



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Metal-ions in Wastewater

Heavy metals have been excessively released into the environment due to rapid industrialization growth that has created a major global concern. Lead, nickel, zinc, and manganese are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc. (Kadirvelu *et al.*, 2001a; Williams *et al.*, 1998). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore, they must be removed before discharge. Researchers have been interested in replacing costly wastewater by using cheaper adsorbents such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis, solvent extraction, etc. (Namasivayam and Ranganathan, 1995).

This work is focused on the adsorption method because it is one of the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions.

Several adsorbents have been used for metal removal from wastewater including;

##### 2.1.1 Removal of Toxic Metal from Wastewater by Plant Wastes as Adsorbent

Wan Ngah *et al.* used plant wastes as adsorbent because they were inexpensive as they had no or very low economic value. Some of the advantages of using plant wastes for wastewater treatment included simple technique, requires little processing, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration. However, the application of untreated plant wastes as adsorbents could also bring several problems such as low adsorption capacity, high COD and BOD as well as TOC due to the release of soluble organic compounds contained in

the plant materials (Gaballah *et al.*, 1997; Nakajima and Sakaguchi, 1990). The increase of the COD, BOD and TOC could cause depletion of oxygen content in water and could threaten the aquatic life. Therefore, plant wastes needed to be modified or treated before being applied for the decontamination of heavy metals. The most common chemicals used for treatment of plant wastes were acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favoured metal uptake. Although chemically modified plant wastes could enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also had to be taken into consideration in order to produce 'low-cost' adsorbents. (W.S. Wan Ngah *et al.*, 2008)

#### 2.1.2 Removal of Toxic Metal from Wastewater by Chitosan as Adsorbent

The uptake of  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  from wastewater was carried out by adsorption and desorption process in chitosan obtained from silkworm chrysalides (ChSC)-packed column which was suitable for the removal of heavy metals. From the economic view point at contact time of 24 h, pH 5.0, particle size of PBZ from 300 to 425  $\mu\text{m}$ , and temperature of  $20 \pm 0.1^\circ\text{C}$ , it could be pointed out that the use of pure ChSC as a low-cost adsorbent of heavy metals such as  $\text{Pb}^{2+}$  might be a solution for industries to treat wastewater. (A.T. Paulino *et al.*, 2008)

#### 2.1.3 Removal of Toxic Metal from Wastewater by Polymeric Chelating

##### Fiber as Adsorbent

Ko *et al.* (2007) synthesized the polymeric chelating fiber with good adsorbing capacity and activated carbon fiber with high specific area to do the comparative study of the adsorption of heavy metal ions on these materials. The adsorption isotherm of various cations on activated carbon fiber and poly(acrylo-amidino diethylenediamine) showed similar adsorption behavior. High adsorptions were found at high pHs. At low pHs, adsorbed  $\text{H}^+$ s on the benzene (in the case of activated carbon fiber) and amine groups (in the case of poly(acrylo-amidino diethylenediamine)) blocked activated carbon fiber–metal complex and poly(acrylo-amidino diethylenediamine)–metal complex formations. Metal ion adsorption on

activated carbon fiber was lower than that on poly(acrylo-amidino diethylenediamine) due to metal crystal growth on poly(acryloamidino diethylenediamine) although activated carbon fiber had high specific area. In the case of anions adsorption, much higher levels of adsorption were observed at lower pHs, but not at higher pHs due to H<sup>+</sup>s. In conclusion, the results suggested that metal crystal growth using functional group on the surface was more effective to remove metal ions in aqueous solution than activated carbon with high specific area.

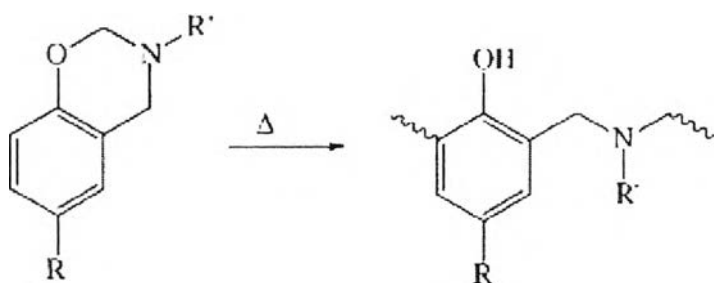
#### 2.1.4 Removal of Toxic Metals from Wastewater by Using Natural Zeolite Scolecite as Adsorbent

Dal Bosco *et al.* (2005) revealed that the natural zeolite “scolecite” could be used as a cation exchanger for the purification of contaminated water. The sorption capacity of scolecite could be related the radius of hydration and the hydration enthalpy of the cations. There was a significant enhancement in the sorption of metals at high temperature. A reduction in the removal of metals observed at lower pH values indicated the occurrence of an ion-exchange process (predominantly at low metal concentrations). The retention of quantities was higher than the expected experimental cation-exchange capacity suggesting the occurrence of another sorption process, probably related to electrostatic interactions among hydrated metal ions and charged surface sites. The desorption processes with sodium and calcium ions showed similar patterns, except for cadmium(II). The mechanism seemed to be dependent on the size of the heavy metal cations. The regeneration process reached equilibrium within the first 60 min. indicating an easy access to the external surface sites. The observed behavior was not related to the formation of hydrolysis products, and it could be conveniently explained by the presence of more easily accessible exchange sites on the scolecite surface. Significant benefit from the usage of scolecite as an ion-exchange material was evident, due to its low cost and high effectiveness in purifying polluted water, allowing a reduction in the concentration of heavy metals from 50 mg L<sup>-1</sup> to valued below the limitation. In such cases, this selective cation exchange might provide an economical way of removing mixed heavy metals from effluents. (S.M. Dal Bosco *et al.*, 2005)

In the present work, polybenzoxazines will be chosen as the absorbent material. By taking advantage of molecular design flexibility, we can design the molecular structures so polybenzoxazine can effectively form complex with metal ions in wastewater. Moreover, polybenzoxazine based-aerogel are composed of particle size in micrometer range. They have very high porosity with pore diameter ranging 5-100 nanometer

## 2.2 Polybenzoxazines

Polybenzoxazines are a relatively new class of versatile materials that have been used in many fields, including electronics and aerospace industries, because they possess several unique features, namely (i) near-zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine based materials,  $T_g$  is much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, and (vi) release of no by-products (even non-toxic) during curing. Polybenzoxazines polymerize via a thermally induced ring-opening reaction to form a phenolic structure characterized by a Mannich base bridge (-CH<sub>2</sub>-NR-CH<sub>2</sub>-) (Figure 2.1).



**Figure 2.1** Benzoxazine polymerization.

Benzoxazine monomers can be prepared simply from inexpensive and commercially available phenols, primary amines, and formaldehyde. Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility. By using appropriate starting materials, properties of polybenzoxazine can be tailored. However, until recently, almost all benzoxazine studies are concerned

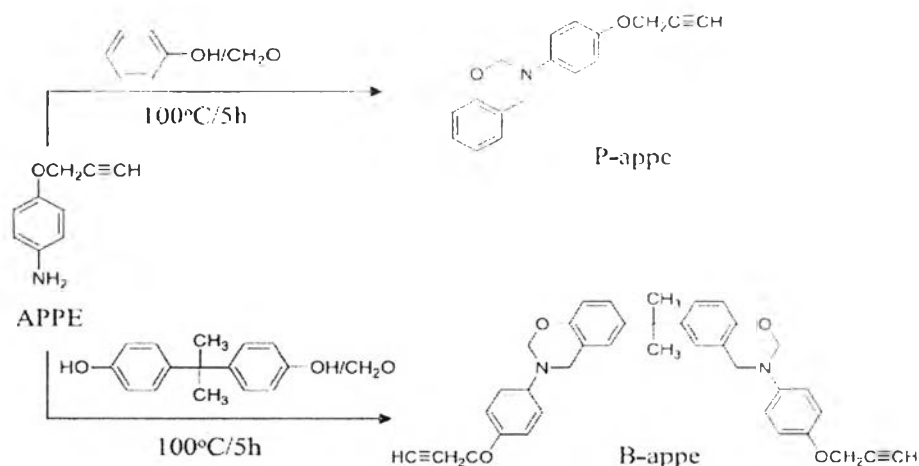
with the polybenzoxazines prepared from the monomer precursors which brings some limitations on their use in practical applications. The monomers are usually in the powder form as a result, processing into thin films is rather difficult. Additionally, the obtained polymers are brittle as a consequence of the short molecular weight of the network structure. (Kiskan *et al.*, 2007)

One approach to enhance the performance of polybenzoxazine is the modification of monomer. The introduction of a flexible and thermally stable structure into the backbone of benzoxazine is considered. For example, a monomer containing a rigid naphthalene structure can be polymerized to give a thermoset having high  $T_g$ . However, the melting temperature of the monomer becomes too high, and ring-opening takes place immediately after the melting of the monomer, resulting in difficult processing. On the other hand, monomer containing an electron-donating alkyl group has higher ring-opening reactivity, and the temperature for the cure shifts to a lower temperature. The  $T_g$  of the obtained polybenzoxazine goes up to approximately 245°C due to high crosslink density.

Another approach for the modification of monomer is the introduction of a crosslink unit into benzoxazine. It is known that polybenzoxazine decomposes by volatilizing aniline fragments during thermal degradation. Therefore, the introduction of an additional cross-linkable site into the aniline part is examined and is shown to be effective for obtaining thermosets with enhanced thermal and mechanical properties. The followings are some examples of the benzoxazines modifications.

### 2.2.1 Addition of a Propargyl Group into Benzoxazine Monomer

The propargyl group was chosen as a possible crosslink site for benzoxazine. Propargyl ether-based monofunctional benzoxazine (P-appe) and bifunctional benzoxazine (B-appe) were prepared as shown in Figure 2.2.

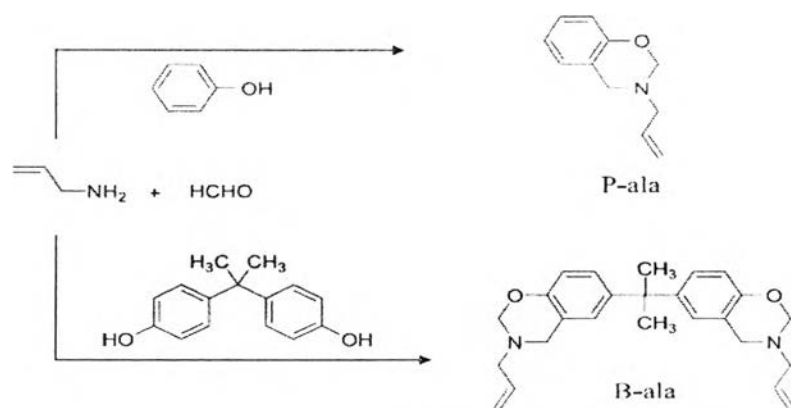


**Figure 2.2** Preparation of P-appe and B-appe.

The thermal properties of the novel polybenzoxazines obtained by heat treatment at 240°C were significantly improved by the incorporation of propargyl group. The result confirmed that the introduction of the propargyl group increased the  $T_g$  of the polybenzoxazine by more than 100°C. Furthermore, The char yield was also increased, indicating that the flame retardant property also increased.

### 2.2.2 Addition of Allyl Group into Benzoxazine Monomer

Another research was the introduction of an allyl group as a crosslink site that worked at moderate temperature. Novel benzoxazine monomers containing allyl groups had been synthesized from phenol and bisphenol A with allylamine and formaldehyde in Figure 2.3.

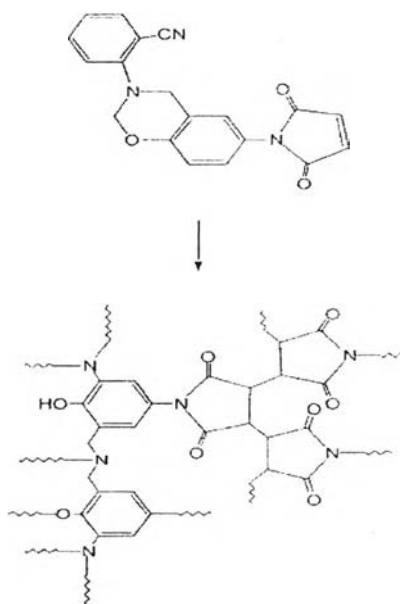


**Figure 2.3** Preparation of P-ala and B-ala.

Thermosets derived from the allyl-functional benzoxazine monomers exhibited significantly improved thermal properties in comparison with the typical polybenzoxazines. The  $T_g$  values of the polybenzoxazine were as high as ca. 300°C due to the introduction of the allyl group. Consequently, the storage moduli of the polybenzoxazine were maintained constant up to much higher temperature than those of typical benzoxazine. (T.Takeichi *et al.*, 2006)

### 2.2.3 Addition of Imide Group into Benzoxazine Monomer

A maleimide and 2-aminobenzonitrile (MIan) based benzoxazine had been synthesized and characterized. This benzoxazine had maleimide and nitrile functionalities that could polymerize, resulting in a highly crosslinked material (Figure 2.4). Incorporation of the imide group increased the shear viscosity compared to monofunctional benzoxazines but not as high as difunctional benzoxazines, allowing good processibility, while maintaining excellent mechanical and thermal properties. Catalysts, epoxy copolymerization, and rubber interlayer methods were utilized to optimize the composite properties. The flexural strength of carbon cloth reinforced composites obtained was higher than 1 GPa. (Chaisuwan *et al.*, 2005)

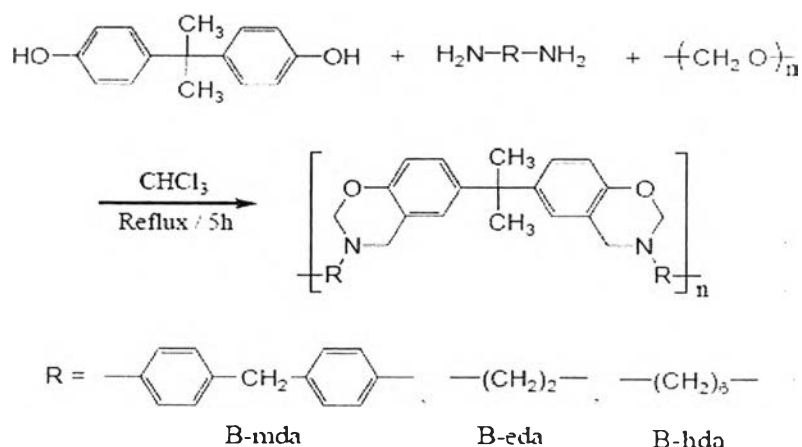


**Figure 2.4** A possible reaction at the maleimide site is the copolymerization of maleimide.

### 2.2.4 Addition of Aromatic or Aliphatic Diamine into Benzoxazine

#### Monomer

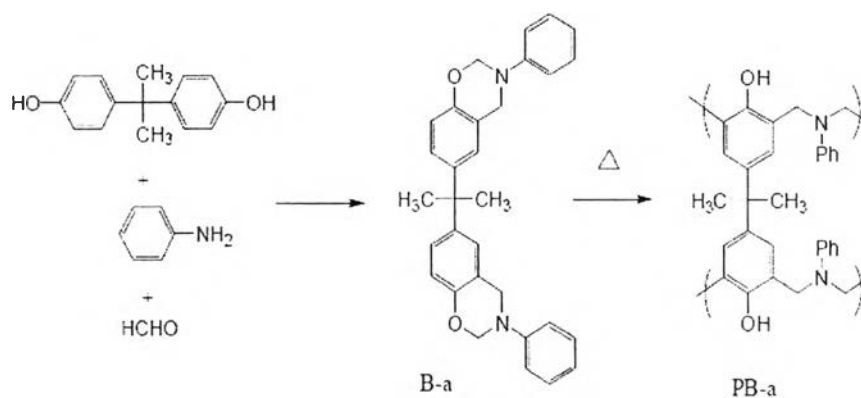
Takeichi *et al.* (2005) synthesized high molecular weight polybenzoxazine precursors which were prepared by reacting bisphenol-A, diamine, and paraformaldehyde as shown in Figure 2.5. The precursors were abbreviated as B-methylenedianiline(mda), B-ethylenediamine(eda) and B-hexamethylenediamine (hda) using the abbreviations of the starting chemicals.



**Figure 2.5** Preparation of polybenzoxazine precursors.

Partially ring-opened structure was observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. Transparent thin precursor films were easily obtained by casting the precursor solution on a glass plate. Heat treatment of the precursor films up to 240°C gave brown transparent polybenzoxazine films. The polybenzoxazine films from the high molecular weight precursors exhibited significantly improved toughness than the typical polybenzoxazine, PB-a, due to the long linear backbone and high crosslink density. The structure of a typical benzoxazine monomer (B-a) prepared from bisphenol-A, aniline and formaldehyde along with the structure of its polybenzoxazine (PB-a) were shown in Figure 2.6.





**Figure 2.6** Structures of B-a and PB-a.

The  $T_g$  values of polybenzoxazines from the high molecular weight precursors were 238–260°C, much higher than the  $T_g$  of the typical PB-a (171°C). Thermal stability of the polybenzoxazine depended on the aromatic content, and polybenzoxazine from aromatic diamine showed higher thermal stability than that of PB-a.

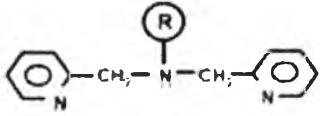
### 2.3 Polymeric Ligand Exchangers (PLE)

As a simple operational technique, adsorption by activated carbon is widely used for removal of metal ion from wastewater. However, it is not suitable for the purpose because activated carbon has less surface area and high cost of disposal. The use of polymeric ligand exchanger is a good alternative for metal ions removal. In recent years ligand exchangers bound with transitional metal ions such as Cu(II) and Fe(III) have demonstrated selective sorption of organic acids (always in anionic form) from solutions of high salinity where the targeted acids can be regarded as ligands owing to the moiety of carboxylic and/or phosphate group. Typically, such sorbent is composed of a supporting matrix (a polymer) and a transition metal (Lewis acid). Its preference towards organic anions is attributed to the concurrent electrostatic and Lewis acid–base interaction.

### 2.3.1 Using Polymeric Ligand Exchanger for Removal of Trace Contaminants from Water

Henry *et al.* (2004) studied the preparation and characterization of an innovative PLE for selective removal of trace organic and inorganic contaminants in the presence of various competing ions. They found that chelating resins with nitrogen donor atoms could serve as excellent metal hosting polymers and pyridine-nitrogen atoms in the polymer phase binds with metal ions more electively than amine-nitrogen atoms. The nitrogen donor atoms in the chelating polymers interacted with various metal ions in accordance with the Irving–Williams series. A novel PLE, designated as DOW3N–Cu, was prepared by immobilizing  $\text{Cu}^{2+}$  ions onto a chelating polymer with high content of pyridine-N donor atoms. Equilibrium and column run results indicated that the PLE was highly selective for trace inorganic contaminants such as phosphate, arsenate and ionizable organic contaminants such as 2,4,6-trichlorophenol (TCP). The ligand exchange (LE) process might provide a cost elective alternative to help water utilities comply with increasingly stringent regulations.

**Table 2.1** Properties of various polymeric sorbents

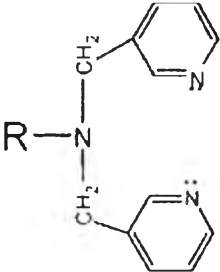
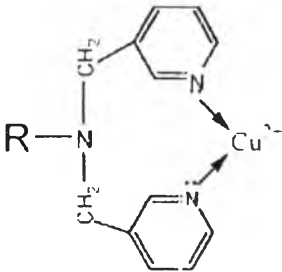
Sorbents	DOW3N
Functional group	 <p>The diagram shows a central nitrogen atom (N) bonded to two pyridine rings (represented as hexagons with an 'N' at the bottom vertex) and a substituent 'R' enclosed in a circle. The pyridine rings are connected to the central nitrogen via methylene groups (-CH<sub>2</sub>-).</p>
Matrix	Polystyrene, macroporous

### 2.3.2 Using Polymeric Ligand Exchanger for Removal of Tartaric Acid

A potential process to selectively separate and preconcentrate tartaric acid from its simulated industrial effluent was reported (Du *et al.*, 2008). A hybrid

sorbent (D-Cu) was prepared by binding Cu(II) onto a polymeric ligand exchanger DowexM-4195. The characteristics of D-Cu and DowexM-4195 sorbent are shown in Table 2.2.

**Table 2.2** Characteristics of DowexM-9145, its Cu(II)-bound derivative D-Cu

Designation	DowexM-9145	D-Cu
Matrix Structure	Polystyrene	Polystyrene
Structure		

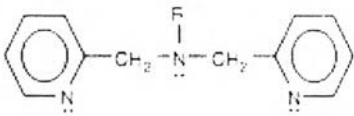
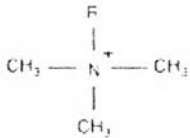
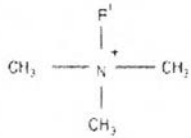
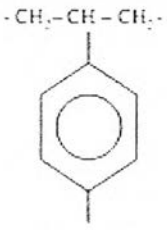
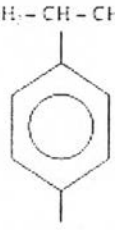
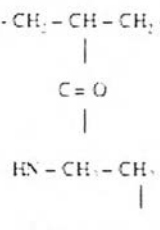
The sorbent exhibited satisfactory performance for tartaric acid sorption from aqueous media even when  $\text{Na}_2\text{SO}_4$  was coexisted at a high level. Moreover, the exhausted sorbent particles were reuseable by using NaCl solution as the regenerant. Continuous sorption–regeneration cycle runs indicated that Cu(II) was firmly bound onto the polymeric ligand exchanger. Column sorption and regeneration tests suggested that D-Cu was a potential sorbent for selective removal of tartaric acid from aqueous media.

### 2.3.3 Using Polymeric Ligand Exchanger for Removal of Arsenate from Drinking Water

An *et al.* (2005) developed an ion exchange process by loading  $\text{Cu}^{2+}$  to a commercially available chelating resin, DOW 3N-Cu. They found that this resin showed unusually high selectivity for arsenate even in the presence of high concentrations of sulfate. Compared to conventional SBA resins (IRA 900 and IRA

958), the arsenic (As) selectivity of DOW 3N–Cu was 60–120 times greater based on the binary arsenate/sulfate separation factor. The characteristics of these sorbents were provided in Table 2.3.

**Table 2.3** Characteristics of DOW 3N, IRA 900, and IRA 958

Sorbent	DOW 3N	IRA 900	IRA 958
Functional group			
Matrix (R or R')	 <p>Polystyrene, Macroporous</p>	 <p>Polystyrene, Macroporous</p>	 <p>Polyacrylic, Macroporous</p>

#### 2.3.4 Using Polymeric Ligand Exchanger for Removal of Phosphate from Reverse Osmosis (RO)

Kumar *et al.* (2007) studied phosphate removal from RO concentrate using Polymeric ligand exchanger (PLE) and to precipitate phosphate from the PLE regenerant solution as struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ).

They concluded that PLE process could be used to remove phosphates from RO concentrate, even though nitrate, sulfate and chloride ions were typically abundant in RO concentrate from reclaimed water applications.