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## Removal of Copper, Lead, and Cadmium Ions in a Fluidized Bed

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### ABSTRACT

In this study, the recovery of copper from synthetic wastewaters prepared from  $\text{CuSO}_4$  was studied using a fluidized bed containing hydrogen-based solid Amberlite. The effects of operating parameters including liquid flow rate, initial copper ions concentration, pH of the influent solution, and Amberlite weight on the breakthrough curves were investigated. It was found that the copper uptake increased with the increase in Amberlite weight, the decrease in initial copper concentration, and decrease in liquid flow rate, but there was no affect with solution influent pH. The recovery of cadmium and lead ions prepared from  $\text{CdSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$ , respectively, was also investigated. Comparison between the adsorption of

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$\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  showed that the adsorption capacity followed the following order:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . It was found that the order of adsorption was independent of the flow rate or the initial feed concentration.

**Key Words:** Adsorption; Fluidization; Waste water; Industrial waste; Heavy metals.

## INTRODUCTION

Contamination of surface waters due to wastewater discharge containing heavy metals is becoming a universal problem. The presence of heavy metals at even very low concentration can cause many ecological and health problems. Copper, cadmium, and lead are examples of these toxic heavy metals. In humans, copper can cause serious problems, such as stomach intestinal distress, kidney damage, and anemia. Studies on humans and experimental animals showed that cadmium has a potential for carcinogenic effects.<sup>[1]</sup>

Different treatment methods have been used and developed for the removal of these heavy metals from aqueous solutions. These methods include chemical precipitation, reverse osmosis, ion exchange, electrodialysis, and adsorption. Adsorption is a well-known equilibrium separation process that has been proven to be effective for heavy metals removal. Abu Al-Rub et al.<sup>[2,3]</sup> have proven the suitability of using adsorption on sheep manure wastes to remove nickel and cadmium. Kandah et al.<sup>[4]</sup> used the sheep manure wastes for the simultaneous removal of nickel–copper and nickel–cadmium from wastewaters. Tee and Khan<sup>[5]</sup> investigated the removal of heavy metals, such as lead, cadmium, and zinc, from wastewater using waste tea leaves. Ferro-Garcia et al.<sup>[6]</sup> studied the removal of heavy metals by adsorption on activated carbons obtained from agricultural by-products, such as almond shells, olive stones, and peach stones. Tobin et al.<sup>[7]</sup> studied the use of *Rhizopus arrhizus* biomass in the removal of heavy metals from wastewater. Reed et al.<sup>[8]</sup> investigated the removal of cadmium ions from aqueous solutions by adsorption on granular activated carbon. Ho and McKay<sup>[9]</sup> studied the removal of lead ions by adsorption on peat.

Ion exchange is another common method used for heavy metal removal. Loureiro et al.<sup>[10]</sup> used the chelating resin Doulite ES 346 for the recovery of individual heavy metals, such as copper, zinc, and lead, from a solution using a packed bed. However, packed beds have some disadvantages, such as high pressure drop and clogging of the beds,<sup>[11]</sup> that may limit their use. Alternatively, ion exchange fluidized beds (IEFBs) do not have such limitations. Hwang et al.<sup>[11]</sup> used a fluidized bed ion exchange for the removal of copper and nickel ions from wastewater.

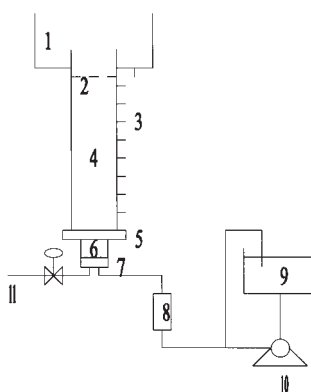


This study aimed at investigating the removal of three individual heavy metals, namely, copper, cadmium, and lead, by IEFB. The effects of different physical and chemical parameters, such as metal concentration, flow rate, and pH, on the performance of the IEFB was studied.

### EXPERIMENTAL PART

The fluidized bed used in this study was a cylinder made of Plexiglas of 1.5 m in length and 0.08 m inner diameter. A liquid distributor was placed at the bottom where a mesh of 0.1 mm in diameter was fixed over it to arrest the flow of fine particles. Glass beads were packed between the mesh and the distributor. At the top of the fluidized bed, a retaining grid was also fixed. Eight holes, 0.15 m apart, were made between the mesh and the retaining grid. A rubber cork, through which a needle could be inserted to withdraw liquid samples for analysis purposes, closed the holes. The reasons for making eight holes was to allow taking more than one sample at the same time and to allow withdrawing samples from the section above the expanded bed (Fig.1).

Adsorption studies on hydrogen-based Amberlite (1R 120 LR S. D. Fine Chem. Ltd.) were carried out using stock water solutions of various concentrations of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , or  $\text{Cd}^{2+}$  ranging from 50 to 170 ppm. The Amberlite had a density of  $1300 \text{ kg/m}^3$ . Its average-particle diameter was  $5 \times 10^{-4} \text{ m}$  and its adsorption capacity for  $\text{Cu}^{2+}$  was  $3.64 \times 10^{-5} \text{ kg Cu}^{2+}/\text{kg Amberlite}$ . Adsorption isotherms of such Amberlite were studied elsewhere.<sup>[11]</sup> The feed



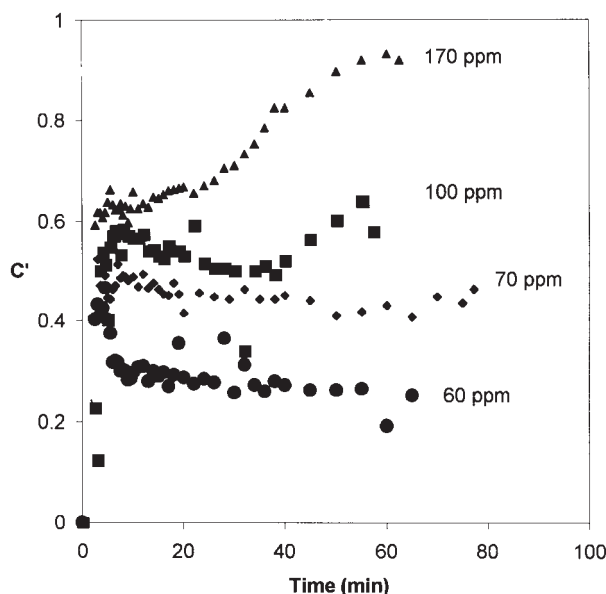
**Figure 1.** Schematic diagram of the apparatus used. (1) Overflow reservoir; (2) retaining grid; (3) sampling ports; (4) fluidized bed; (5) mesh; (6) glass bead; (7) liquid distributor; (8) rotameter; (9) feed tank; (10) pump; (11) drain.

solutions were prepared from  $\text{CuSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{CdSO}_4$ , respectively. The effect of the flow rate was studied by carrying out the experiments at different flow rates ranging from 4 to 9 L/min. These flow rates correspond to 2–4.5 times the minimum fluidization flow rate (2 L/min). The concentration of the ions in the feed and the effluent streams was measured by taking samples and analyzing them using an atomic absorption spectrophotometer. Some of the experiments were duplicated to confirm the reproducibility of the experimental results.

The effect of the amount of the adsorbent was studied by charging the bed with 100, 150, and 200 g of Amberlite. These amounts of Amberlite occupy 1.3%, 1.9%, and 2.6% of the total bed volume, respectively. The effect of pH was also studied by performing experiments at pH values ranging from 2 to 6. All of the experiments were performed at room temperature.

## RESULTS AND DISCUSSION

Figure 2 shows the effect of the initial  $\text{CuSO}_4$  on the efficiency of  $\text{Cu}^{2+}$  adsorption on Amberlite surface at a feed flow rate of 4 L/min,

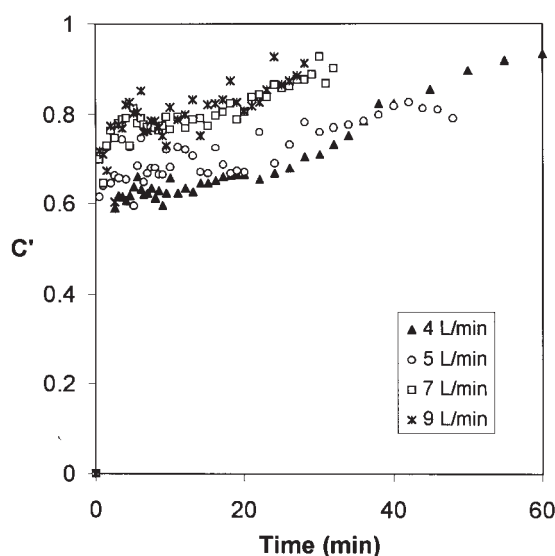


**Figure 2.** Dimensionless concentration of  $\text{Cu}^{2+}$  vs. time for various feed concentration. The feed flow rate is 4 L/min, pH = 5.78, and the weight of Amberlite is 100 g.



pH = 5.78, and the weight of Amberlite is 100 g. As can be seen from the figure, the  $\text{Cu}^{2+}$  concentration in the effluent stream was larger as the initial  $\text{Cu}^{2+}$  concentration was raised. It is obvious that due to the availability of  $\text{Cu}^{2+}$ , the surface of the Amberlite reached saturation and no more  $\text{Cu}^{2+}$  could be adsorbed, leading to higher  $\text{Cu}^{2+}$  in the effluent stream.

The effect of the feed flow rate on the efficiency of  $\text{Cu}^{2+}$  adsorption for feed concentration of 170 ppm, pH of 5.78, and bed weight of 100 g Amberlite is depicted in Fig. 3. It can be seen from Fig. 3 that as the flow rate increased, the concentration of  $\text{Cu}^{2+}$  in the effluent stream was higher. One would expect that more  $\text{Cu}^{2+}$  would be adsorbed as the flow rate increases since the diffusion rate is usually proportional to the flow rate. Moreover as the flow rate increases the bed expands, giving more time for the liquid in the bed,  $L_{\text{bed}}/v$ . The above two points result in lower  $\text{Cu}^{2+}$  concentration in the effluent stream. However, as the flow rate increases, the copper ions are not given enough time to diffuse toward the resin surface, leading to higher  $\text{Cu}^{2+}$  concentration in the effluent stream. A competition between the facts exists, leading to the trend exhibited in Fig. 3. The trend can be also explained from another point of view, as follows. As the flow rate increases, more  $\text{Cu}^{2+}$  is fed to the bed. This is equivalent to increasing the feed concentration,



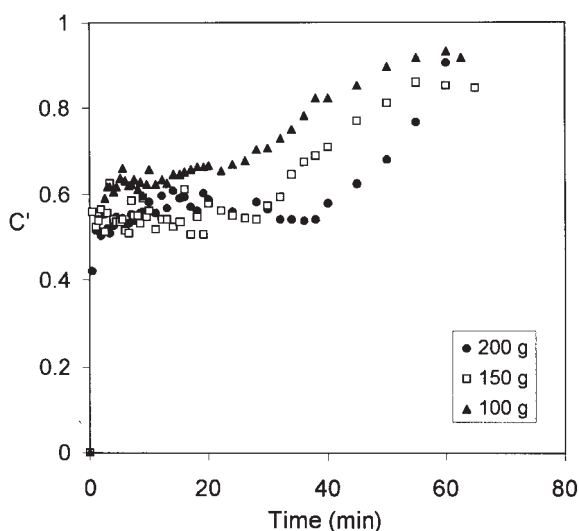
**Figure 3.** Dimensionless concentration of  $\text{Cu}^{2+}$  vs. time for various feed flow rates. The feed concentration is 170 ppm, pH = 5.78, and the bed contains 100 g of Amberlite.



which leads to higher  $\text{Cu}^{2+}$  concentration in the effluent stream, similar to the results shown in Fig. 2. It should be mentioned that Hwang et al.<sup>[11]</sup> found that as the flow rate increases, the concentration of  $\text{Cu}^{2+}$  was lower. A result opposite to the one found in this study. They explained the results by the fact that the residence time is larger due to bed expansion, only without mentioning the other two factors.

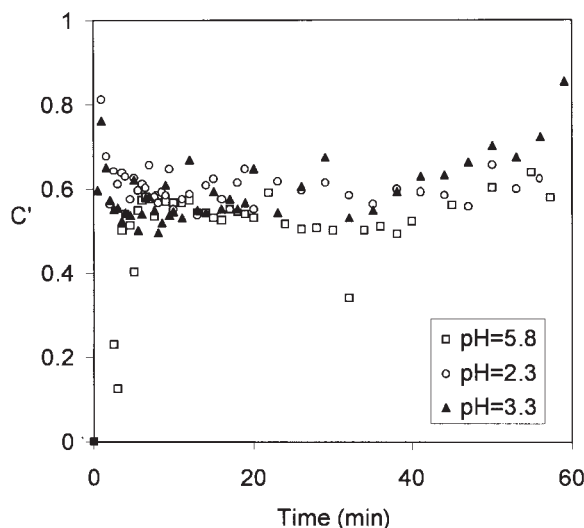
The effect of the amount of resin charged to the bed at a flow rate of 4 L/min, pH of 5.78, and feed concentration of 170 ppm  $\text{Cu}^{2+}$  is portrayed in Fig. 4. As expected, the larger the amount of resin (indicating the higher the surface area available for adsorption), the more the  $\text{Cu}^{2+}$  was adsorbed. This results in a lower  $\text{Cu}^{2+}$  concentration in the effluent stream, which agrees with the results obtained by Hwang et al.<sup>[11]</sup>

The effect of the pH of the feed on the adsorption at a flow rate of 4 L/min, Amberlite weight of 100 g, and feed concentration of 170 ppm  $\text{Cu}^{2+}$  is shown in Fig. 5. As can be seen from the figure, the initial pH has no influence on the rate of adsorption. This is due to the fact that the pH of the liquid phase in the fluidized bed is determined mainly by the amount of  $\text{H}^+$  released from the resins, and this pH is constant for various values of the pH of the inlet solution used in experiments. Therefore, the breakthrough curve of  $\text{Cu}^{2+}$  was not affected by the pH of the influent solution.



**Figure 4.** Dimensionless concentration of  $\text{Cu}^{2+}$  vs. time for various Amberlite weights. The feed flow rate is 4 L/min, feed concentration = 170 ppm, and pH = 5.78.





**Figure 5.** Dimensionless concentration of  $\text{Cu}^{2+}$  vs. time for various pH value of the feed. Feed flow rate = 4 L/min, concentration = 170 ppm, and weight of Amberlite = 100 g.

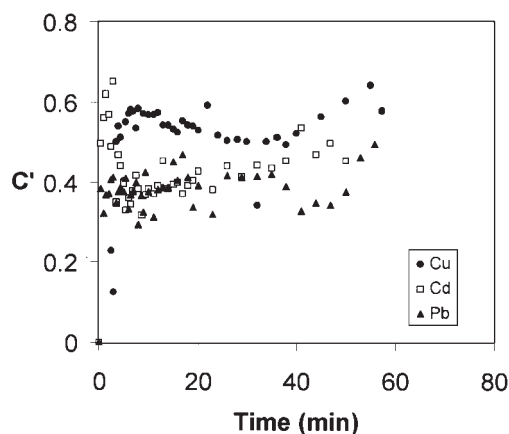
Adsorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  at an initial concentration of 100 ppm, a flow rate of 4 L/min, pH of 5.78, and Amberlite weight of 100 g for each case was also performed. A comparison between the adsorption of the three ions ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ ) is shown in Fig. 6. It can be noticed that the adsorption rate of the ions follows the following order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . This indicates that the adsorption rate is directly proportional to the size of the ion, implying that the adsorption process was not diffusion controlled. The same result was obtained when the experiments were repeated at an initial concentration of 150 ppm, a flow rate of 4 L/min and weight of Amberlite of 100 g, as shown in Fig. 7. To further fortify this point, the experiments were repeated at 100 ppm, weight of Amberlite of 100 g, pH of 5.78, and a flow rate of 8 L/min, as shown in Fig. 8. It can be seen that the order of adsorption was still the same.

## CONCLUSION

From the results obtained in this research, the following can be concluded. Heavy metals, such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ , can be removed from

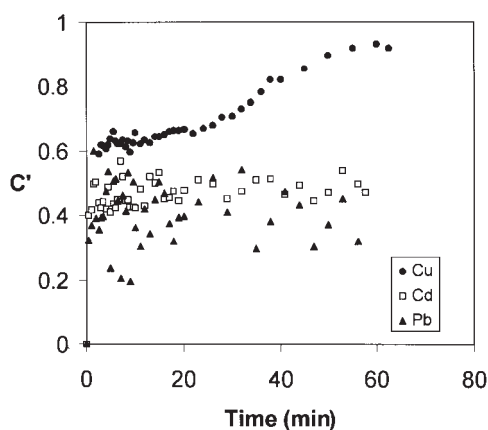






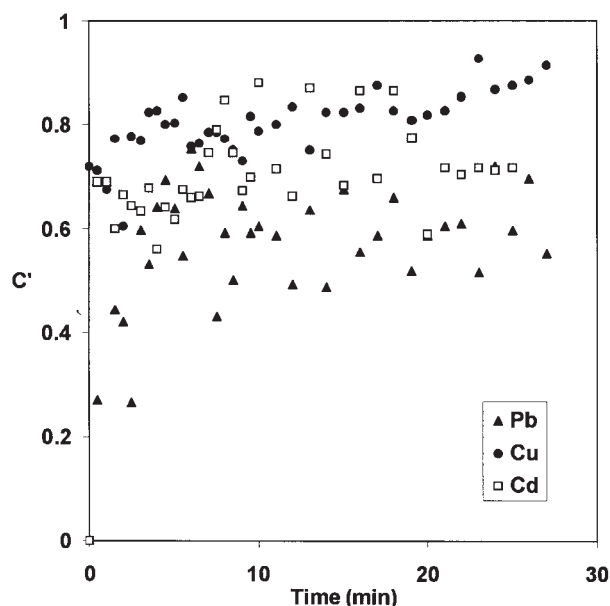
**Figure 6.** Dimensionless concentration of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  vs. time at a flow rate of 4 L/min and initial concentration of each ion of 100 ppm. The pH = 5.78 and the weight of Amberlite = 100 g.

wastewater in a fluidized bed. The adsorption rate is proportional to the amount of resin. The pH value has no influence on the adsorption of  $\text{Cu}^{2+}$  to Amberlite. In the range of flow rate studied, adsorption of  $\text{Cu}^{2+}$  ions was inversely proportional to the flow rate. The adsorption of the ions studied in this research followed the following order:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . Under



**Figure 7.** Dimensionless concentration of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  vs. time at a flow rate of 4 L/min and initial concentration of each ion of 150 ppm. The pH = 5.78 and weight of Amberlite = 100 g.





**Figure 8.** Dimensionless concentration of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  vs. time at a flow rate of 8 L/min and initial concentration of each ion of 100 ppm. The pH = 5.78 and weight of Amberlite = 100 g.

the experimental conditions studied in this research, the adsorption process was not diffusion controlled.

## NOMENCLATURE

$C'$	dimensionless concentration = $C(t)/C_0$
$C_0$	initial concentration, ppm
$L_{\text{bed}}$	bed length, m
$v$	fluidization velocity, m/s

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