

Full Length Research Paper

Preconcentration and removal of heavy metal ions from aqueous solution using modified charcoal

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Levels of Pb(II), Cu(II), Zn(II), Mn(II), and Co(II) ion in aqueous solutions were determined by atomic absorption spectrometry (AAS) technique after preconcentration on diethyl dithiocarbamate supported by EDTA modified charcoal from *Khaya senegalensis* wood. The sorbed elements were eluted with acid and subsequently analyzed. The influence of pH, contact time and initial metal ion concentration by the modified charcoal was investigated. At 90 min contact time the uptake level of metal ions from solution was found to depend on the metal ion-substrate contact time, ion concentration and ion type. The percentage recovery of the metals ions retained by modified charcoal was highest at pH 5. The sorption recovery for the metal ions was within the range of 95.1-99.8%. It was observed that EDTA modification of charcoal significantly improved the percentage recovery of the metal ions. The results obtained from the study showed EDTA modified charcoal to be favourable for preconcentration and removal of heavy metal ions from aqueous solution.

Key words: Preconcentration, removal, heavy metals, modified charcoal, environmental pollution.

INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide (Iqbal and Saeed, 2007; Jimoh, 2010). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Guo et al., 2008). The presence of heavy metal ions is a major concern due to their toxicity to many life forms. It therefore becomes imperative to determine these metal ion concentrations in the water bodies.

In some cases, however there are many difficulties in determining traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. Thus, a preconcentration and/or separation step is often recommended (Unob et al., 2005). The atomic absorption spectrometry (AAS) technique, which offers fast multi-elemental analysis, suffers from a poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real

samples. This drawback can be overcome by a combination of a suitable preconcentration technique with subsequent AAS determination. These preconcentration methods provide low detection limits and also help to avoid matrix interferences in the analysis of real samples (Suvardhan et al., 2003).

Consequently, many methods have been developed for the preconcentration and separation of heavy metals from various samples before being discharged into the environment. These include liquid-liquid extraction (LLE), co-precipitation, resin chelation, electrochemical deposition, ion exchange, coagulation or flocculation and solid - phase extraction (SPE) (Juang and Shiau, 2000; Amuda and Amoo, 2006; Amuda and Alade, 2006; Amuda et al., 2006). These techniques however, have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products (Ahalya et al., 2003).

Thus preconcentration by solid-liquid extraction considered in this work is one of the most efficient methods used to remove heavy metals from effluents using naturally available material as an adsorbent. This technique has an edge over the other methods due to its sludge free clean operation and complete removal of toxic

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metals even from dilute solution (Ahalya et al., 2003). Preconcentration procedures of metals by dissolving metal-substrates with acid and determining the metal concentration by atomic absorption spectrometry have been reported by (Wu et al., 2000; Rhazi et al., 2002; Ngah et al., 2004; Unob et al., 2005).

The objective of this work was to use EDTA modified charcoal in simultaneous preconcentration and removal of Pb(II), Co(II), Mn(II), Cu(II) and Zn(II) ion from aqueous solutions.

MATERIALS AND METHODS

Aqueous solution preparation

All the reagents used were of analytical grade and were prepared with high quality distilled-deionised water. The aqueous solutions containing Pb, Co, Mn, Cu and Zn was prepared from Pb(NO₃)₂, CuSO₄·5H₂O, MnCl₄, CoCl₂·6H₂O, and Zn(NO₃)₂·6H₂O. 1000 mgdm⁻³ stock solution of each of the salts was prepared. Other concentrations of 5, 10, 20, 30, 40 and 50 mgdm⁻³ were prepared from each stock solution by serial dilution.

Sample collection

The charcoal used in this work was obtained from *Khaya senegalensis* tree along Government House, Minna. Sampling was done at random within this area. A composite sample was made from where the representative samples were collected for this study. The charcoal was obtained by burning the wood in a limited supply of air.

Sample pretreatment

The samples were deoiled by soaking in hot deionized water with detergent for 24 h. They were then rinsed in hot deionized water to remove all debris, after which they were air dried for a period of one week. The dried samples were ground using a clean blender and sieved through a 400 µm mesh screen. The fine powder retained on the 400 µm clean sieve was then used for the preconcentration studies.

Adsorbent preparation for preconcentration studies

Charcoal was modified by soaking with 0.5 moldm⁻³ EDTA (ethylene diamine tetra acetic acid) for 24 h. This was done to significantly improve the uptake levels of these heavy metal ions.

Preconcentration procedure

1 moldm⁻³ each of these metals (Lead, Zinc, Copper, Cobalt and Manganese) was extracted as metal diethyl dithio-carbamates with 2:5 acetone-chloroform by varying the pH from 1 to 8. The pH of solutions was adjusted to the desired value by using either 0.5 moldm⁻³ NaOH or concentrated HCl. These metals were then adsorbed on a 2 g column of modified charcoal in 5:4:1 mixture of Tetrahydrofuran, Ethylene glycol and 6.0 moldm⁻³ HCl. Successive elution was effected with 6.0 mol.dm⁻³ HCl for Co, Cu, Mn and Pb while 2.0 moldm⁻³ HNO₃ was used for Zn. The elements of interest

in the eluates were analyzed by flame atomic absorption spectrophotometer, model Pye Unicam SP-9 Cambridge, UK.

Sorption experiment

The experimental procedure described by Okieimen and Okieimen, (2001) was modified as follows: 0.5 g of the pretreated powdered samples were taken and shaken with 100 cm³ of a metal ion solution whose concentration was 5 mgdm⁻³. The bottles were shaken at various time intervals of 30 to 180 min at room temperature in a reciprocating shaker at 300 rpm. At the end of each contact period the mixture was filtered using Whatman filter paper No. 42 and the filtrate was stored in sample bottles in a refrigerator prior to analysis. The filtrate was analysed for the heavy metal ions using FAAS, model Pye Unicam SP-9 Cambridge, UK.

Multimetal batch adsorption study

The experiments were carried out in the batch mode for the measurement of adsorption capabilities at 33°C using different concentrations of 10, 20, 30, 40 and 50 mgdm⁻³ for the various heavy metal ions studied. 100 cm³ of various concentrations (10.0 mgdm⁻³ to 50.0 mgdm⁻³) of the metal ions were placed in 250 cm³ conical flasks, and 0.5 g of the substrate was each added. The corked conical flask was shaken in a reciprocating shaker at 300 rpm for constant metal ion-substrate contact period of 90 min at 33°C. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an flame atomic absorption spectrophotometer (FAAS).

Data analysis

The adsorptive capacity of metal ions per unit adsorbent (mg metal g⁻¹ dry biosorbent) was determined using the following expression:

$$q = \frac{V(C_i - C_{eq})}{M} \quad \text{----- 1}$$

Where q is the metal uptake (mg metal ions g⁻¹ dry weight of adsorbent entrapped), V is the volume of metal solution (cm³), C_i is the initial concentration of metal ions in the solution (mgdm⁻³), C_{eq} is the final concentration of metal ions in the solution (mgdm⁻³), and M is the dry weight of adsorbent. Percentage removal of heavy metal ions from initial solution concentration calculated from the following Equation.

$$R_{em} = \frac{C_o - C_t}{C_o} \times 100\% \quad \text{----- 2}$$

where C₀ is the initial metal ion concentration (mgdm⁻³), and C_t is the metal ion concentration at time t (mgdm⁻³).

RESULTS

The percentage recovery was calculated from the amount of metals (1 moldm⁻³) in starting solution (N_s) and the amount of metals eluted from the column (N_{fi}) as in

Table 1. Recovery of metals with column preconcentration based on pH variation.

pH	Recovered amount (mgdm ⁻³)									
	Pb ²⁺	% Recovery	Zn ²⁺	% Recovery	Cu ²⁺	% Recovery	Co ²⁺	% Recovery	Mn ²⁺	% Recovery
1	0.25	75.00	0.27	73.00	0.30	70.00	0.33	67.00	0.42	58.00
2	0.19	81.00	0.21	79.00	0.26	74.00	0.29	71.00	0.34	66.00
3	0.17	83.00	0.19	81.00	0.24	76.00	0.28	72.00	0.30	70.00
4	0.14	85.70	0.20	80.30	0.21	78.90	0.25	75.40	0.35	64.60
5	0.01	99.80	0.10	98.00	0.11	97.90	0.20	96.00	0.24	95.10
6	0.10	97.50	0.15	96.30	0.12	97.10	0.21	94.90	0.25	93.70
7	0.12	96.00	0.15	94.90	0.20	93.20	0.23	92.40	0.29	90.40
8	0.12	93.80	0.17	91.40	0.20	89.90	0.23	88.40	0.30	85.00

Equation 1.

The results are summarized in Table 1

$$\% \text{ recovery} = \frac{N_{fi}}{N_s} \times 100 \dots \dots \dots 3$$

DISCUSSION

From Table 1, at pH 5, the recovery of the metals ions is in the range of 95.1 – 99.8%. The acceptable range of percentage recovery is 80-110% as reported by many authors (Wu et al., 2000; Rhazi et al., 2002; Ngah et al., 2004; Unob et al., 2005). The obtained results therefore agree with the findings of Unob et al. (2005) who had earlier studied the preconcentration of heavy metals from aqueous solution using chitosan flake at pH 5. Similar results were also obtained by Ngah et al. (2004) who investigated the preconcentration of Zn(II) and Pb(II) using chitosan flake column in which the metals were optimally retained by chitosan at pH 5.

Effect of varying pH on the adsorption of metal ions

Metal sorption is critically linked to pH and the effect of pH of the solution is an important controlling factor in the adsorption process (Ngah et al., 2004; Faria et al., 2004). For this, the role of hydrogen ion concentration was examined at different pH. The effect of pH on the preconcentration of metals ions extracted as diethyldithiocarbamates complexes, that was adsorbed on a 2 g column packed with modified charcoal in 5:4:1 mixture of tetrahydrofuran, methyl glycol and 6 moldm⁻³ HCl was examined. It was observed that with the increase in the pH of the solution the percentage removal of metal ions increased up to the pH 5 as shown in Table 1. At pH 5 maximum recoveries were obtained for all the metal ions studied. The preconcentration experiment showed that the highest removal by modified charcoal

was 99.8% for Pb(II) ions in the aqueous solution at pH 5.

The improved removal levels of Pb(II) ion and other metal ions by EDTA modified substrates may be ascribed to the chemical reaction of the metal ions with the EDTA on the charcoal which result to the formation of the metal complexes. These metal complexes however, remain in solution and are recovered as metal ion upon addition of acids. The rate of recovery was based on their ionic radii and atomic weight (Jimoh, 2010). It should be noted that the increase in the percentage recovery was not directly proportional to the substrates suggesting that other factors play a role in the adsorption and desorption mechanism. It is quite plausible that an initial high adsorption rate (possibly by ion exchange) followed by chelation of the metal ions with the carboxyl group may have been the case. A similar behaviour was shown by column packed with chitosan flake biomass where the percentage of Pb(II) ion removal was much higher than other metal ions at pH 5 (Unob et al., 2005).

The increase in percentage removal of metal ions due to increase in pH may be explained on the basis of a decrease in competition between proton (H⁺) and positively charged metal ion at the surface sites and also by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ion. pH values of 7 to 8 suggest increase in alkalinity level and as such, there was a further decrease in the rate of adsorption by modified charcoal for Pb(II), Cu(II), Zn(II), Co(II) and Mn(II) ions in the aqueous solution. With increase in pH from 7 to 8, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased. A close relationship between the surface basis of the adsorbents and the anions is evident. This is similar to other findings where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the columbic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (Faria et al., 2004; Oyebamiji et al., 2009; Egila et al., 2010).

The low percentage recovery at pH 1 and 2 may be ascribed to the fact that the higher mobility of H⁺ ions

Table 2. Results of the effect of contact time on the amount of metal ions bound (mg/100 cm³) on Modified charcoal at 33°C.

Contact time(min)	Pb ²⁺	Zn ²⁺	Mn ²⁺	Cu ²⁺	Co ²⁺
30	1.5	1.7	1.8	1.8	1.9
60	2.3	2.4	2.7	2.7	2.8
90	2.7	2.9	3.3	3.4	3.0
120	2.5	2.7	3.1	2.5	2.6
150	2.2	2.3	2.5	2.2	2.3
180	1.2	1.3	1.4	1.9	2.0

present favoured the preferential adsorption of hydrogen ions compared to metal ions. This trend is not far from what was observed by Ajmal et al., (2000) and Wong et al. (2003) who independently suggested that at lower pH value, the surface of the adsorbent is surrounded by hydroxonium ions (H₃O⁺), thereby preventing the metal ions from approaching the binding sites of the sorbent. This means that at higher H⁺ ions concentration, the biosorbent surface becomes more positively charged such that the attraction between modified charcoal and metal cations is reduced (Saeed et al., 2004; Jimoh, 2010). However, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal ions removal. It is commonly agreed that the preconcentration of metal cations increases with increasing pH as the metal ionic species become less stable in the solution (Unob et al., 2005).

Therefore, the column packed with modified charcoal is suitable for the preconcentration of these metals in aqueous solution. At pH 5, the recovery of metal ions from the column was in the range of 95.10-99.80%. This is the pH at which maximum recovery was obtained for the metal ions present in the aqueous solution. The effectiveness of the used method was presented in terms of percentage recovery of metal ions ranging from 95.10 to 99.80 at pH 5. The column packed with modified charcoal from *Khaya senegalensis* was able to recover 99.8% Pb (II) ions after successful elution with 6 moldm⁻³ HCl. This value is within the acceptable limits.

Effect of contact time on the adsorption of metal ions

Tables 2 show the percentage removal of the various metal ions by the modified charcoal. For all the metal ions present in the aqueous solution, there were a progression in the rate of adsorption but it was not linear at any time. It was also observed that the rate of adsorption increased significantly for all the metal ions present for 90 min of contact time.

This result is essential, as equilibrium time is one of the important parameters for an economical wastewater treatment system. The trend observed for the various metal ions under the same experimental conditions revealed that the pattern of adsorption is a function of the

substrate as well as that of the metal ions (Egila and Okorie, 2002; Egila et al., 2010; Jimoh, 2010). The increase of contact time further from 90 to 180 min had no significant effect on the percentage sorption of all metal ions.

Further more, manganese with small ionic size was observed to have adsorbed at a faster rate than the other metal ions. The trend of adsorption in the modified charcoal is Mn(II)>Co(II)>Cu(II)>Zn(II)>Pb(II). This occurrence may be explained by considering the ionic radii which was observed for Mn(II) (0.67Å), Co(II), Cu(II) with higher rate of adsorption at equilibrium time than Zn(II), Pb(II) ions (1.20Å). According to Abia and Asuquo (2006) during sorption of metal ions, the ions of smaller ionic radii tend to move faster to potential adsorption. Similar observation had been reported by several other researchers (Mohsen, 2007; Oboh and Aluyor, 2008; Oyebamiji et al., 2009; Egila et al., 2010).

The effect of initial metal ions concentrations on the adsorption of the metal ions

The uptake level of Mn(II), Co(II), Cu(II), Zn(II) and Pb(II) ions from solutions containing various amounts of the metal ions by modified charcoal is shown in Table 3 as the metal ions concentration increases from 10 to 50 mg/100 cm³. The obtained results show that the amount of the metal ions bound by the modified charcoal depended on the type of metal ions and its concentration. The uptake levels of metal ions followed this order Mn (II) >Co(II) >Cu(II)>Zn(II)>Pb(II). The difference in the uptake levels of the metal ions can be explained in terms of the difference in the ionic size and atomic weight of the metal ions, the mode of interaction between the metal ions and the substrate.

The initial faster sorption rate of each metal ion could be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005; Egila et al., 2010; Jimoh, 2010). The trend could also be explained in terms of the progressive increase in the columbic interaction between the metal ions and the adsorbent active sites. Moreover, more adsorption sites were being covered as the metal ions concentration

Table 3. Results of the effect of varying metal ions concentration on the adsorption of metal ions on modified charcoal at 33°C for 90 min.

Initial metal ions concentration (mg/100 cm ³)	Amount of metal ions adsorbed				
	Pb ²⁺	Zn ²⁺	Mn ²⁺	Cu ²⁺	Co ²⁺
10	3.50	3.55	4.83	4.85	4.90
20	9.36	10.20	12.43	12.30	12.50
30	17.50	17.80	18.50	19.00	20.50
40	19.04	20.20	23.02	25.00	23.02
50	23.00	24.00	34.60	35.20	34.29

Table 4. Results of the Freundlich constants for modified charcoal.

Heavy metal ions	1/n (Freundlich Constant)	K _f (Freundlich Constant)	R ² (Correlation coefficient)
Pb ²⁺	0.65	2.05	0.965
Cu ²⁺	0.74	2.57	0.968
Zn ²⁺	0.73	2.58	0.975
Mn ²⁺	0.76	2.73	0.976
Co ²⁺	0.75	2.68	0.975

increased (Egila et al., 2010; Jimoh, 2010), and higher initial concentrations led to an increase in the affinity of the metal ions towards the active sites (Oboh and Aluyor, 2008).

The decline in the uptake level despite increase in the initial metal ions concentration is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at higher concentrations (Somasekhara et al., 2007). The results obtained from this research work conformed to the findings by Oboh and Aluyor (2008) that studied Sour sop seeds as biosorbent to remove heavy metals ions from aqueous solution.

Adsorption isotherms

The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherms which is usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. Most often biosorption equilibria are described with adsorption isotherms of Langmuir or Freundlich types. Since the adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical for design purposes, therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation. When the sorption data of the metal ions investigated on modified charcoal were plotted logarithmically, they all fitted the Freundlich adsorption isotherm.

The values of correlation coefficient as contained in Table 4 indicate that the adsorption process conforms to

the Freundlich isotherms (Igwe et al., 2005; Kurniawan, 2008; Oyebamiji et al., 2009). The results also show that the R² values for substrate was greater than 0.9 for Freundlich Isotherm, so the adsorption was multi layered and physio-sorption type. Mn(II) ion with small ionic size was observed to have the highest value for 1/n, R² and K_f than the other metal ions. The trend of occurrence was Mn(II)>Co(II)>Cu(II)>Zn(II)>Pb(II). This phenomenon may be explained by considering that Mn (II) ion has an ionic radius of 0.67Å while Pb(II) ion has is 1.20Å. Since Mn (II) ion has a smaller ionic radius, it tends to diffuse to the potential adsorption sites easier than other metal ions. The smaller ionic radius of Mn(II) might probably be attributed to its greater adsorptivity.

The value of 1/n which is less than 1 indicates that the metal ions are favourably adsorbed by the modified charcoal. A smaller value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent (Egila and Okorie, 2002; Egila et al., 2010; Jimoh, 2010).

Conclusion

The obtained results from this work have confirmed the potential of preconcentration by solid-liquid extraction as one of the most selective method for determination of metal ions in low concentrations. It has also proved the effectiveness of heavy metal removal from aqueous solution by EDTA modified charcoal sourced from *Khaya senegalensis*. This has the potential to be used in metal ion removal from wastewater and assist in reducing environmental pollution from such metals as well to save

the fund of purchasing the commercial adsorbents.

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