

## CHAPTER FOUR

### REUSABILITY OF ADSORBENTS IN MULTIPLE CYCLES OF ZINC ADSORPTION AND DESORPTION

#### 4.1 General Background

To design and optimise a batch metal removal based on adsorption for commercial applications, it is important to elucidate the adsorption as well as desorption behaviour of the adsorbent so that the adsorbent can be reused in multiple cycles, increasing substantially the cost-effectiveness of the process. In addition, it is equally important to select an efficient and cost-effective desorbing agent to strip adsorbed metals from the adsorbent. The effectiveness of nitric acid as a desorbing agent in stripping adsorbed zinc and copper from the POFA and activated carbon adsorbents had already been investigated in detail in Chapter Three.

This Chapter addresses the issue of reusability of the two adsorbents in multiple cycles of zinc adsorption and desorption. The zinc-POFA and zinc-carbon systems were selected for further investigation because excellent desorption efficiency was obtained when nitric acid with a strength of 0.125% was employed as the desorbing agent, as reported in Chapter Three.

## 4.2 Materials and Methods

### 4.2.1 Materials

The two adsorbents used in this study were palm oil fuel ash (POFA) obtained from boilers using oil-palm waste products as fuel and granular activated carbon derived from coconut shells. The properties of the two adsorbents and information on all chemicals used in the course of this study had already been described in detail in Section 3.2.1, Chapter Three, and will not be repeated here.

### 4.2.2 Methods

Each of the two adsorbents was first loaded with zinc by conducting batch adsorption experiments. The initial zinc concentration and solution pH were fixed at 305.95  $\mu\text{mol/L}$  (20 mg/L) and 5.0. About 0.5 g of each adsorbent was added to a flask containing 150 mL zinc solution. The flasks were incubated according to the experimental conditions which have been found to be optimal for metal uptake by the POFA adsorbent (Hashim *et al.*, 1996) and activated carbon (Chiew and Sekhar, 1996). After equilibration, the slurry was filtered and the residual zinc concentration in the filtrate determined with an inductively coupled plasma spectrometer. The amount of zinc bound to the adsorbent was calculated from a mass balance.

The zinc-laden adsorbent was filtered and washed repeatedly with distilled water to remove any residual zinc solution attached to the adsorbent. After washing, excess water was removed from the adsorbent. The adsorbent was then placed in a flask containing 150 mL of nitric acid with a strength of 0.125%. The flask was incubated at 25 °C and 150 rpm for 24 hours. As reported in Chapter Three, three hours of contact time was in fact experimentally confirmed to be sufficient for the attainment of desorption equilibrium. A contact period of 24 hours used in the present study was therefore more than enough to allow the desorption process to reach equilibrium. Following desorption of the adsorbent with nitric acid, the slurry was filtered and the zinc concentration of the filtrate determined. The amount of desorbed zinc was calculated from a mass balance. The eluted adsorbent retained by the filter membrane was washed repeatedly with distilled water to remove any residual nitric acid attached to the adsorbent. The adsorbent was ready for reuse after removing excess water. The above adsorption and desorption procedures were repeated for another four cycles using the same adsorbent to assess the effect of desorption on the ability of the adsorbent to repeatedly take up zinc.

### **4.3 Results and Discussion**

The potential of multiple reuse of the POFA and activated carbon adsorbents was tested for five consecutive cycles of zinc adsorption and desorption. It has generally

been accepted that for a desorbing agent to be efficient it must fulfil the following two major criteria:

- 1) Complete desorption in each cycle; and
- 2) Metal uptake capacity of the adsorbent remains unchanged in each cycle.

A desorbing agent that can fulfil the above two requirements is considered a high-performance desorbing agent. The desorption efficiency defined according to Equation (3.1) in Chapter Three for a single cycle of adsorption-desorption can be used as a parameter to assess quantitatively whether a desorbing agent is able to meet the first criterion. The desorption efficiency of a cycle comprising one adsorption step and one desorption step can therefore be calculated according to Equation (3.1), reproduced here and labelled as Equation (4.1):

$$\text{Desorption Efficiency} = \frac{\text{Amount of metal desorbed in one cycle}}{\text{Amount of metal loaded in one cycle}} \times 100\% \quad (4.1)$$

The ability of a desorbing agent to meet the second criterion in multiple cycles of adsorption-desorption can be assessed on a quantitative basis by defining a parameter called 'adsorption efficiency':

$$\text{Adsorption Efficiency} = \frac{\text{Amount of metal loaded in higher cycle}}{\text{Amount of metal loaded in first cycle}} \times 100\% \quad (4.2)$$

Equation (4.2) allows one to assess the reusability of an adsorbent by comparing metal uptake in subsequent cycles to metal uptake by the virgin adsorbent in the first cycle.

The discussion of the experimental results presented in Chapter Three has suggested that 0.125% nitric acid was an effective desorbing agent for the recovery of zinc initially held by the POFA and activated carbon adsorbents in a single cycle of adsorption-desorption. The present work describes the results of the experimental investigation of zinc desorption and reloading in five consecutive cycles of adsorption-desorption using 0.125% nitric acid as the desorbing agent.

Figures 4.1 and 4.2 show the experimental results obtained for the zinc-POFA and zinc-carbon systems, respectively. The open bars depict the amount of zinc adsorbed while the solid bars represent the amount of zinc desorbed in each cycle. In both systems, Figures 4.1 and 4.2 clearly show a drastic decrease in zinc uptake after the first cycle of adsorption-desorption.

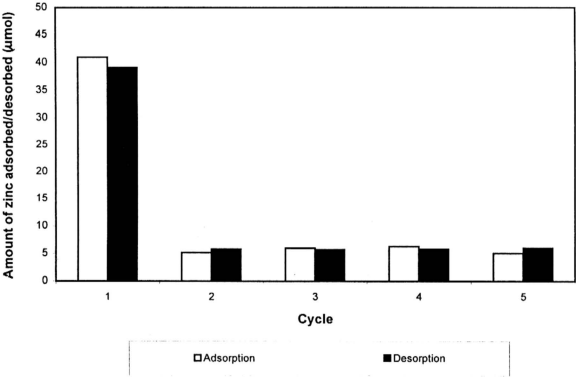


Figure 4.1: The amount of zinc adsorbed and desorbed from POFA during five cycles of adsorption-desorption.

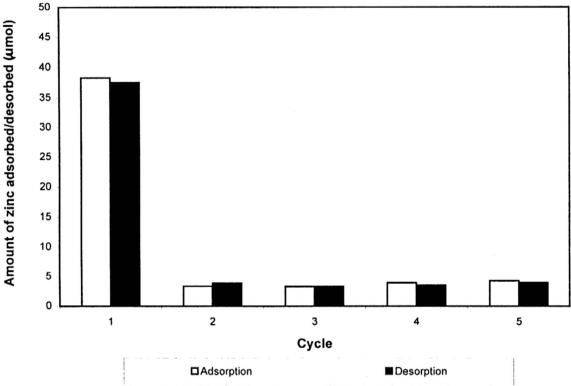


Figure 4.2: The amount of zinc adsorbed and desorbed from activated carbon during five cycles of adsorption-desorption.

The results presented in Figures 4.1 and 4.2 were analysed on a quantitative basis according to Equations (4.1) and (4.2). Calculated values of the desorption and adsorption efficiencies of the five cycles are tabulated in Tables 4.1 and 4.2.

Table 4.1: Desorption efficiency and adsorption efficiency of the zinc-POFA system.

Cycle	Desorption Efficiency (%)	Adsorption Efficiency (%)
1	96	-
2	112	13
3	96	15
4	93	15
5	119	12

Table 4.2: Desorption efficiency and adsorption efficiency of the zinc-carbon system.

Cycle	Desorption Efficiency (%)	Adsorption Efficiency (%)
1	98	-
2	116	9
3	100	9
4	89	10
5	93	11



Tables 4.1 and 4.2 show that the desorption efficiency ranges from 93 to 119% for the zinc-POFA system and from 89 to 116% for the zinc-carbon system, indicating that the 0.125% nitric acid was effective in stripping adsorbed zinc from the two adsorbents over consecutive cycles of adsorption-desorption. An interesting trend in desorption was observed in Cycles 2 and 5 in the zinc-POFA system and in Cycle 2 in the zinc-carbon system: the amount of zinc desorbed was higher than the amount of zinc adsorbed (desorption efficiency > 100%). The excess zinc must have come from the zinc that was not desorbed in the preceding cycles. For example, a fraction of the zinc loaded in the first cycle remained with the adsorbent following the application of the desorbing agent. This fraction of zinc together with zinc loaded in the second cycle was stripped off in the desorption step of the second cycle.

Table 4.3 shows the cumulative amounts of zinc adsorbed and desorbed over the entire five cycles. The quantity of zinc desorbed over the five cycles was very close to the quantity loaded, indicating that almost complete desorption was eventually achieved. It is clear that zinc uptake by the two adsorbents is reversible with very little accumulation of irreversibly bound zinc on the adsorbents. This observation indicates that the 0.125% nitric acid desorbing agent has successfully fulfilled the first criterion stated earlier, i.e., complete desorption of adsorbed metal.

Table 4.3: Total amounts of zinc adsorbed and desorbed over five cycles of adsorption-desorption.

System	Zinc Loaded ( $\mu\text{mol}$ )	Zinc Desorbed ( $\mu\text{mol}$ )
Zinc-POFA	63.36	62.35
Zinc-Carbon	53.08	52.12

Tables 4.1 and 4.2 show that while the 0.125% nitric acid was efficient in releasing the adsorbed zinc into solution in each cycle, its application negatively affected subsequent zinc uptake (reloading) of the two adsorbents. After the first cycle, zinc uptake by the POFA adsorbent in Cycles 2 - 5 was reduced to 12 - 15% of the original zinc uptake observed in the first cycle. A similar reduction was observed in the zinc-carbon system with adsorption efficiencies ranging from 9 to 11% in Cycles 2 - 5.

It appears that a 90% loss in zinc uptake by the two adsorbents from the second cycle onwards was observed when 0.125% nitric acid was used as the desorbing agent. This drastic reduction is very significant for process applications since it allows only 10% of the adsorbent capacity to be reused in multiple cycles of adsorption-desorption. Such a low reusable portion of the adsorbent capacity can increase substantially the cost of a technical application of the process. The adsorbent would have to be replaced on a frequent basis due to its short service life

time, making the economics of the process unfavourable owing to the high cost of the adsorbent. This is especially true in the case of the activated carbon adsorbent whose cost is much higher than that of the POFA adsorbent.

The results presented in Figures 4.1 and 4.2 therefore suggest that the 0.125% nitric acid desorbing agent has failed to meet the second criterion which requires a desorbing agent to cause little reduction in the metal uptake capacity of an adsorbent in multiple cycles of adsorption-desorption.

The drastic reduction in the zinc reloading capacity of the two adsorbents may be attributed to one or both of the following possible causes:

- 1) Release of residual nitric acid during the zinc uptake step in Cycles 2 - 5; and
- 2) Damage to functional groups responsible for zinc binding following the stripping of adsorbed zinc in the first cycle.

Following the stripping of adsorbed zinc with nitric acid in each cycle, the adsorbent was repeatedly washed with distilled water to remove any residual acid adhered to the structure of the adsorbent. The adsorbent was then reloaded with zinc. If the nitric acid was not completely removed, the release of the residual acid during the zinc reloading step would lower the pH of the zinc solution. At low pH

values, it has been reported that metal uptake by the two adsorbents was generally low (Hashim *et al.*, 1996; Chiew and Sekhar, 1996).

Figure 4.3 shows the solution pH measured at the end of the zinc uptake step in each cycle. The initial pH of the zinc solution was fixed at 5.0. In both the zinc-POFA and zinc-carbon systems, the solution pH increased to 6.6 - 6.8 at the end of the zinc uptake step in the first cycle (the fresh adsorbent had not been exposed to nitric acid). By contrast, the zinc uptake step in Cycles 2 - 5 resulted in solution pH values ranging from 3.5 to 3.6 for the zinc-POFA system and from 3.3 to 3.4 for the zinc-carbon system. The observed very limited zinc uptake in Cycles 2 - 5 could therefore be the result of low solution pH values which inhibit metal uptake. The drop in pH values may be attributed to the release of residual nitric acid which was not removed in the preceding desorption step. The results obtained were in agreement with that of Netzer and Hughes (1984) where at pH around 3, there was only slight metal adsorption. At pH 4 and above, there was a dramatic increase in metal adsorption

A large fraction of the functional groups on the surface of the two adsorbents responsible for zinc binding could have been destroyed by the 0.125% nitric acid solution following the stripping of the adsorbed zinc in the first cycle. Repeated

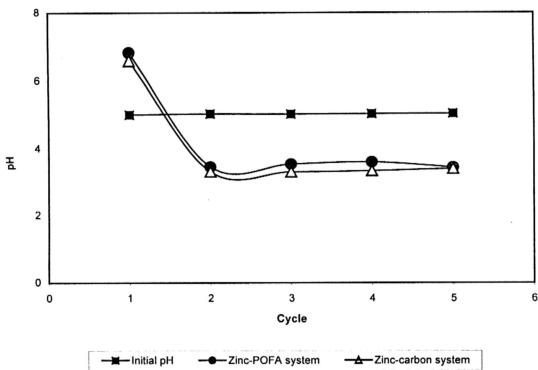


Figure 4.3: Solution pH measured at the end of the zinc loading step in five cycles of adsorption-desorption.

exposure of the adsorbents to a strong acidic environment could lead to a reduction in the number of metal binding sites on the adsorbents. Consequently, the zinc reloading capacity of the two adsorbents was severely reduced, limiting zinc uptake in Cycles 2 - 5.

#### **4.5 Conclusions**

Nitric acid solution with a strength of 0.125% was found to be effective in stripping adsorbed zinc from the POFA and activated carbon adsorbents over five consecutive cycles of adsorption-desorption. The quantity of zinc desorbed over the five cycles corresponded well to the quantity loaded, indicating that almost complete recovery of the adsorbed zinc from the two adsorbents was readily achieved. Unfortunately, following the completion of the first cycle the zinc uptake capacity of the two adsorbents deteriorated drastically in subsequent cycles. It was found that less than 15% of the zinc uptake capacity of the fresh POFA adsorbent and less than 11% of the zinc uptake capacity of the fresh activated carbon could be reused in Cycles 2 - 5. It can therefore be concluded that the 0.125% nitric acid does not appear to be very attractive as a desorbing agent although it possesses excellent desorption efficiency. Two possible causes for the observed drastic reduction in zinc uptake by the two adsorbents were proposed. Firstly, the very high hydrogen ion concentration of the desorbing solution could be damaging to a large fraction of

the zinc binding sites on the adsorbents. These binding sites lost their ability to re-adsorb zinc in subsequent cycles. Secondly, during the zinc uptake step the release of residual nitric acid from the adsorbent particles which had been subjected to the nitric acid treatment in the preceding cycles could have caused a reduction in solution pH which inhibits zinc uptake.