Removal and Recovery of Lead from Aqueous Solution by Low Cost Media

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Abstract: Problem statement: To remove Pb(II) from wastewater using local UAE sand and then to recover the removed Pb(II). **Approach:** Removal efficiency of Pb(II) from wastewater was investigated using white, yellow and red United Arab Emirates sand with pore sizes < 300 μm. Two methods were employed: batch equilibrium and column filtration. In the batch equilibrium study, the effect of sand type and dosage on Pb(II) removal efficiency was investigated. In the column filtration study, removal efficiencies were measured using yellow sand at 0.100 dm^3 intervals while continuously injecting 300 ppm Pb(II) solution into the column. Pb(II) concentrations were determined using inductively coupled plasma- atomic emission spectrometer (ICP-AES). Measurements were carried out until saturation of the column by Pb(II) was attained. Recovery efficiency of Pb(II) was initially investigated using distilled water, 0.100 mol dm^{-3} HNO$_3$ and pH 8.0 aqueous solutions. Recovery via chelation with Ethylenediaminetetraacetic Acid (EDTA) was then attempted. **Results:** Batch experiments showed that yellow sand was more efficient than either white or red sand in removing Pb(II), with a maximum removal capacity of 0.030 kg Pb(II) per kg yellow sand. Accordingly, yellow sand was selected for column filtration experiments. In column filtration, the removal capacity rose to a maximum of 0.086 kg Pb(II) per kg sand. When sand containing removed Pb(II) in batch experiments was equilibrated overnight with EDTA solutions in stoichiometric excess, 86.6% recovery was observed. By comparison, recovery using EDTA in column filtration was 94.7%. Recovery by injection of either water or 0.100 mol dm^{-3} HNO$_3$ solution was either negligible or much lower than that obtained with EDTA. **Conclusion:** Column filtration using UAE yellow sand is an efficient and inexpensive method to remove Pb(II) from wastewaters. Pb(II) can be efficiently recovered from yellow sand columns by chelation with EDTA.

Key words: UAE sand, lead removal, lead recovery, Ethylenediaminetetraacetic Acid (EDTA), recovery agents, recovery heavy metals, non-renewable resources, aqueous mixtures, sieved using brass, distilled water, Column filtration, contaminating groundwater, dilute EDTA solution

INTRODUCTION

Heavy metals are released into the environment by many industrial activities in both developed and developing countries, contaminating groundwater and soil. Lead is a ubiquitous heavy metal, used by humans since ancient times. As is the case with other heavy metals, such as cadmium, chromium, copper and mercury, lead is found in most contaminated sites and it poses a hazard to human and animal health. Exposure to high level of lead causes intellectual and other neurologic defects. Heavy metals can be removed from aqueous solutions by adsorption and/or filtration on different substrates. The possibility to use low cost substrates to remove lead is thus of particular significance (Issabayeva *et al.*, 2006; 2010; Hussain *et al*., 2009; Pandley *et al.*, 2009; Zwinowanda *et al*., 2010).

The removal efficiency of several heavy metals from aqueous mixtures by sands from the United Arab Emirates (UAE) has been investigated and reported by researchers from this laboratory (Pappalardo *et al*., 2010; Khamis *et al*., 2009). A recent issue of interest is the possibility of recovery of heavy metals from substrates. Indeed, substrates used in the removal of these metals are not easily disposed of safely in the environment. In addition, some heavy metals are considered non-renewable resources (Jnr *et al.*, 2006;

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Pandey *et al.*, 2009). This study aims to investigate the removal and recovery of lead from aqueous solutions by using UAE sands as substrates and acidic and chelating reagents as recovery agents.

MATERIALS AND METHODS

All primary chemicals used were of analytical reagent grade. $Pb(NO_3)_2$ was purchased from Pancreac (Spain). Ethylenediaminetetraacetic Acid (EDTA) was purchased as the disodium salt from VWR (England). White, yellow and red sand grab samples were obtained from several locations within the UAE and randomized.

Metal ion concentrations were determined using a Varian Liberty axial sequential inductively coupled plasma-atomic emission spectrometer "ICP-AES" (Australia). pH was measured on a 550A Thermo Orion pH meter (USA) equipped with a combined glass electrode. Solutions were shaken at $25.0 \pm 0.1^{o}C$ using an Edmund Buhler KS-15/TH-15 shaker (Germany). Sand samples were sieved by means of impact test sieves from Standard Sieve (USA), mesh model BS410, 1986 ST. Solutions were injected continuously into the column using a peristaltic pump Master flex C/L 300 RPM, Cole Parmer (USA).

Sand samples were successively sieved using brass frames with sieve sizes 600, 300, 150 and 75 μm. For each sand type, the three fractions with pore sizes less than 300 μm were combined and used in Pb(II) removal experiments. Prior to removal by either batch equilibration or column, each sand sample was washed repeatedly with deionized distilled water and dried to a constant weight at 110°C.

All batch equilibrations were performed on 0.100 dm^3 aqueous solutions containing 300 ppm Pb(II). The pH of all mixtures was adjusted to 4.0 using 50% (v/v) HNO_3. Sand dosages were varied in the range 0-0.040 $kg\ dm^{-3}$. Experiments were conducted using a batch reaction process in triplicate. A known mass of sand was added to the Pb(II) solution in a 0.250 dm^3 flask and then shaken at $25.0^{o}C$ for 2 h at 200 rpm. Following equilibration, ion concentrations were determined using ICP.

Subsequently, the supernatant liquid was decanted and 0.100 dm^3 each of distilled water, 0.100 M HNO_3 and aqueous pH 8.0 solution were added in three separate experiments and the flask was again shaken for 2 h. In each case Pb(II) was determined in the solution. Next, Pb(II) recovery was attempted by adding 0.100 dm^3 of 0.010 mol dm^{-3} EDTA to the sand. The flask containing EDTA was shaken for two periods at

25.0°C: 2 h and overnight. Following each shaking period, the liquid was decanted and the Pb(II) in the solution determined.

Pb(II) removal was also investigated using a column 0.025 m in diameter containing yellow sand to a height of 0.050 m. Yellow sand was selected because equilibration data showed its Pb(II) removal efficiency to be highest. After washing the column with 1.5 dm^3 of distilled deionized water, 300 ppm Pb(II) solution was added to the column, using a peristaltic pump. The flow rate was adjusted to 0.30 $dm^3\ h^{-1}$. The quantity of Pb(II) present in the effluent was measured at 0.100 dm^3 intervals. Addition of solution and measurement of Pb(II) concentration was continued until saturation was attained.

Recovery of Pb(II) that was removed by yellow sand inside the column was investigated as follows: the column was first washed with 0.500 dm^3 distilled deionized water followed by the same volume of 0.100 mol dm^{-3} HNO_3. In each case the effluent was analyzed for Pb(II). This was followed by the injection of aqueous EDTA at pH 8.0. The concentration of Pb(II) recovered in the effluent was measured at 0.025 dm^3 intervals. In all cases, the injection flow rate was maintained at 0.30 $dm^3\ h^{-1}$.

RESULTS

Table 1 gives the percent retention of the three sand types on each of the brass frames and in the pan (< 75 μm). All experimental results were obtained on the combined lowest three portions in the Table, i.e., particle size less than 300 μm.

Batch equilibrium: The dependence of Pb (II) removal efficiency on sand dosage for the three sand types is shown in Fig. 1. It is apparent that, for all sand dosages, the removal efficiency of yellow sand is significantly higher than that of either white or red sand. For example, at a sand dosage of 0.0060 kg dm^{-3}, removal efficiencies were 37.9, 76.0 and 28.2 for white, yellow and red sands, respectively. Additionally, white sand is more efficient than red sand at low sand dosages but this is reversed at sand dosages above 0.014 kg dm^{-3}.

Table 1: Percent retention on sieves for white, yellow and red sands

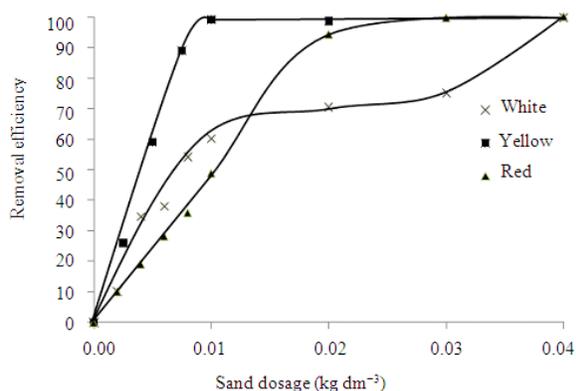| Sieve size (μm)	Percent retention		
	White sand	Yellow sand	Red sand
600	0.04	0.02	0.06
300	0.52	6.27	5.30
150	38.49	34.84	65.74
75	58.45	56.18	26.42
Pan (< 75 μm)	2.21	2.50	2.21

Fig. 1: Pb(II) removal efficiency in batch equilibrium experiments as a function of white, yellow and red sand dosage. Volume of solution = 0.100 dm^3. Initial [Pb(II)] = 300 ppm. T= 25.0°C. Equilibration time: 2 h
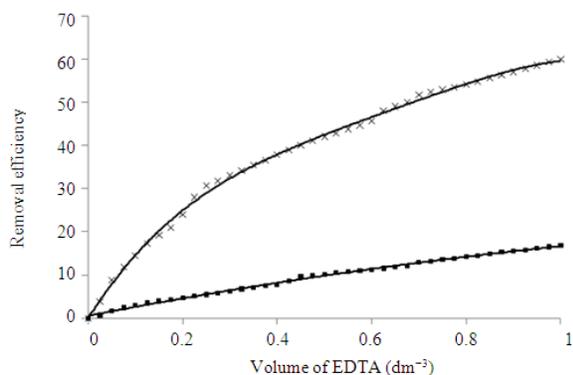

Fig. 2: Pb(II) recovery efficiency in column filtration experiments with 0.010 and 0.100 mol dm^{-3} EDTA pH=8.0. Pb(II)= 3.30×10^{-3} kg, yellow sand: 0.0385 kg. Flow rate 0.30 dm^3 h^{-1}, T= 25.0°C

The maximum removal capacity of yellow sand in the batch equilibration experiments, defined as mass of lead removed/mass of sand present in the batch, is found to be 0.030 kg Pb(II)/kg sand.

Sand column filtration: Under industrial conditions it is more practical to use columns, rather than batch equilibration, to treat wastewater containing heavy metals. Since yellow sand exhibited the highest Pb(II) removal efficiency, it was selected for column filtration experiments. It was found that saturation of the 0.050 m column containing 0.0385 kg yellow sand was attained after the injection of 11.0 dm^3 of the 300 ppm Pb(II)

solution. The removal capacity of yellow sand, as determined by the first appearance of Pb(II) in the effluent, as detected on ICP, was found to be 0.086 kg Pb(II) /kg sand.

Lead recovery after batch equilibrium: Following equilibrium in batches, the solution was filtered and the yellow sand was equilibrated for 2 h in the shaker, in separate experiments, with deionized water and with pH 8.0 and 1.0 aqueous solutions. In each of these three cases 0.100 dm^3 was added to 1.00×10^{-3} kg sand containing the removed Pb(II) and the solution was shaken for 2 h at 25°C. The percent Pb(II) recovery was observed to be 0.13, 3.15 and 36.4 in water, pH 8.0 and pH 1.0, respectively.

In another experiment, 0.100 dm^3 of 0.010 mol dm^{-3} EDTA was added to the sand containing the removed Pb(II) and shaken for 2 h. This process resulted in a 78.7% recovery of Pb(II), as determined by ICP measurements. The 1-1 EDTA-Pb(II) complex has a formation constant of 1.0×10^{18} at 25.0°C (Mortveldt, 1991) and since EDTA is in stoichiometric excess (1.4×10^{-4} mol Pb(II) to 1.00×10^{-3} mol EDTA), it is apparent that the EDTA added is sufficient to complex all free, or labile, Pb(II) ions. When the equilibration period with EDTA was extended to overnight in the shaker, the percent Pb(II) recovery rose to 86.6%.

Lead recovery after column filtration: The column containing removed lead was washed by continuously injecting, in separate experiments, 0.500 dm^3 each of distilled deionized water and 0.100 mol dm^{-3} HNO$_3$. It was not necessary to attempt recovery via injection of base as this would have resulted in the formation of the insoluble Pb(OH)$_2$ which does not appear in the effluent. This has indeed been found to be the case in batch equilibration. For HNO$_3$ injection, by stark contrast to the results from batch experiments, no measurable amount of Pb(II) was observed in the effluent.

Next, Pb(II) recovery experiments were performed using 0.010 and 0.100 mol dm^{-3} EDTA solutions. In each run, the amount of yellow sand in the column was 0.0385 kg and contained 3.30x10^{-3} kg Pb(II). Fig. 2 shows that recovery efficiencies following continuous injection of 1.00 dm^3 of 0.010 and 0.100 mol dm^{-3} EDTA solutions are 16.8% and 60.0%, respectively. In a separate run, injection of 1.75 dm^3 of 0.100 mol dm^{-3} EDTA in the same column resulted in 94.7% recovery.

DISCUSSION

The high Pb(II) removal efficiency by yellow sand in batch equilibration studies, when compared to that for either white or red sand, is consistent with earlier results obtained in this laboratory on mixtures of heavy metal ions, including Pb(II) (Pappalardo *et al.*, 2010).

Whereas shaking 1.00×10^{-3} kg of yellow sand containing removed Pb(II) with 0.100 dm^3 aqueous solution at pH 1.0 resulted in 36.0% recovery, virtually no Pb(II) was recovered when 0.500 dm^3 of the acid solution was injected into the sand column saturated with Pb(II). This observation indicates that the removed Pb(II) is not labile and that sufficient contact time with the acid, such as that provided in using the shaker, is needed for recovery. In a similar vein, the higher Pb(II) recovery efficiency in column experiments (when concentrations are considered) of the more dilute EDTA solution can be attributed to a 'kinetic' effect (Sun *et al.,* 2001). For example, when 1.00 dm^3 0.0100 mol dm^{-3} EDTA is added to the column, 16.8% of the removed Pb(II) was recovered (Fig. 2). To achieve the same recovery with 0.100 mol dm^{-3} EDTA requires 0.114 dm^3, i.e. 11.4% more moles EDTA than the in the dilute EDTA case. Since the flow rate was kept constant at 0.30 dm^3 h^{-1}, the contact time of the dilute EDTA solution with sand in the column, for the passage of the same amount of EDTA, was 10 fold higher than that for the more concentrated solution, thereby affording more time for the mobilization of Pb(II) and for their subsequent chelation and elution.

The results emphasize the differences between the two modes of Pb(II) removal and recovery, batch equilibrium vs. column filtration as well as the effect of contact time and EDTA concentration on recovery efficiency. Nevertheless, while column filtration remains the more practical, recovery by EDTA in both modes is highly efficient.

CONCLUSION

UAE sands are highly effective in removing Pb(II) from wastewaters. In particular, column filtration using yellow sand, with a removal capacity of 0.086 kg Pb(II)/kg sand, has been demonstrated to be most efficient. In addition, EDTA has been shown to be very effective in the recovery of Pb(II) after being removed in both batch or column experiments. However, the recovery efficiency in column filtration remains better than that in batch processes. Attempted recovery by neutral, acidic or basic solutions is not effective in column experiments. Recovery by pH 1.0 aqueous solutions in batch experiments amounted up to 36.0%. Though moderately successful, this was far less than the 86.6% and the 94.7% recovery efficiencies obtained with EDTA in batch equilibration and column filtration, respectively.

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