

CHAPTER TWO

LITERATURE REVIEW

2.1 Zinc and Copper

Heavy metals are often present in industrial wastewater. Because of their toxicity, they must be removed prior to discharge. The common heavy metal contaminants include arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. In this study, zinc and copper were selected as model metals because they are present at relatively high concentrations in numerous industrial waste streams. In this section, the chemical properties as well as toxicity of zinc and copper are reviewed. This is followed by a brief review of the significance of zinc and copper in industrial wastewater.

2.1.1 Chemical Properties of Zinc and Copper

Zinc is the first member of Group IIb in the periodic classification of elements. Zinc exhibits only the 2+ valence in aqueous solution. Zn(II) forms soluble complexes with ammonia, chloride, sulphide, sulphate and hydroxide. The hydrolysis of Zn(II) results in the formation of the mononuclear species $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2^0$, $\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$ and polynuclear species $\text{Zn}_2\text{OH}^{3+}$ and $\text{Zn}_2(\text{OH})_6^{2-}$.

(Eichenberger and Chen, 1982; Stumm and Morgan, 1981). Reported zinc (II) chloride complexes include ZnCl^+ , ZnCl_2^0 , ZnCl_3^- , ZnCl_4^{2-} and ZnCl_5^{3-} (Lu and Chen, 1974). The zinc chloride complexes are relatively weak and are only of importance at fairly high chloride concentrations (Heslop and Robinson, 1967).

Copper is the first member of Group Ib in the periodic classification of elements. Copper occurs in the 1+, 2+ and 3+ oxidation states in aquatic systems. The stable oxidation state of copper is 2+. Cu(I) readily disproportionate in water to form Cu^{2+} and Cu^0 (Latimer, 1952). Only small amounts of Cu^+ can exist unless it forms stable complexes such as $\text{Cu}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{CN})_3^{2-}$ (Heslop and Robinson, 1967). Cu(II) forms soluble complexes with ammonia, disulfide, borate, carbonate, chloride, glycine and histidine. Allen *et al.* (1980) reported that in freshwaters, copper is predominantly associated with organic colloidal matter. The adsorption of dissolved copper onto suspended particles may be inhibited to a large extent by the formation of dissolved Cu-organic complexes (Skolkovitz and Copland, 1981).

Cu(II) hydrolyses to form the mononuclear species CuOH^+ , $\text{Cu}(\text{OH})_3^-$, $\text{Cu}(\text{OH})_4^{2-}$ and the polynuclear complex $\text{Cu}_2(\text{OH})_2^{2+}$. The solubility of Cu(II) increases in carbonate-bearing water by the formation of stable carbonate complexes CuCO_3^0 and $\text{Cu}(\text{CO}_3)_2^{2-}$ (Stumm and Morgan, 1981).

2.1.2 Toxicity of Zinc and Copper

Zinc has no known adverse physiological effects upon man except at very high concentrations. Soluble zinc is rarely present in natural waters in significant concentrations. Zinc in tap water from galvanised pipes may range from 3 to 2100 µg/L (Kopp, 1970). Its presence in drinking water in concentrations up to 40 mg/L appears to have no health significance, but it does impart an astringent taste to water and it will precipitate as $Zn(OH)_2$ or $ZnCO_3$ in alkaline waters to produce a milky turbidity. The recommended limit of 5 mg/L in the U.S. drinking water standards is to avoid the taste problem (Camp and Meserve, 1974).

Copper is not considered to be a cumulative systematic poison like lead or mercury. Most of the copper ingested is excreted by the body and very little is retained (McKee and Wolf, 1963). Chronic copper poisoning is said to cause gastrointestinal catarrh and to be related to hemochromatosis, but the amount of copper required for poisoning is far in excess of the concentrations permitted in drinking water (Camp and Meserve, 1974).

The restriction of 1.0 mg/L (U.S. EPA Proposed Secondary Drinking Water Regulations) of copper is primarily to avoid the taste that occurs at higher levels. There is no evidence to indicate that copper is detrimental to public health at

aesthetically acceptable levels. In surface waters, copper is toxic to aquatic plants at concentrations below 1.0 mg/L and has frequently been used as the sulphate salt to control growth of algae in water supply reservoirs. Concentrations near 1.0 mg/L can be toxic to some fish (Sawyer and McCarty, 1978). In Malaysia, water quality standards for zinc and copper in surface waters as well as marine waters to protect public health and the aquatic ecosystems have been proposed (Table 2.1).

Table 2.1: Water quality standards for Malaysia.

Interim National Water Quality Standards (Class III: suitable for public water supply after extensive treatment and tolerant aquatic species)

Zinc	= 0.35 mg/L
Copper	= 0.01 mg/L

Interim Marine Water Quality Standards

Zinc	= No recommendation
Copper	= 0.1 mg/L

2.1.3 Zinc and Copper in Industrial Wastewater

Zinc is present in the wastewater of a number of industries producing steel works with galvanising lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fibre production, ground wood pulp production and newsprint paper

production. Zinc salts are also used in the inorganic pigments industry (e.g. zinc chromate), and high zinc levels have been reported in acid mine drainage water. Plating solutions typically contain 5,000 - 34,000 mg/L zinc (Patterson, 1985). The concentration of zinc in a plating rinse water will be a function of the bath zinc concentration, plated part drainage time over the bath and the volume of rinse water used. Most zinc and all brass plating and rinse solutions contain cyanide.

Copper is present in the wastewater of a number of industries producing chemicals using copper salts or copper catalyst, metal-processing products and metal-plated products. For example, the concentration of copper in a plating bath depends upon the bath type, and may range from 3,000 to 50,000 mg/L. For a given bath, copper concentration in rinse water will be a function of many factors including drainage time over the bath, shape of the part and total surface area, method of rinsing and the rate of rinse water flow. Copper concentration in rinse water may range from 0.02 to 1.0% of the process bath concentration (Patterson, 1985).

2.2 Adsorption of Heavy Metals by Fly Ash

Fly ash adsorption is a new process for the treatment of industrial wastewater containing heavy metals. Weng and Huang (1994) showed that fly ash obtained from coal-fired power plants can be an effective metal adsorbent for Zn(II) and

Cd(II) in dilute industrial wastewaters. The fly ash adsorption capacities for the above mentioned metals were 0.27 mg/g and 0.05 mg/g, respectively. The percent removal of Zn(II) and Cd(II) increased with increasing fly ash concentration. It was shown that 70% of Zn(II) removal was observed at 50 g/L fly ash dosage. Nearly 100% of Zn(II) removal could be achieved with 100 g/L fly ash.

Huang and Rhoads (1989) showed that with the high content of silica, alumina and iron oxide in fly ash, it exhibits high affinity towards heavy metals and therefore is a good metal adsorbent.

Hashim *et al.* (1996) investigated the feasibility of using fly ash obtained from oil-palm waste products to remove copper from aqueous solutions. At pH 4.5 and 25°C, the maximum adsorption capacity of the fly ash for copper was 220 $\mu\text{mol/g}$ (14 mg/g). Kinetic results showed that copper adsorption by the fly ash reached equilibrium in only about 40 min.

Many factors affect the adsorption of heavy metals by fly ash. pH is probably the most important factor affecting the extent of adsorption of heavy metals by fly ash because it influences the metal chemistry in solution as well as the surface chemistry of fly ash. Hashim *et al.* (1996) showed that at pH 2 copper adsorption

was very low. When the pH was raised from 2 to 5, copper adsorption increased dramatically.

Other factors such as temperature also affect the metal adsorption onto fly ash. Panday *et al.* (1985) showed that copper adsorption increased with increasing temperature. It may be due to the desolvation of the adsorbing species, changes in the pore size of the fly ash and the enhanced rate of the intra-particle diffusion of cupric ions. However, subsequent studies conducted by the same group of researchers indicate that the adsorption of other metals like cadmium and lead by the same fly ash decreased with increasing temperature (Hashim *et al.*, 1996). It appears that the effect of temperature may depend on the nature of the adsorbate.

2.3 Adsorption of Heavy Metals by Activated Carbon

Activated carbon adsorption is commonly used to remove trace organic compounds from aqueous streams. Such streams also may contain heavy metals which can be adsorbed concurrently with the organic contaminants. One of the earliest reports on metal adsorption by activated carbon appeared in 1929 (Watanabe and Ogawa, 1929). In the mid-1970's, the U.S. Environmental Protection Agency conducted a series of pilot plant studies to investigate the effectiveness of physical and chemical processes including coagulation, filtration, sedimentation and carbon adsorption to

remove 23 trace metals from wastewater (Maruyama *et al.*, 1975; Hannah *et al.*, 1977). The overall process was found to be very efficient in removing most of the trace metals. For example, activated carbon increased the efficiency of metal removal by as much as 80% for certain metals.

In adsorption equilibrium studies, it is important to allow sufficient time for the batch adsorption system to reach equilibrium. Such information can be obtained from kinetic studies. Huang and Ostrovic (1978) showed that cadmium adsorption by activated carbon reached equilibrium within the first 30 min to 1 hour. At pH 7, for instance, 98% of the cadmium was removed from solution within 30 min. Netzer and Hughes (1984) evaluated the adsorption of copper, lead and cobalt by activated carbon. Their kinetic studies showed that the time required for adsorption to reach equilibrium was approximately 120 min. It is clear that in most cases equilibrium is reached within a relatively short period of time under intense agitation, e.g. 1 to 2 hours. However, in practice most studies employ a much longer contact time to allow the experimental system to reach equilibrium. For example, Huang and Ostrovic (1978) employed a contact time of 20 hours while Budinova *et al.* (1994) used a time of 24 hours to generate adsorption equilibrium data.

Many factors affect the adsorption of heavy metals by activated carbon. The pH of the metal solution is probably one of the most important factors affecting the extent of carbon adsorption of heavy metals. Huang and Ostrovic (1978) showed that pH influences the surface charge of activated carbon. This implies that the extent of metal uptake by activated carbon can be varied by changing the pH of the adsorption environment which in turn determines the surface charge of the carbon. For example, Netzer and Hughes (1984) showed that adsorption of lead, copper and cobalt was relatively low at pH 2. At pH 4 and above a dramatic increase in metal uptake was observed. The results of Budinova *et al.* (1994) who investigated the adsorption of copper, lead, zinc and cadmium by three activated carbons derived from different raw materials are in agreement with that of Netzer and Hughes (1984). In general, the extent of metal adsorption is high at relatively high pH values (4 - 5).

Other factors such as activated carbon type and size of carbon also play an important role in metal adsorption. Due to the large number of variables in the adsorption of metals by activated carbon and the complexity of the carbon surface and water chemistry, no single carbon property appears to be dominant in determining its metal adsorption characteristics.