Adsorption of heavy metals by exhausted coffee grounds as a potential treatment method for waste waters

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The adsorption of the heavy metal ions Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution by used coffee grounds has been investigated as a potential low-cost treatment method for heavy metal-containing waste waters that is based on a readily available natural by-product. The results show that metal ion adsorption is efficient over a fairly wide pH range and adsorbed metals are reversibly leached from the exhausted coffee by dilute acid without significant loss of the adsorptive capacity for subsequent re-use. [DOI: 10.1380/ejsnt.2006.504]

Keywords: coffee; adsorption; heavy metals; waste water treatment

I. INTRODUCTION

The re-use of natural waste materials that arise through various industrial processes for additional purposes, rather than simple disposal, makes both environmental and commercial sense [1]. Thus there has been a recent focus on agricultural and food industry wastes such as tea, coffee grounds and rice hull [2] as alternatives to synthetic ion-exchange resins or activated carbon for treating metal-containing waste streams. Tannin-containing materials such as exhausted coffee contain metal-binding polyhydroxy polyphenol functional groups [1] and are available in large quantities from the manufacture of instant coffee [3]. While there have been several studies of metal ion adsorption by tea and coffee [4, 5] the detailed chemistry causing their affinity for different metal ions is not yet well-known.

Here we report the use of exhausted coffee grounds as an adsorbent for the heavy metal ions Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution. We present results describing adsorption isotherms for the metal ions, and the effects of adsorbent concentration, pH and metal ion concentration. In addition, we present results for the use of the adsorbent in a flow-through column.

II. METHODS

Commercial ground coffee (Blue Mountain variety) was sieved through an ASTM 18 stainless steel sieve (1 mm mesh size). It was then repeatedly leached with excess 0.01 M NaOH solution (30 g coffee in 800 mL solution) at $\sim 60^\circ\text{C}$ for 10-30 min with decanting and replacement of the NaOH until the yellow colour of the solution was no longer observed (4-6 solution changes). After this the coffee grounds were suspended in 0.01M HNO_3 and poured through a filter funnel containing a Whatman 114 filter and then washed repeatedly with deionized water (Millipore Milli-Q system) until a pH close to 6.0 was achieved. Finally the grounds were oven dried at 100°C for 2 h, cooled to room temperature and sealed with parafilm. Earlier experiments [6] employed coffee leached with deionized water only, and our subsequent

work showed that this adsorbent continued to release soluble coffee material on subsequent exposure to aqueous solution. This complicates adsorption by competing for the metal cations. However, the alkali-leached material released very little coloured material.

Batch experiments measuring adsorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} were conducted by adding known concentrations of each metal ion to a suspension of coffee adsorbent in water and equilibrating overnight at room temperature with occasional shaking. Typical conditions were $3\text{ g}\cdot\text{L}^{-1}$ of coffee grounds and $200\text{ }\mu\text{M}$ of metal ion. The pH of the suspension was then adjusted to the required value by addition of dilute NaOH or HNO_3 as required. pH buffers were avoided since these could compete as ligands for the metal cations. After equilibration, the suspensions were filtered through a Whatman 114 filter, the filtrate was analyzed for metal ions by atomic absorption spectrometry and the amount adsorbed calculated by difference. The effects of pH and the concentrations of adsorbent and metal ion were studied.

Column adsorption experiments were also conducted in which solutions of metal ion concentration were pumped through a column containing 0.5 g of exhausted coffee adsorbent using a peristaltic pump, with aliquots of the effluent collected for metal ion analysis. The efficiency of recycling was investigated by repeated leaching of metal ions from the column using 0.1 M HCl and then re-adsorption of the same metal ions.

III. RESULTS AND DISCUSSION

All of the metal ions exhibited a strong affinity for exhausted coffee grounds as an adsorbent. Figure 1 shows how the percentage of metal ion adsorbed at pH ~ 5 increases with the concentration of coffee adsorbent, reaching a plateau (75-90% adsorbed) at $\sim 20\text{ g coffee L}^{-1}$.

The adsorption equilibria were investigated using pH 5.0 solutions containing $3.0\text{ g}\cdot\text{L}^{-1}$ of coffee grounds and metal ion concentrations in the range 20-200 μM . The results were then fitted to a Langmuir isotherm [7] as follows:

$$\frac{1}{X} = \frac{1}{bX_m c_e} + \frac{1}{X_m} \quad (1)$$

where X is the amount of metal ion adsorbed per g of adsorbent, X_m is the maximum amount of metal ion that

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FIG. 1: Percentage of metal ion adsorbed from 200 mL solutions containing 10 mg·L⁻¹ of Cu(II) or Pb(II) or 1.0 mg·L⁻¹ of Cd(II) or Zn(II) at pH 5.0 as a function of the mass of coffee adsorbent.

FIG. 2: Langmuir plot of Eq. (1) for adsorption of Zn(II) at pH 5.0 on coffee adsorbent by 3 g·L⁻¹ of coffee adsorbent. The least-square regression line and equation are shown.

can be adsorbed per g of adsorbent, c_e is the final equilibrium concentration of the metal ion in solution (M) and b is effectively the equilibrium constant for adsorption.

Figure 2 shows the Langmuir adsorption plot for Zn²⁺ adsorption. Linear least-squares regression was used to calculate b and X_m from the best-fit line. Table I presents the resultant values for all of the metal ions studied.

Figure 3 shows the pH dependence of metal ion adsorp-

TABLE I: Langmuir adsorption parameters for the 4 metal ions for 3 g·L⁻¹ coffee grounds at pH 5.0. The least-squares regression line and regression coefficient r^2 for the Langmuir plot (Fig. 2) are also shown.

Metal Ion	r^2	X_m (mmol·g ⁻¹)	b (L·mmol ⁻¹)
Pb ²⁺	0.9911	0.2388	1.229
Cd ²⁺	0.9951	0.1032	2.414
Zn ²⁺	0.9967	0.0575	4.356
Cu ²⁺	0.9670	0.0306	6.291

FIG. 3: Percentage of metal ion adsorbed by 10 g·L⁻¹ of coffee adsorbent as a function of pH from solutions containing 10 mg·L⁻¹ of Cu(II) or Pb(II) or 1.0 mg·L⁻¹ of Zn(II) or Cd(II).

FIG. 4: Percentage of metal ion adsorbed as a function of metal ion concentration at pH 5.0 by 10 g·L⁻¹ of coffee adsorbent.

tion at fixed concentrations of metal ions and coffee adsorbent. The extent of adsorption was largely independent of pH over a wide pH range, but was significantly reduced at very low (pH < 4) and to a lesser extent at high pH (pH > 10). Good adsorption efficiency is observed at intermediate pH values likely to be encountered with many waste waters.

Figure 4 shows the percentage of metal ion adsorbed at pH 5.0 from a suspension containing 10 g·L⁻¹ of coffee as a function of the metal ion concentrations. In each case, the fraction adsorbed was fairly constant at metal ion concentrations below about 10 mg·L⁻¹ but at levels above 100 mg·L⁻¹ the adsorptive capacity of the coffee

TABLE II: Maximum adsorbed concentration of each metal X_m (from Table I) and the corresponding maximum solution concentration for 10 g·L⁻¹ of coffee.

Metal	X_m (mmol·g ⁻¹)	C_{max} (mg·L ⁻¹)
Pb	0.2388	494.8
Cd	0.1032	115.6
Zn	0.0575	37.6
Cu	0.0306	19.4

TABLE III: Percentages of Cd(II) and Zn(II) adsorbed ($1.0 \text{ mg}\cdot\text{L}^{-1}$, pH 4.0) and then eluted in 0.1 M HCl during 4 repeated adsorption-elution cycles on a column containing 0.5 g of coffee adsorbent.

	Cd		Zn	
	Adsorbed	Eluted	Adsorbed	Eluted
1	91.3	83.1	91.0	82.7
2	98.9	99.5	99.7	100.0
3	100.0	98.4	100.9	100.3
4	100.0	98.4	100.9	99.7

FIG. 5: Percentage of Cu(II) adsorbed by a column containing 0.5 g coffee adsorbent at pH 5.0 and flow rate $3.3 \text{ mL}\cdot\text{min}^{-1}$ as a function of the volume of $10 \text{ mg}\cdot\text{L}^{-1}$ Cu(II) solution passed through the column.

was exceeded.

Table II shows the theoretical adsorption capacity for this concentration of coffee adsorbent calculated from the X_m values presented in Table I, from which it is clear that Pb(II) should exhibit the greatest limit for adsorption and Cu(II) the least. This is approximately in agreement with

the results shown in Figure 4.

Column experiments indicated almost 100% initial removal of metal ion from solution, with breakthrough occurring after the adsorption capacity of the adsorbent was exceeded, depending on pH, flow rate, amount of column adsorbent and metal ion concentration. This is illustrated by Figure 5 for Cu(II). Using the X_m value reported in Table I for this cation, it was calculated that breakthrough should occur after 97 mL of $10 \text{ mg}\cdot\text{L}^{-1}$ Cu(II) solution had been passed through the column containing 0.5 g of coffee, which agrees very well with the breakthrough at $\sim 100 \text{ mL}$ actually observed in this case.

Table III shows the result of repeated adsorption-elution experiments for Cd(II) and Zn(II). In each case, $100 \mu\text{g}$ of metal ion comprising 100 mL of $1.0 \text{ mg}\cdot\text{L}^{-1}$ solution was passed through a column containing 0.5 g of coffee. After rinsing with 50 mL of Milli-Q water, the column was eluted with 100 mL of 0.1 M HCl which was retained for analysis. The results show that after the first adsorption-elution cycle, both metal ions are quantitatively adsorbed by, and then eluted from, the column. However, there is some initial loss on the first cycle.

IV. CONCLUSION

Our preliminary results indicate that exhausted coffee grounds offer considerable promise as a low-cost natural medium for waste water treatment. The adsorption is efficient over a fairly wide pH range and adsorbed metals are reversibly leached from the exhausted coffee by dilute acid without significant loss of the adsorptive capacity for subsequent re-use.

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