) was used for desorption experiments. Deionized water was used in all experimental work.

#### 4.3.2 Measurements

The FT-IR spectra of benzoxazine precursor were obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrument. The sample was loaded on the platinum pan and heated from 30° to 800°C at a heating rate of 10°C/min under  $N_2$  flow of 50 mL/min. Scanning electron microscope, JEOL/JSM model 5200, was used to observe the surface morphology of polybenzoxazine-based aerogel. The specimens were coated with gold under vacuum before observation. Transmission electron microscope, JEOL model JEM-2100, was used to observe the porous structure of polybenzoxazine-based aerogel. TEM samples were prepared using the ultramicrotome. Nuclear magnetic resonance was used to characterize the chemical structure of polybenzoxazine.  $^1H$  NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. The solvent used was deuterated dimethyl sulfoxide (DMSO). DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a rate of 10°C/min under a  $N_2$  atmosphere with a flow rate of 10 ml/min.  $N_2$

adsorption-desorption isotherms were obtained at  $-196^{\circ}\text{C}$  on a Quantachrome Autosorb-1. Samples were degassed at  $150^{\circ}\text{C}$  during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Dubinin-Astakhov (DA) method using the adsorption branch of the nitrogen isotherm. A 50 ml of 1 ppm  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{2+}$ ,  $\text{Sn}^{2+}$  and  $\text{Zn}^{2+}$  solutions and polybenzoxazine-based aerogel (10 to 80 mg) were placed in a glass bottle and shaken for 4 to 48 hr. The quantitative analysis of metal ions was carried out with Inductively Coupled Plasma Spectrometer (ICP) mass spectrometer, Optima 4300DV model PE.

### 4.3.3 Methodology

#### 4.3.3.1 Synthesis of Organic Aerogel from Polybenzoxazine

The benzoxazine aerogel was synthesized by dissolving bisphenol-A (BPA,  $\text{C}_{15}\text{H}_{16}\text{O}_2$ ) in dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ ). Formaldehyde ( $\text{CH}_2\text{O}$ ) and triethylenetetramine (TETA,  $\text{C}_6\text{H}_{18}\text{N}_4$ ) were then added in the solution. The mole ratio of bisphenol A: formaldehyde: diamine is 1:4:1. The mixture was stirred continuously while the reaction was cooled with an ice bath; yielding partially-cured benzoxazine which was in the form of homogeneous yellowish viscous liquid. The precured benzoxazine was then placed in the oven at  $80^{\circ}\text{C}$  for 72 hr. in a closed system to evaporate solvent at ambient condition, followed by fully curing with a heating rate of  $10^{\circ}\text{C}/\text{min}$  for 10 hr. under  $\text{N}_2$  atmosphere. The organic aerogel was then obtained.

#### 4.3.3.2 Characteristics of Polybenzoxazine-based Aerogel

The structural characteristics of polybenzoxazine-based aerogel were investigated using FTIR and  $^1\text{H}$ -NMR. The thermal properties were measured using DSC and TG/DTA. The morphology was observed by SEM. The porous structure of polybenzoxazine-based aerogel was characterized by TEM. Furthermore, the surface area and pore distribution were measured using SAA.

#### 4.3.3.3 Adsorption Experiments

Experimental solutions with different amounts of polybenzoxazine-based aerogel were mixed in glass bottle at a given temperature and constant total ion

normality in solutions. Essentially, 50 ml of a solution containing the metal-ions with 1 ppm of initial concentration ( $C_0$ ) was mixed with polybenzoxazine-based aerogel weighted varied from 20 to 80 mg, under constant magnetic stirring, at 298 K. After a time period from 4 to 48 h, the suspension were filtered through 2.5  $\mu\text{m}$  membrane filters and the metal solutions were analyzed.

The control experiments were done in order to confirm that the adsorption of specific metals on the walls of glass bottle or in the filtration systems was negligible.

#### 4.3.3.4 Desorption Experiments

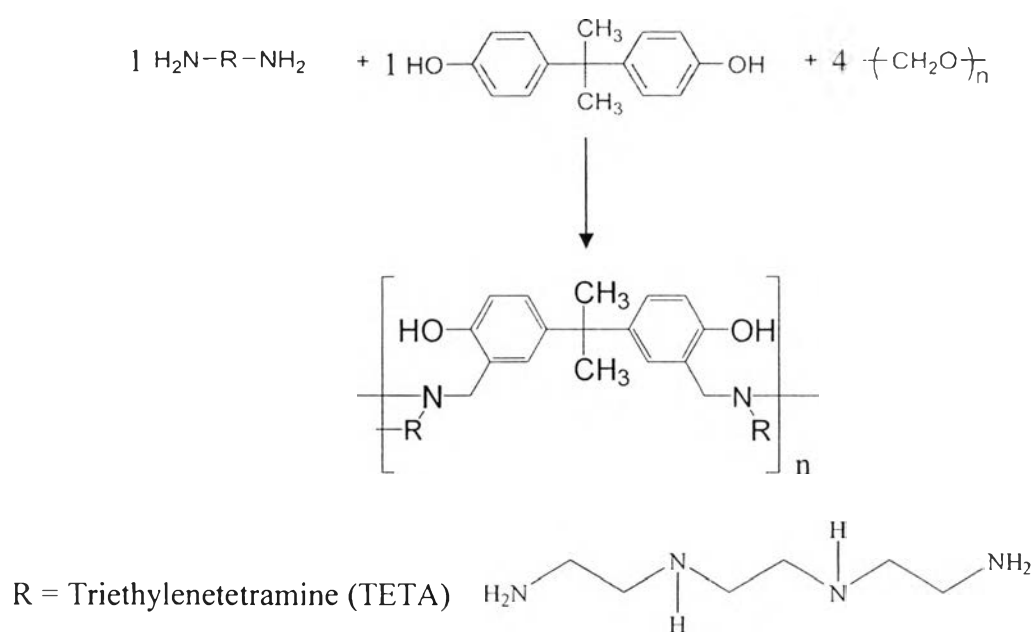
The polybenzoxazine-based aerogel (80 mg) with adsorbed  $\text{Sn}^{2+}$ , obtained from the metal sorption study, was placed in contact with (a)  $\text{H}_2\text{O}$  or (b) 2% (w/v) NaCl solutions at pH 4, 7, 9 while stirring continuously. After 24 hour, the aqueous phase was separated by filtration and the amount of metal released from the polybenzoxazine-based aerogel was determined.

### 4.3 Results and Discussion

#### 4.4.1 Preparation Polybenzoxazine-based Aerogel

The synthesis of polybenzoxazine precursor derived from “quasi-solventless method” is our first recovery, unlike the traditional method requiring solvent and long reaction, as first described by Takeichi *et al.* [7]. Our method used dioxane to facilitate the mixing of all reactants to accelerate the synthesis process to produce benzoxazine precursor, within one hour, as shown in Figure 4.1. The benzoxazine precursor was evaporated the dioxane at ambient condition before fully being cured to polybenzoxazine-based aerogel.

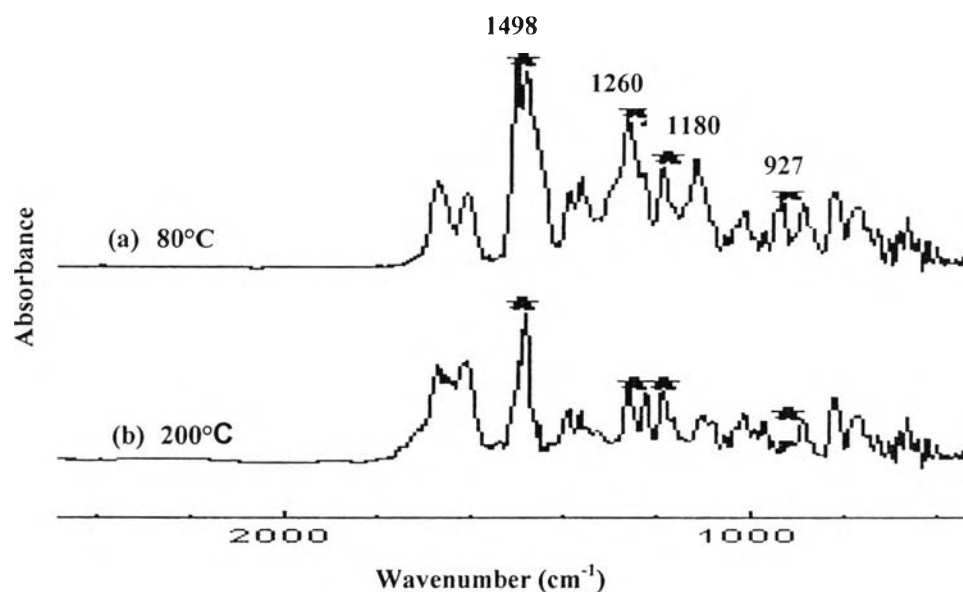
According to Du *et al.* [5], the higher numbers of nitrogen donor atom has higher strongly basic anion exchanger. Triethylenetetramine (TETA) was, thus, chosen as one of the reactants for benzoxazine synthesis due to high numbers of nitrogen donor atom which could form complex with metal ions when polybenzoxazine was used as a polymeric ligand exchanger.



**Figure 4.1** Chemical reaction of polybenzoxazine-based aerogel synthesis.

#### 4.4.2 Characterization of Polybenzoxazine-based Aerogel

The polymerization process of benzoxazine precursor to polybenzoxazine-based aerogel, denoted as [Poly (BA-TETA)], was followed using FT-IR, as shown in Figure 4.2.

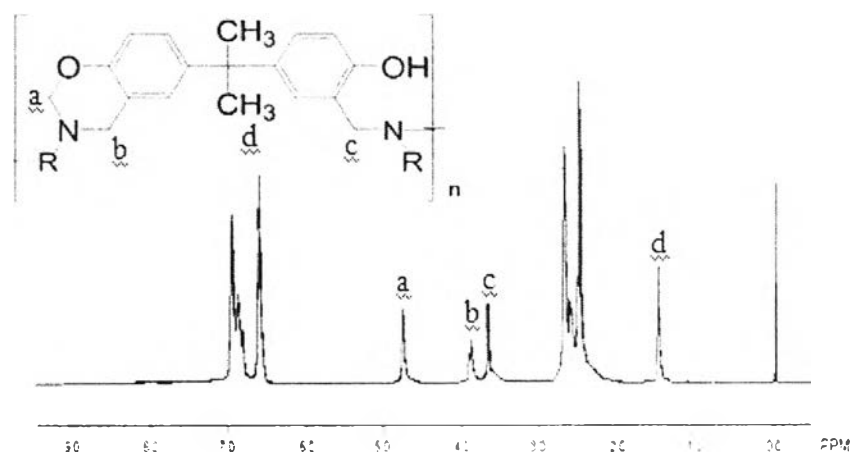


**Figure 4.2** FTIR spectra of polybenzoxazine precursor after drying at 80°C (pre-cured) (a) and after heat treatment at 200°C (fully-cured) (b).

FTIR spectrum confirmed that polybenzoxazine precursor was obtained, as shown in Figure 4.2 a. The asymmetric stretching band of C–N–C ( $1180\text{ cm}^{-1}$ ), C–O–C ( $1260\text{ cm}^{-1}$ ) and  $\text{CH}_2$  wagging of oxazine ( $1370\text{--}1380\text{ cm}^{-1}$ ) were observed. Additionally, the characteristic absorption peaks assigned to trisubstituted benzene ring and out of plane bending vibrations of C–H were observed at  $1498$  and  $927\text{ cm}^{-1}$ , respectively [12].

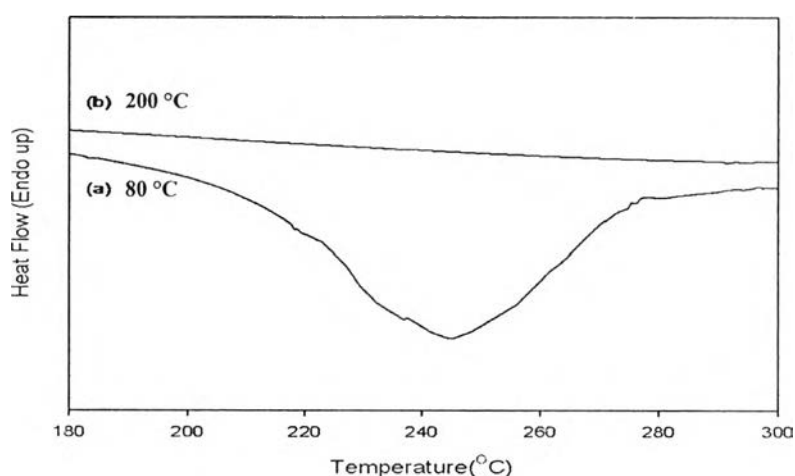
The intensity of the characteristic absorption bands at  $927\text{ cm}^{-1}$  decreased significantly after polybenzoxazine was completely polymerized, as shown in Figure 4.2 b. This FTIR result agrees with the study of Dunkers *et al.* [12], suggesting the change of the characteristic absorption due to the ring-opening polymerization of benzoxazine.

$^1\text{H-NMR}$  was also used to confirm the chemical structure of partially cured polybenzoxazine, as can be seen in Figure 4.3. According to the study of Dunkers *et al.* [12], the resonances at  $4.83$  and  $3.98$  ppm correspond to the methylene protons of  $\text{O-CH}_2\text{-N}$  and  $\text{Ar-CH}_2\text{-N}$  of oxazine ring, respectively. The methylene protons of  $\text{Ar-CH}_2\text{-N}$  obtained from ring-opening was observed at  $3.72$  ppm. The resonance at  $1.52$  ppm corresponds to the methyl protons of bisphenol-A.



**Figure 4.3**  $^1\text{H-NMR}$  spectrum of partially cured polybenzoxazine.

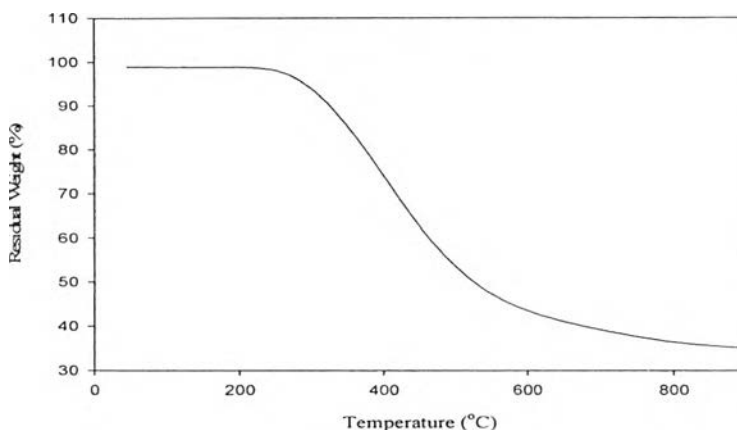
Thermal behavior of both benzoxazine precursor and partially-cured polybenzoxazine was studied using DSC and TGA, respectively. The ring-opening polymerization monitored by DSC is depicted in Figure 4.4. In case of partially-cured BA-TETA, the exothermic peak was observed from 180°-245°C, indicating the incomplete polymerization. However, after the heat treatment at 200°C, the obtained thermogram was rather flat, implying that the polymerization is complete. This DSC result is in agreement with the study of Su *et al.* [13], showing the decrease of the exotherm peak with the increase of temperature, which was disappeared after the fully cure (Figure 4.4 b).



**Figure 4.4** DSC thermograms of benzoxazine precursor (pre-cured) (a) and polybenzoxazine (fully-cured) (b).

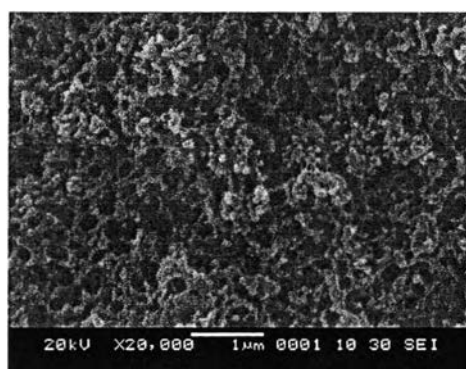
Thermal stability of partially-cured polybenzoxazine by TGA is shown in Figure 4.5. The decomposition of organic materials from benzoxazine precursor started at 250°C, and the maximum weight loss was observed between 250° and 600°C. The weight loss still decreased after 600°C. Su *et al.* [13] also identified the decomposition of polybenzoxazines through TGA technique, and found that the decomposition was from the crosslink of aliphatic and amines.





**Figure 4.5** TGA thermogram during the pyrolysis of the partially-cured polybenzoxazine.

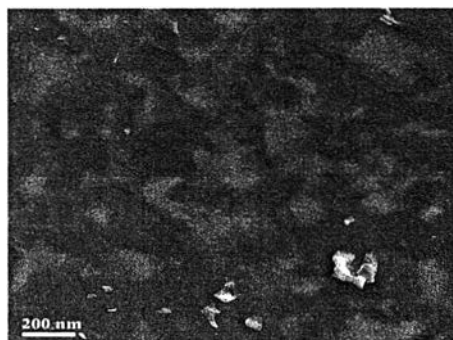
Scanning electron microscopy (SEM) was employed to investigate the microstructure of the polybenzoxazine-based aerogel, as shown in Figure 4.6. The porous structure of organic aerogel was obtained due to the removal of the solvent from the aerogels. From the SEM micrograph, the obtained organic aerogel was in the form of continuous polymer network incorporated with pores ranging from nanometers to micrometers. According to the study of Wang *et al.* [14], polybenzoxazine-based aerogel surface gives a rough surface, possessing both micro- and nanoscale binary structures.



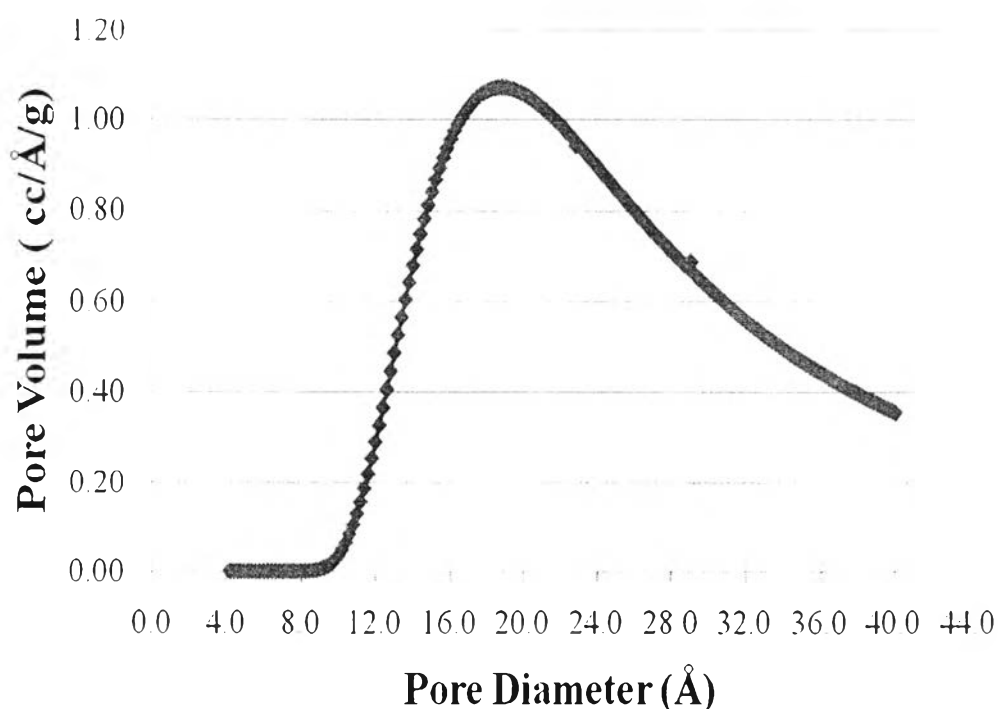
**Figure 4.6** SEM micrograph of polybenzoxazine-based aerogel.

Microstructure of polybenzoxazine-based aerogel was investigated using TEM and SAA, respectively. Pore sizes and pore structure of polybenzoxazine-based aerogel (Figures 4.7 and 4.8) indicated that polybenzoxazine-based aerogel consisted of different pore sizes, including nanopores, mesopores and macropores. Similar to

the study of Kim *et al.* [15], showing that the pore distribution of the resorcinol/formaldehyde resin aerogel was broadly spread with diameters ranging from nanopores to macropores.



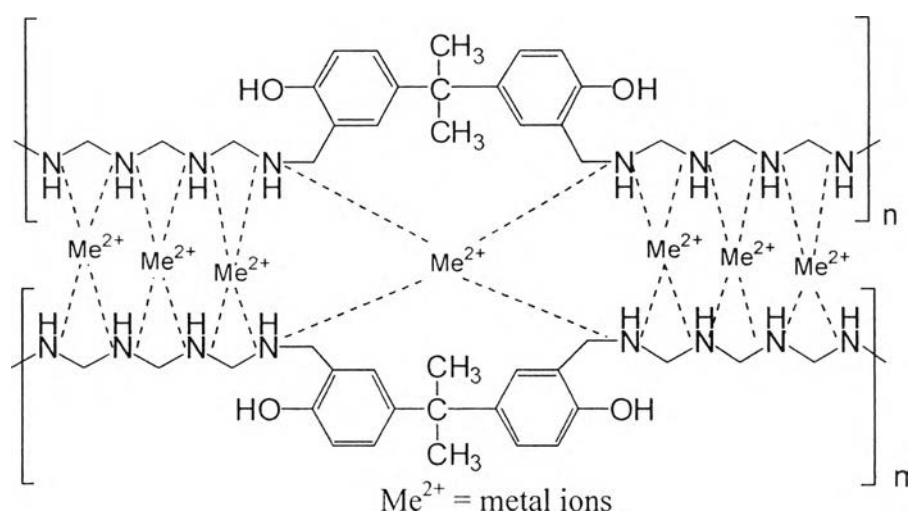
**Figure 4.7** TEM micrograph of polybenzoxazine-based aerogel.



**Figure 4.8** The pore size distribution of polybenzoxazine-based aerogel particle.

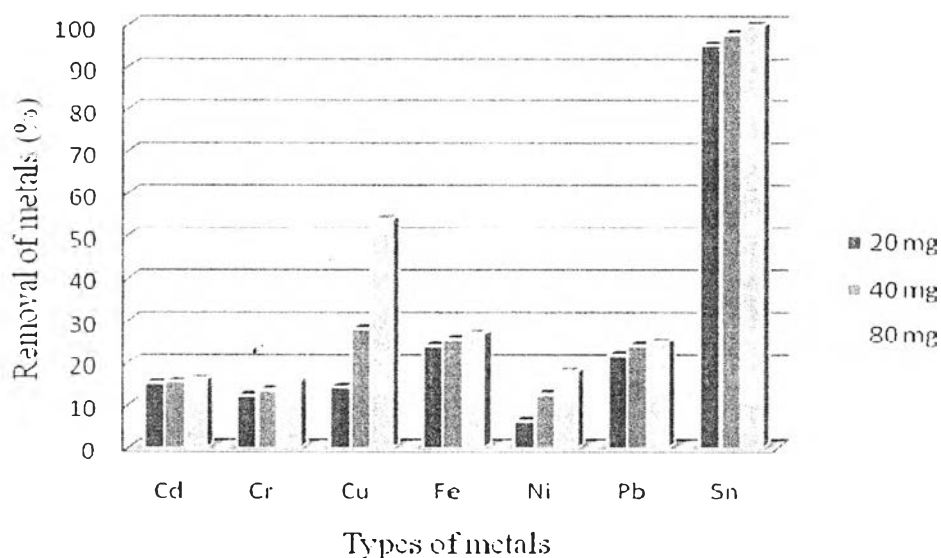
#### 4.4.3 Adsorption Experiments

The adsorption onto polybenzoxazine-based aerogel could be envisioned as the metal-ligand complex process [15-16], as shown in Figure 4.9.



**Figure 4.9** The adsorption onto polybenzoxazine-based aerogel.

Effects of metal types on adsorption by polybenzoxazine based aerogel were examined and the results are presented in Figure 4.10.



**Figure 4.10** The adsorption onto polybenzoxazine-based aerogel in single metal solution at various weights of polybenzoxazine-based aerogel.

The results indicated that removal of metal ions using polybenzoxazine-based aerogel as the ligand was in the following order:  $\text{Sn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{2+}$ . The stability of metal-ligand complexes in homogeneous system was generally explained using the Irving-Williams rule [18]. Henry *et al.* [2] also found that the sequence of complex stability followed this rule. The rule is related to

the molecular orbital stabilization energy and the crystal field stabilization energy. These two types of energies are explained in term of stability constants. Since the magnitudes of stability constants are proportional to the anti-logarithms of standard free energy changes,  $-\Delta G^\circ$ , the order is, thus, that of the  $-\Delta G^\circ$  values for the formation reactions. Theoretically, the standard free energies of formation are related to the enthalpies and the entropies, as followed;

$$-\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ$$

Indeed in a few case, direct measurement of the  $\Delta H^\circ$  values have proved this order to be true.

According to this rule, the following sequence of the complex stability holds for a given ligand:  $\text{Cd}^{2+} < \text{Cr}^{2+} < \text{Fe}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$  which indicates that  $\text{Cu}^{2+}$  may be the best candidate for forming with ligand because  $\text{Cu}^{2+}$  has the lowest enthalpy of hydration ( $\Delta H^\circ$ ). Enthalpy of hydration,  $H_{\text{hyd}}$ , of an ion is the amount of energy released when a mole of the ion dissolves in a large amount of water, forming an infinite dilute solution in the process,



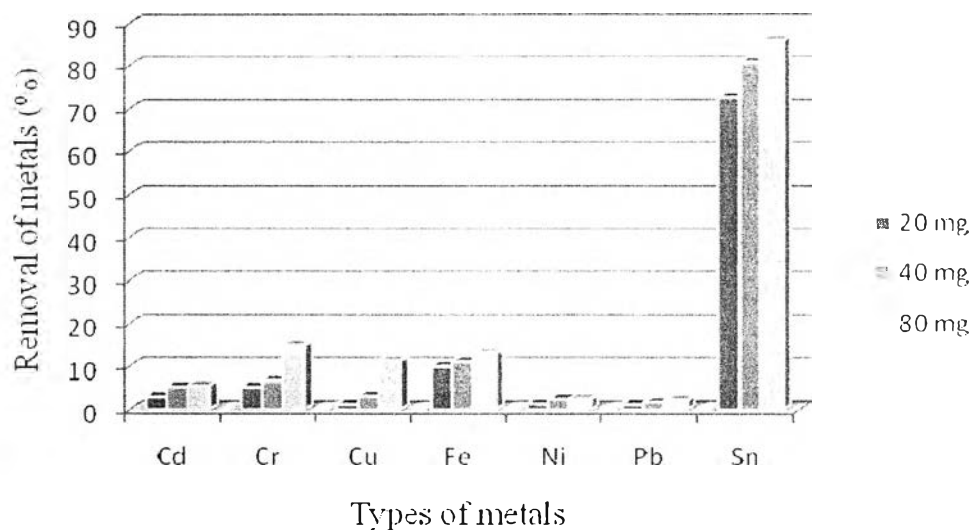
where  $\text{M}^{2+} (\text{aq})$  represents ions surrounded by water molecules and dispersed in the solution [18].

However, in our study, the results indicated that  $\text{Sn}^{2+}$  had the highest percentage of sorption probably due to the highest Van der Waals radius of  $\text{Sn}^{2+}$ , determined from measurements of atomic spacing between pairs of unbonded metal atoms in crystals [18]. Therefore, it could be concluded that both Irving-Williams rule and Van der Waals radius played significant effects on the sorption of the metal-ions.

Ngeontae *et al.* [19] explained that the adsorption is strongly influenced by the weight of absorbent. This statement can be implied to our case since the increase of the polybenzoxazine-based aerogel amount, from 20 to 80 mg, resulted in the higher amount of metal ions removed from the solutions. According to the detection limits of ICP, we observed that after 24 hr of binding,  $\text{Sn}^{2+}$  was completely removed from the solution with  $C_0$  equals to  $1 \text{ mgL}^{-1}$  when 80 g of polybenzoxazine-based aerogel was used. The overall results obtained clearly indicated that

polybenzoxazine-based aerogel was the most selectively to  $\text{Sn}^{2+}$  in regardless of the weight of polybenzoxazine-based aerogel used as the absorbent.

The effect of mixed metal solution on the removal of metals (Figure 4.11) was evaluated and compared with the effect of single metal solution (Figure 4.10).



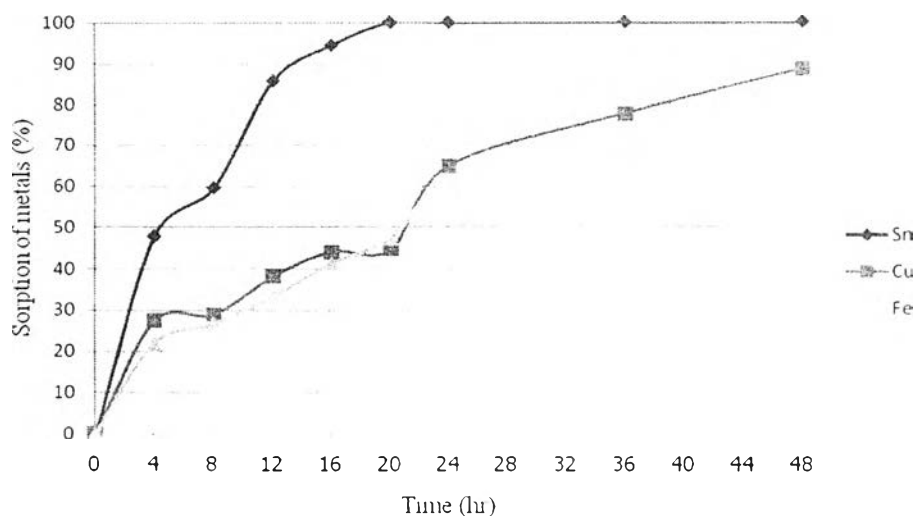
**Figure 4.11** The adsorption onto polybenzoxazine-based aerogel in mixed metal solutions at various weights of polybenzoxazine-based aerogel.

The maximum adsorption capacity of mixed metal solutions was lower than that of single metal solutions for all types of metals at room temperature, when the contact time used was 24 hr at pH 2.45 using less than 150  $\mu\text{m}$  particle size of polybenzoxazine absorbent, and 500 rpm stirring speed. The difference between the maximum adsorption capacities of the single and the mixed metal solutions was attributed to several factors, such as enthalpy of hydration, and Van der Waals radius [18].

Tokuda *et al.* [20] found that at certain pH the results obtained from both single-metal and multi-metal systems were not significantly different. Comparatively, our case provided different results of the metal absorption between single and mixed metal solutions for all kinds of metals at pH 2.45.

To define the time necessary for the attainment of sorption equilibrium [2-6], a study of the uptake rates of metal ions by polybenzoxazine-based aerogel was undertaken at 298°K, as shown in Figure 4.12. The results indicated that the amount of metal ions removed from the solutions increased as the contact time. Furthermore,

the equilibrium was reached after 20 hr for the  $\text{Sn}^{2+}$  case, whereas, the cases of the  $\text{Cu}^{2+}$  and the  $\text{Fe}^{2+}$  did not reach equilibrium within 48 hr.



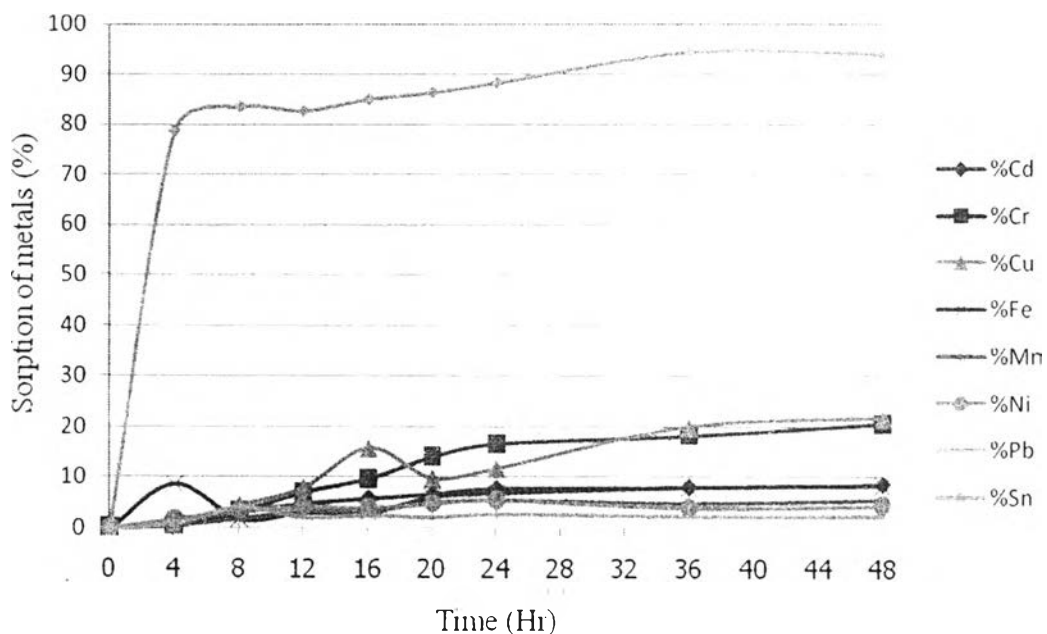
**Figure 4.12** The adsorption onto polybenzoxazine-based aerogel in single metal solutions at various contact times.

The sorption series obtained could be a result of two phenomena that might influence the process, namely, physisorption and chemisorption. The physisorption is a classification of adsorption characterized by a weak Van der Waals force, as opposed to chemisorptions which is characterized by a strong interaction between adsorbent and metal ions.  $\text{Sn}^{2+}$  has the highest Van der Waals radius; therefore physisorption through Van der Waals force was more significant than chemisorption. On the other hand, other metal ions have lower Van der Waals radius, as a result, the interaction with adsorbent occurred through chemisorption.

Paulino *et al.* [10] obtained different results when using chitosan as an adsorbent. They demonstrated that the chitosan and the  $\text{Cu}^{2+}$  solutions did reach equilibrium within 24 hr, and used the pore sizes of chitosan to adsorb  $\text{Cu}^{2+}$  to explain why the chemisorption occurred slower than the physisorption.

The effect of the contact time in the single and the mixed metal solutions on the removal of metals was evaluated at room temperature. The results were compared between Figures 4.12 and 4.13. It was found that the results were in agreement with those of the adsorbent weight effect. That is, the maximum adsorption capacity of

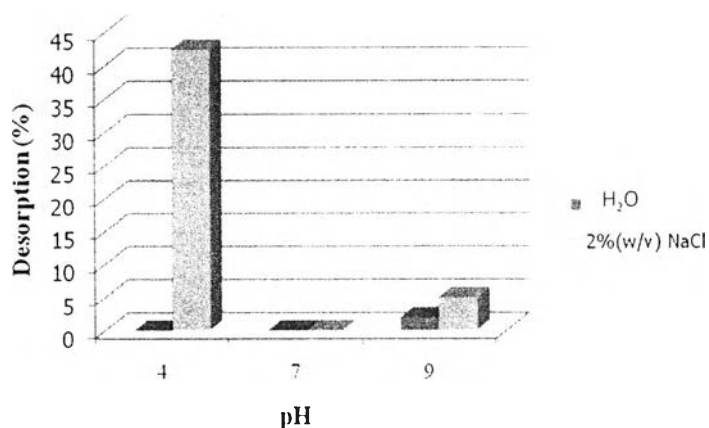
mixed metal solutions was lower than that of single metal solutions for all types of metal at the same conditions.



**Figure 4.13** The adsorption onto polybenzoxazine-based aerogel in mixed metal solutions at various contact times.

#### 4.4.4 Desorption Experiments

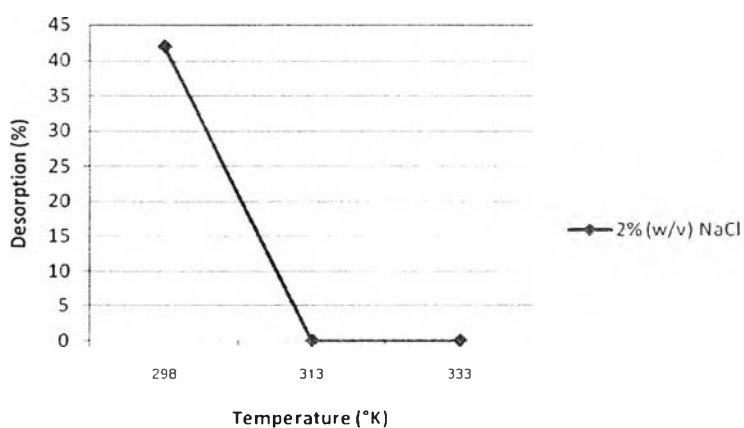
The effect of media types on desorption was evaluated by using H<sub>2</sub>O and 2% (w/v) NaCl (Figure 4.14). When H<sub>2</sub>O was used as media, the Sn<sup>2+</sup> desorption was negligible. However, when the desorption experiments were done in 2% (w/v) NaCl at pH 4, 40% of Sn<sup>2+</sup> was recovered which might be because NaCl has much higher ionic dissociation than H<sub>2</sub>O, as observed by Bosco *et al.* [8] using NaCl and Ca(NO<sub>3</sub>)<sub>2</sub> as media.



**Figure 4.14** The desorption process of H<sub>2</sub>O and 2% (w/v) NaCl at various pHs.

H<sub>2</sub>O and 2% (w/v) NaCl with pH 4, 7, and 9 were prepared to investigate the effect of pH on Sn<sup>2+</sup> desorption. From the results, the greatest desorption was observed when the acidic pH (4) media was used. The results indicated that more than 40% of sorbed Sn<sup>2+</sup> was recovered within 24 hr. Obviously, the participation of H<sup>+</sup> in the ligand exchange reaction at acidic pH significantly improved the desorption efficiency. Paulino *et al.* [10] observed similar behavior for other absorbents. Their results indicated that desorption increased with the increase of pH when solution was in the acidic range.

In order to investigate the effect of temperature, the metal desorption studies were conducted at 298°, 313°, and 333°K using 2% (w/v) NaCl at pH 4. The desorption values of metal ions from polybenzoxazine-based aerogel as a function of temperature were shown in Figure 4.15. When temperature was increased, the Sn<sup>2+</sup> desorption was negligible, which might be due to the difficulty of formation between sodium ion in media with ligand since the entropy was increased, as also observed by Özer *et al.* [21] that the desorption capacity decreased at higher temperature.



**Figure 4.15** The desorption process 2% (w/v) NaCl at pH 4 by various temperatures.



#### 4.5 Conclusions

This study revealed that polybenzoxazine aerogel could be used for metal removal from wastewater. The sorption capacity of polybenzoxazine-based aerogel for metals at 298°K was in the following order:  $\text{Sn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{2+}$ . This order could be related to both Irving-Williams rule and Van der Waals radius. Moreover, the results indicated that the amount of metal ions removed from the solutions depended on both the weight of adsorbent as well as the sorption time. The maximum adsorption capacity of mixed metal solutions was less than that of single metal solutions for all types of metal at the same conditions because of enthalpy of hydration and Van der Waals radius. For desorption process, 40% of  $\text{Sn}^{2+}$  could be optimally recovered when 2% (w/v) NaCl with pH 4 was employed which might be due to the ionic dissociation of NaCl and amount of protons in acid solutions.

#### 4.6 Acknowledgements

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#### 4.7 References

- [1] Bosco, S.M.D., Jimenez, R.S., and Carvalho, W.A. (2005). Removal of toxic metals from wastewater by Brazilian natural scolecite. Journal of Colloid and Interface Science. 281, 424–431.
- [2] Henry, W.D., Zhao, D., SenGupta, A.K., and Lange, C. (2004). Preparation and characterization of a new class of polymeric ligand exchangers for selective removal of trace contaminants from water. Reactive & Functional Polymers, 60, 109-120
- [3] Zhao, D., and SenGupta, A.K. (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. Water Research, 32, 1613-1625.

- [4] Li, P., and SenGupta, A.K. (2004). Sorption of hydrophobic ionizable organic compounds (HIOCs) onto polymeric ion exchangers, Reactive & Functional Polymers, 60, 27-39.
- [5] Du, W., Pan, B., Jiang, P., Zhang, Q., Zhang, W., Pan, B., Zhang, Q., and Zhang, Q. (2008). Selective sorption and preconcentration of tartaric acid using a copper (II)-bound polymeric ligand exchanger. Chemical Engineering Journal, 139, 63-68.
- [6] An, B., Steinwinder, T.R., and Zhao, D. (2005). Selective removal of arsenate from water using a polymeric ligand exchanger. Water Research, 39, 4993-5004.
- [7] Takeichi, T., and Agag, T., (2006). High Performance Polybenzoxazines as Novel Thermosets. High Performance Polymers, 18, 777-797.
- [8] Bosco, S.M.D., Jimenez, R.S., and Carvalho, W.A. (2005). Removal of toxic metals from wastewater by Brazilian natural scolecite. Journal of Colloid and Interface Science, 281, 424-431.
- [9] Ngah, W.S.W., and Hanafiah M.A.K.M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresource Technology, 99, 3935-3948.
- [10] Paulino, A.T., Santos, L.B. and Nozaki, J. (2008). Removal of  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Fe^{3+}$  from battery manufacture wastewater by chitosan produced from silkworm chrysalides as a low-cost adsorbent. Reactive & Functional Polymers, 68, 634-642.
- [11] Gârea, S.-A., Iovu, H., Nicolescu, A., and Deleanu, C. (2007). Thermal polymerization of benzoxazine monomers followed by GPC, FTIR and DETA. Polymer Testing, 26, 162-171.
- [12] Dunkers, J., and Ishida, H. (1995). Vibrational assignments of 3-alkyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazines in the fingerprint region. Spectrochimica Acta, 51, 1061-1074.
- [13] Su, Y. C., Chen, W.-C., Chang F.-C. (2004). Investigation of the Thermal Properties of Novel Adamantane-Modified Polybenzoxazine. Journal of Applied Polymer Science, 94, 932-940.

- [14] Wang, C.-F., Wang, Y.-T., Tung, P.-H., Kuo, S.-W., Lin, C.-H., Sheen, Y.-C., and Chang, F.-C. (2006). Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range. Langmuir, 22, 8289-8292.
- [15] Kim, P.-H., Kwon, J.-D., and Kim, J.S. (2004). The impregnated synthesis of polypyrrole into carbon aerogel and its applications to photovoltaic materials. Synthetic Metals, 142, 153-160.
- [16] Schubert, U.S., and Heller, M. (2001). Metallo-Supramolecular Initiators for the Preparation of Novel Functional Architectures. Chemistry a European journal, 7(24), 5252-5259.
- [17] Sesalan, B. S., Koca A., Gül. A. (2008). Water soluble novel phthalocyanines containing dodeca-amino groups. Dyes and Pigments, 79, 259–264.
- [18] Cotton, F. A., Wilkinson, G. (1980). *Advanced Inorganic Chemistry*. pp 685-686. John Wiley & Sons, New York.
- [19] Ngeontae, W., Aeungmaitrepirom, W., and Tuntulani, T. (2007). Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II). Talanta, 71, 1075-1082.
- [20] Tokuda, H., Kuchar, D., Mihara, N., Kubota, M., Matsuda, H., and Fukuta, T. (2008). Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H<sub>2</sub>S in single-metal and multi-metal systems. Chemosphere, 73, 1448-1452.
- [21] Özer, A., and Özer, D. (2003). Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats. Journal of Hazardous materials, 100, 219–229.