CHAPTER THREE

DESORPTION CHARACTERISTICS OF ZINC AND COPPER

3.1 General Background

Although the metal accumulation capability of fly ash and activated carbon derived from agricultural wastes has been known for some time, the application of the two adsorbents in the treatment of metal-bearing wastewater has been explored only recently in conjunction with metal recovery processes. For the establishment of metal removal and recovery by fly ash or activated carbon as an alternative to the conventional chemical precipitation method, potent fly ash and activated carbon types have to be identified and the mechanism of the adsorption process better understood. An important aspect of the exploration of metal removal and recovery by fly ash and activated carbon is investigation of an efficient desorption process and regeneration of the adsorbent.

Recovery of adsorbed metal can be achieved by the use of an appropriate desorbing solution capable of effectively stripping the adsorbed metal from the adsorbent and bringing it back into solution. It is desirable that the desorption be complete or that irreversibly held metal be kept to a minimum. In addition, it is desirable that the

least possible damage occurs to the adsorption properties of the adsorbent so as to allow the reuse of the adsorbent in subsequent adsorption-desorption cycles. The reuse capability would also improve substantially the economics of the adsorption process.

Palm oil fuel ash (POFA) obtained from boilers using oil palm waste as fuel and granular activated carbon derived from coconut shells have been shown to act as very effective adsorbent for a wide range of heavy metals. The adsorption equilibrium and kinetic aspects of the two adsorbents have been reported in detail (Chiew and Sekhar, 1996; Hashim *et al.*, 1996; Lee, 1999; Ng, 1999). In the present investigation, the desorption of copper and zinc from the two adsorbents was experimentally studied. A mineral acid, namely nitric acid, was tested for its desorption capability because of the familiarity of the waste treatment industry with its use and its relatively low cost. Furthermore, the available metal adsorption equilibrium data have suggested that hydrogen ions can compete very effectively with metals for the binding sites on POFA and activated carbon and result in reduced metal uptake at low pH values (Chiew and Sekhar, 1996; Hashim *et al.*, 1996). A relatively concentrated acid solution could therefore act as a desorbing agent.

3.2 Materials and Methods

3.2.1 Materials

The fly ash obtained from oil-palm waste products, called palm oil fuel ash (POFA) in this study, contains large amounts of partially burnt low-calorific waste like fibres, bark and shells. Table 3.1 summarises the properties of the POFA which was supplied by the Palm Oil Research Institute of Malaysia.

Table 3.1: Properties of the palm oil fuel ash (POFA).

Surface area, m^2/g	23.4
Weight loss on ignition	64%
Moisture content	6%
Size, mm	0.5 - 1.0

The granular activated carbon used in this study was derived from coconut shells and supplied by Phoenix Engineering, Klang, Malaysia. Its physical properties are listed in Table 3.2.

Table 3.2: Properties of the coconut shell-based activated carbon.

Surface area, m^2/g	1,100
Bulk density, g/cm^3	0.52
Pore volume, cm^3/g	6.62
Size, mm	0.5 - 1.0

Nitric acid, sodium hydroxide, copper nitrate trihydrate, zinc nitrate hexahydrate, copper and zinc standard solutions (1,000 mg/L) were of analytical reagent grade and supplied by Fluka Chemika (Switzerland). Cellulose nitrate membrane filters (0.45 μm) were obtained from Sartorius (Germany).

3.2.2 Methods

3.2.2.1 Preparation of POFA

The palm oil fuel ash (POFA) particles were washed with distilled water and dried in an oven. The particles were sieved in a mechanical shaker. POFA particles in the size range of 0.5 - 1.0 mm were used in the experiments.

3.2.2.2 Preparation of activated carbon

The activated carbon was washed with distilled water and crushed in a grinder. Particles in the size range of 0.5 - 1.0 mm collected from a mechanical sieve were dried in an oven and store until required.

3.2.2.3 Preparation of metal solutions

All glassware was washed with detergent and rinsed thoroughly with distilled water. They were then soaked overnight in 10% nitric acid and rinse with distilled water. 1000 ppm of metal stock solutions were prepared by dissolving copper nitrate trihydrate and zinc nitrate hexahydrate salts in distilled water. The solutions were acidified with 1 - 2 drops of concentrated nitric acid and store in the refrigerator prior use.

3.2.2.4 Adsorption experiments

The experimental conditions for adsorption are based on the results obtained in previous studies (Chiew and Sekhar, 1996; Hashim *et al.*, 1996). About 0.5 g of POFA or activated carbon was added to Erlenmeyer flasks containing 150 mL of zinc and copper solutions with a concentration of 20 mg/L (Zn = 305.95 μmol/L; Cu = 314.76 μmol/L). The initial pH of the solutions was fixed at 5.0. The flasks were agitated in a rotary shaker (ISV-1-V, Kuhnar, Switzerland) at 150 rpm and

25°C for a period of 24 hours. Previous studies indicate that adsorption equilibrium was reached within two hours of contact time in adsorption experiments using the coconut shell-based activated carbon (Chiew and Sekhar, 1996) while adsorption experiments based on the POFA adsorbent reached equilibrium within 40 min of contact time (Hashim *et al.*, 1996). Based on these kinetic studies, the contact time of 24 hours employed in the present study was more than enough to allow the adsorption to reach equilibrium.

At the end of the adsorption experiments, the metal solutions were filtered using membrane filters of 0.45 μm. The filtrates were analysed for their metal content by Inductively-Coupled Plasma Atomic Emission Spectro-photometry (ICP-AES) using a Baird ICP 2000 instrument (Baird, Switzerland). The amounts of metal loaded onto the adsorbents were determined from the difference in the initial and final equilibrium concentrations of the metal solutions.

3.2.2.5 Desorption experiments

In the present study, preliminary desorption experiments were conducted to investigate the effect of acid strength on the desorption behaviour of the POFA adsorbent initially loaded with zinc. Nitric acid solutions with acid strengths of 0.125%, 0.5%, 1.0% and 2.5% were tested for their effectiveness in stripping

adsorbed zinc from the POFA adsorbent. The zinc-laden adsorbent from the adsorption experiments were separated from the zinc solution and washed with distilled water to remove any zinc solution attached to the surface of the adsorbent. The adsorbent was then transferred to Erlenmeyer flasks containing 150 mL of nitric acid solution with a specified strength (0.125%, 0.5%, 1.0% and 2.5%). The flasks were agitated in a rotary shaker at 150 rpm and 25 °C for a contact period of 24 hours. At the end of the desorption period, the desorbing solutions were analysed for their zinc content by ICP-AES. The amounts of zinc desorbed were determined from the difference in the initial and final zinc concentrations of the desorbing solutions. To generate the time profiles of zinc and copper desorption from the POFA and activated carbon adsorbents, the zinc and copper-laden adsorbents from the adsorption experiments were transferred to Erlenmeyer flasks containing 150 mL of nitric acid solution with a strength of 0.125%. The flasks were agitated in a rotary shaker at 150 rpm and 25°C. The desorbing solutions were sampled at fixed time intervals to generate the desorption kinetic profiles. The experiments were terminated after a contact period of 24 hours. The samples were then analysed for their metal content by ICP-AES. An additional kinetic experiment was conducted using POFA loaded with zinc and nitric acid with a strength of 0.5% to investigate the effect of acid strength on desorption kinetics.

3.3 Results and Discussion

3.3.1 Adsorption of zinc and copper

Before conducting desorption studies, two sets of zinc and copper must first be loaded onto the two adsorbents, palm oil fuel ash (POFA) and coconut shell-based activated carbon respectively. The mean values of the adsorption results are shown in Table 3.3. The amount of metal loaded onto the adsorbent is expressed in terms of total amount of metal loaded as well as metal loaded per gram of adsorbent.

Table 3.3: Loading of zinc and copper onto POFA and activated carbon.

	POFA	Activated Carbon
Zinc		
a) Initial amount in solution	45.89 μmol	45.89 μmol
b) Final amount in solution	4.87 μmol	7.89 μmol
c) Amount loaded (a-b)	41.02 μmol	38.00 μmol
d) Amount loaded per gram $(\frac{c}{0.5})$	82.04 μmol/g	76.00 μmol/g
e) Percent loading $(\frac{c}{a} \times 100)$	89%	83%
Copper		
a) Initial amount in solution	49.58 μmol	49.58 μmol
b) Final amount in solution	2.21 μmol	1.76 μmol
c) Amount loaded (a - b)	47.37 μmol	47.82 μmol
d) Amount loaded per gram $(\frac{c}{0.5})$	94.74 μmol/g	95.64 μmol/g
e) Percent loading $(\frac{c}{a} x 100)$	96%	97%

Table 3.3 shows that both adsorbents have a slightly higher capacity for copper than for zinc. The two adsorbents were shown to remove a similar fraction of copper from solution. However, the POFA adsorbent was able to remove a larger fraction of zinc compared to the activated carbon, indicating that the POFA adsorbent is a more efficient adsorbent for zinc removal. This observation is interesting considering the fact that the activated carbon has a much larger specific surface area (1,100 m^2/g) owing to its porous structure than the POFA adsorbent which is essentially non-porous with a specific surface area of 23.4 m^2/g (Tables 3.1 and 3.2). It can therefore be concluded that most of the internal surface area of the activated carbon was probably not involved in metal uptake and that virtually all the metals were very likely loaded onto the external surface of the two adsorbents.

3.3.2 Desorption of zinc and copper

Nitric acid was selected as the desorbing agent in the course of the present work. Four acid concentrations of 0.125%, 0.5%, 1.0% and 2.5% were evaluated for their abilities to desorb zinc from the POFA adsorbent which had earlier been loaded with zinc. Results are presented in Figure 3.1 in terms of the amounts of zinc adsorbed and desorbed as well as on the basis of the desorption efficiency. The desorption efficiency reported in this study is defined as follows:

$$\text{Desorption Efficiency} = \frac{\text{Total amount of metal desorbed}}{\text{Total amount of metal loaded}} \times 100\% \qquad (3.1)$$

For these preliminary desorption experiments, it was assumed that the zinc-POFA system reached equilibrium after a contact period of 24 hours. The amount of zinc desorbed after 24 hours was therefore taken as the total amount of zinc desorbed. The justification for this assumption is discussed later.

Figure 3.1 shows that the desorption efficiencies for the 0.125% and 0.5% nitric acid solutions are about 95% while almost complete zinc desorption was obtained with the 1.0% and 2.5% desorbing solutions (desorption efficiency > 98%). For subsequent desorption experiments, it was decided to employ the 0.125% nitric acid as the desorbing agent because its desorption efficiency of 95% was considered satisfactory. In addition, the use of low strength nitric acid would increase substantially the cost effectiveness of the process.

Using the 0.125% nitric acid as the desorbing agent, further experiments were conducted to generate the kinetic profiles of zinc and copper desorption from the POFA and activated carbon adsorbents. Figures 3.2 and 3.3 show the time profiles of zinc and copper desorption from the two adsorbents.

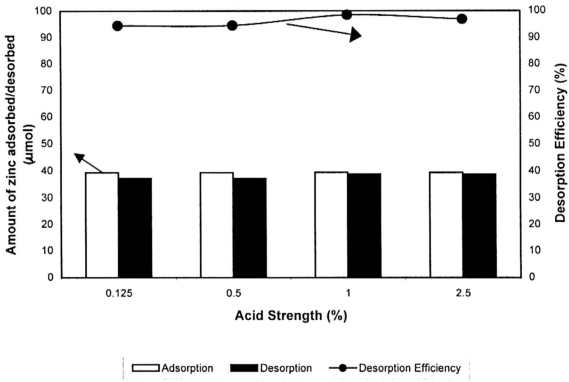

Figure 3.1: Effect of acid strength on the desorption of zinc from POFA.

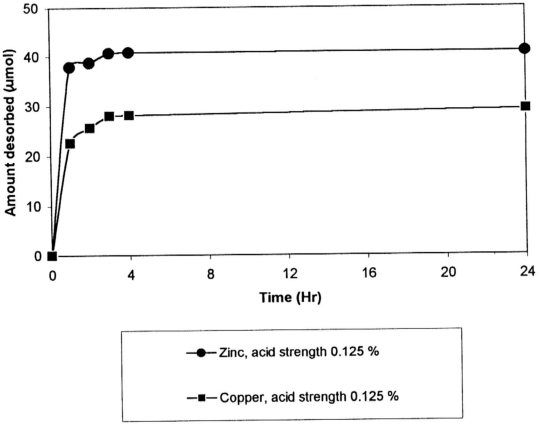

Figure 3.2: Kinetic profiles of zinc and copper desorption from POFA.

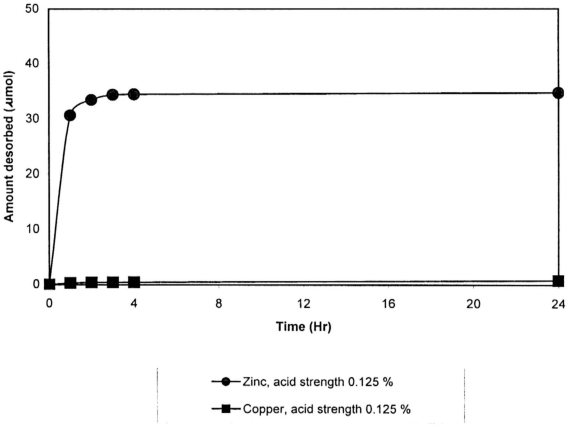

Figure 3.3: Kinetic profiles of zinc and copper desorption from activated carbon.

As seen in Figure 3.2, there was a rapid rate of zinc desorption within the first hour of contact time followed by a very slow rate of desorption up to a period of 24 hours when the experiment was terminated. At the first hour of contact, the amount of zinc desorbed from the POFA adsorbent reached 92% of the total amount desorbed over the entire period of 24 hours. The amount of zinc desorbed measured at the third, fourth and 24th hour of contact was very similar, indicating that the desorption process reached equilibrium after a contact period of three hours. The desorption efficiency for the zinc-POFA-0.125% nitric acid system calculated according to Equation (3.1) is approximately 99%, slightly higher than the 95% obtained from a similar experiment shown in Figure 3.1. This slight difference in desorption efficiency is expected due to possible variation in the properties of the POFA adsorbent which is a by-product of boilers which use various oil-palm waste products as fuel.

In the case of copper desorption from the POFA adsorbent, the kinetic profile is very similar to that of zinc desorption (Figure 3.2). A desorption pattern comprising a rapid rate of copper desorption within the first hour of contact followed by a very slow rate of desorption was again observed. At the first hour of contact, the amount of copper desorbed reached 77% of the total amount desorbed over 24 hours of contact. The desorption efficiency in this case is 62%, indicating that the 0.125%

nitric acid failed to strip 38% of the adsorbed copper from the POFA adsorbent although the system reached equilibrium within three hours of contact.

The results presented in Figure 3.2 indicate that the 0.125% nitric acid was an effective desorbing agent, yielding a desorption efficiency of 99% for the zinc-POFA system which reached equilibrium after three hours of contact. The kinetic result therefore justifies the use of a contact period of 24 hours in the preliminary experiments which investigated the effect of acid strength on zinc desorption from the POFA adsorbent (Figure 3.1). A contact period of 24 hours was in fact more than enough to ensure that equilibrium was attained. By contrast, the performance of the 0.125% nitric acid in the copper-POFA system was not satisfactory, yielding a desorption efficiency of 62%.

Another experiment was conducted to investigate the effect of acid strength on the kinetic profile of zinc desorption from the POFA adsorbent. Nitric acid with a strength of 0.5% was used to desorbed zinc initially loaded onto the POFA adsorbent. The kinetic profile is shown in Figure 3.4 for comparison. It is obvious that both the 0.125% and 0.5% nitric acid solutions produced almost identical kinetic profiles. It can be concluded that increasing the acid strength from 0.125% to 0.5% did not lead to faster desorption kinetics.

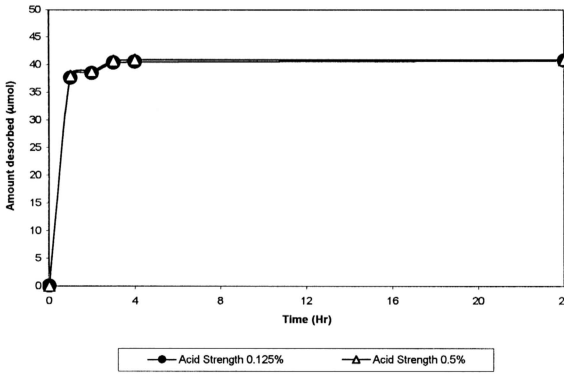

Figure 3.4: Kinetics profiles of zinc desorption from POFA.

The time profiles of zinc and copper desorption from the metal-laden activated carbon by the 0.125% nitric acid are shown in Figure 3.3. For the zinc-carbon system, the observed kinetic profile is similar to that of zinc desorption from the POFA adsorbent: a rapid rate of desorption followed by a very slow rate of desorption. The amount of zinc desorbed after one hour of contact reached 88% of the total amount desorbed over a period of 24 hours. The zinc-carbon system reached equilibrium after three hours of contact. The desorption efficiency estimated according to Equation (3.1) is 93%, indicating that the 0.125% nitric acid was effective in stripping adsorbed zinc from the activated carbon.

By contrast, Figure 3.3 clearly shows that the 0.125% nitric acid was a poor desorbing agent for the copper-carbon system. The nitric acid was shown to result in minimal copper desorption even after a contact period of 24 hours. The desorption efficiency calculated according to Equation (3.1) is about 2%.

The results presented in Figures 3.2 and 3.3 indicate that hydrogen ions are able to disrupt the attractive interactions between zinc and the functional groups on the surface of the two adsorbents responsible for binding. During desorption with the 0.125% acid, the increased competition towards zinc by the hydrogen ions for binding sites on the adsorbents can be driving forces that reverse the equilibrium in

favour of the liquid phase, thus returning the zinc initially held by the adsorbents back into solution. However, the hydrogen ions are not able to dislodge a large fraction of the adsorbed copper from the two adsorbents, especially in the copper-carbon system. This observation indicates that copper forms much stronger attractive interactions with the two adsorbents compared to zinc.

3.4 Conclusions

The experimental data and the analysis of the present work suggest the following conclusions:

1) Under the experimental conditions chosen for the desorption experiments, it was shown that a contact period of approximately three hours was sufficient to allow the zinc-POFA and copper-POFA systems to reach equilibrium using 0.125% nitric acid as the desorbing agent. Almost complete stripping of the adsorbed zinc from the POFA adsorbent was observed while the desorption efficiency for the copper-POFA system is about 62%. Increasing the acid strength from 0.125% to 0.5% in the zinc-POFA system did not lead to a faster desorption rate.

2) Desorption of zinc that has been taken up by the coconut shell-based activated carbon is possible by using 0.125% nitric acid as the desorbing agent. A contact

period of three hours was required to allow the desorption process to reach equilibrium. The desorption efficiency for the zinc-carbon system is 93%. By contrast, the 0.125% nitric acid was not able to strip adsorbed copper from the activated carbon. A very low desorption efficiency of 2% was obtained for the copper-carbon system.