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ORIGINAL PAPER

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Sorption of trace metals on human hair and application for cadmium and lead pre-concentration with flame atomic absorption determination

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Abstract Human hair shavings were characterized as a sorbent for trace metals. At pH 7.0 metal sorption follows the order Pb(II)>Cd(II)>Cr(VI)>Fe(III)>Cu(II)>Ni(II)>Mn(VI). Metal recovery is quantitative for Pb and Cd after 30 min of equilibration. Recovery of other metals is less quantitative and varies with pH. For example, while Cu is best recovered at pH 5, Ni and Mn are sorbed optimally in the basic pH region. Sorbed metals can be washed off the sorbent with 0.5 mol L^{-1} strong mineral acids or more completely with 0.1 mol L^{-1} ethylenediaminetetraacetic acid (EDTA). Typical sorption isotherms were obtained for Cd and Pb with sorption capacities of 39 and 26 μmol g^{-1}, respectively.

Hair sorbent was used for 40-fold pre-concentration of Cd and Pb from treated wastewater samples followed by flame atomic absorption spectroscopic (FAAS) determination. Comparison of the data obtained for lead and cadmium by the proposed pre-concentration method with that by graphite furnace atomic absorption spectroscopy (GFAAS) showed 79 to 86% recovery and comparable analytical precision. Common cations and anions at the levels normally present in natural water do not interfere in the proposed pre-concentration-FAAS method.

Keywords Atomic absorption · Cadmium · Hair · Lead · Preconcentration · Sorption

Introduction

The ever-increasing environmental pollution by toxic metals has triggered a parallel increase in demand for accurate and sensitive quantitative metal analysis in environmental samples. Flame atomic absorption spectroscopy (FAAS) is the most widely used technique for such determinations because of simplicity and low initial and running cost. However, this technique suffers from lack of sensitivity for the ultra-trace metal concentrations usually encountered in environmental samples. Therefore, sample pre-concentration is becoming an essential treatment step before flame atomic absorption determination [1, 2, 3, 4, 5, 6, 7, 8].

Ion-exchange resins and chelating materials immobilized on or bonded to some solid support are gaining popularity for metal ion pre-concentration prior to FAAS. This is attributed to its simplicity, reduced potential for contamination, reasonable control of selectivity and high capacity.

A single hair is a fibrous protein called keratin that can be viewed as a bundle of thousands of α-helical polypeptide chains imbedded in amorphous protein cells [9]. Hair polypeptides contain an abundant fraction of cysteine (2-amino-3-mercaptopropionic acid) which holds parallel polypeptide chains by sulfur–sulfur bridge bonds. Hair accumulates trace metals by complexation with polypeptides through the available sulfhydryl, amino, and carboxylate groups of the constituent amino acids [10, 11, 12, 13]. Many cells in living organisms synthesize metal binding proteins as a mechanism for de-toxification, in response to elevated levels of toxic metals [14]. Recently, protein-based sensors were used for the determination of low concentrations of metal ions [15].

Literature survey showed that limited work has been performed on sorption of metals on hair. The bulk of the published work is focused on other types of protein, such as wool, silk, egg-shell membrane [16, 17], moss peat [18], and types of microorganism [19, 20]. The purpose of such research was aimed at studying the nature of metal–ligand binding with the hope of applying such materials for environmental decontamination. The concentration of metals in hair has been reported for persons with frequent contact with lead and cadmium-polluted workplaces such as gasoline vending stations and battery-manufacturing facilities [21]. However, it is not known if the observed metal accumulation in hair is due to internal ingestion or external adsorption.

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This work is the first report on the sorption characteristics of metal ions by human hair, and the potential application of hair for metal ion pre-concentration and determination.

Experimental

Sorbent preparation

Electrically shaved hair (0.25 to 1 mm long) was collected from four donors age 32 to 48. Hair was stirred in distilled water and the supernatant liquid was decanted to remove floating skin debris, and non-hair objects. The residue was washed with synthetic liquid detergent in an ultrasonic bath for 1 h to get rid of greasy materials and rinsed thoroughly with distilled water. Next, the hair shavings were freeze dried in liquid nitrogen and pulverized to pass 100 mesh. The fines were rejected by repeated suspension in distilled water and decantation. This treatment breaks up the layer of amorphous protein surrounding the hair strand and facilitates accessibility of metal ions to polypeptide chains. Next, the hair shavings were agitated in an ultra sonic bath for 2 h in 0.5 mol L^{-1} HNO_3 solution to remove residual sorbed metals, rinsed thoroughly with distilled water and dried at 50 °C in a vacuum drying oven.

Chemicals, solutions, and chemical analysis

Unless otherwise stated, all reagents used are of analytical reagent quality. Stock solutions were prepared by dissolving the reagents using distilled de-ionized water. Working solutions were prepared by serial dilution of the above stocks.

Chemical analysis for different elements by FAAS was performed on an ATI Unicam double-beam spectrometer model 929. Associated hardware and software components have been described earlier [22, 23]. For solutions with metal concentrations below the limit of quantification of FAAS analyses were performed on a Perkin–Elmer model 700 graphite furnace atomic absorption spectrometer (GFAAS). Details of hardware and software components of this instrument have been reported elsewhere [24]. Instrumental conditions used for both instruments were those recommended by the manufacturer and are presented in Table 1.

Effect of pH on metal sorption

An solution (100 mL) was buffered to the proper pH and spiked with 0.4 µg mL^{-1} of the element of interest (1.0 µg mL^{-1} for lead). The buffer used was the low metal-complexing 0.05 mol L^{-1} PIPES, piperazine-*N*, *N*′-bis(2-ethanesulfonic acid), in the pH range 6.75 to 8.25. The spiked solution was split in to four 25-mL aliquots; one aliquot was kept for elemental analysis of the initial concentration, C_i, while the other three were agitated for 2 h with 1.000 g of the hair sorbent at room temperature of 22±2 °C. Agitation was performed in 50-mL disposable plastic centrifuge tubes with end-on-end tumbling in a mechanical shaker that was set at low speed. Next, the adsorbent was settled by centrifugation, and the clear supernatant solution was aspirated into the flame atomic absorption spectrometer for the determination of equilibrium metal concentration, C_e. Buffered standard solutions and non-spiked buffer solution served as a calibration set for the above analyses.

The distribution ratio, D, of the metal ion between the adsorbent phase and the solution phase was calculated by mass balance from the equation:

$$D = [(C_i - C_e)\,V/m]\,/C_e$$

The numerator of the above equation is the metal concentration in the solid phase in µg g^{-1}, where V is the volume of the aqueous solution in mL and m is the mass of hair adsorbent in grams.

Table 1 Instrumental conditions for the determination of metals by flame (FL) and graphite furnace (GF) atomic absorption spectroscopy

Parameter	Cd		Pb		Cu		Cr		Ni		Mn		Fe	
	FL	GF	FL	GF	FL	GF	FL	GF	FL	GF	FL	GF	FL	GF
Wave- Length (nm)	228.8	228.8	217.0	283.3	324.7	324.7	357.9	357.9	232.0	232.0	279.5	279.5	248.3	248.3
Lamp Current (mA)	3	4	7	10	8	30	10	25	8	25	10	20	7	30
Slit Width (nm)	0.5	0.7	0.5	0.7	0.5	0.7	0.2	0.7	0.2	0.2	0.2	0.2	0.2	0.2
Background correction	ON	ON	ON	ON	ON	ON	ON	OFF	ON	ON	ON	ON	OFF	ON
Flame oxidant	AIR	-	AIR	-	AIR	-	N_2O	-	AIR	-	AIR	-	AIR	-
Heating Cycle (°/s^{-1})														
Drying (1)	-	100/15	-	100/20	-	100/20	-	100/20	-	100/20	-	100/5	-	100/20
Drying (2)	-	140/20	-	140/15	-	140/15	-	140/15	-	140/15	-	140/15	-	140/15
Ashing	-	850/20	-	700/20	-	1000/20	-	1650/20	-	1400/20	-	1400/20	-	1400/20
Atomization	-	1650/5	-	1800/5	-	2300/5	-	2500/5	-	2500/5	-	2200/5	-	2400/5

Effect of agitation time on metal sorption

A solution (0.40 µg mL^{-1} (1.0 µg mL^{-1} for lead), 1 L) of the element of interest buffered at pH 7.0 was agitated with 1.000 g of hair sorbent for different intervals of time (5 min to 4 h). At the end of each time interval 10 mL of the solution was drawn through a disposable cellulose acetate filter (0.45 µm porosity) into a 10-mL plastic syringe. After proper dilution, the equilibrium metal concentration (C_e) was determined by FAAS or GFAAS. The solution was also analysed for the target element before agitation with the sorbent (C_i). The percentage of metal sorbed was calculated from mass balance from the relation:

$$\%\text{Adsorbed metal} = [(C_i - C_e)/C_i] \times 100\%$$

Isotherm of sorption

Aqueous solution (50 mL) spiked with 10 µg mL^{-1} of lead or cadmium, was buffered to pH 7.0 and shaken for 1 h with variable masses of hair sorbent (0.000 to 2.000 g) as described in the section above. After sorbent separation by centrifugation the equilibrium metal concentration (C_e) in the aqueous phase was determined by FAAS against matching standards. The metal concentration in the sorbent phase (C_{ads}, µmol g^{-1}) was calculated from the equation:

$$C_{ads} = [(C_i - C_e) \times V/m]/\text{atomic mass}$$

where C_i is the metal concentration in the sorbent-free solution.

Effect of diverse ions

About 800 mL of distilled water was spiked with 25, 50 or 100 µg L^{-1} of either Cd or Pb plus the interferent ion at the proper concentration and buffered to pH 7.0. Next, the solution was diluted to 1 L and equilibrated with 1.000 g of the sorbent for 1 h at room temperature (22 24 °C). Then, the sorbent was filtered and leached for 15 min with 25 mL of 0.10 mol L^{-1} EDTA (pH 8.0) and the metal content of the leaching solution was determined by FAAS.

Results and discussion

Metal contamination of sorbent

Analysis of the acid leachate of the adsorbent showed that hair shavings contain zinc (530 µg g^{-1}), iron (39 µg g^{-1}), copper (34 µg g^{-1}), and nickel (5.1 µg g^{-1}). Further leaching with 0.20 mol L^{-1} HCl or HNO_3 or with 0.10 mol L^{-1} ethylenediaminetetraacetic acid (EDTA) (pH 8.0) gave metal concentrations statistically similar to those of the control blank leaching solution. Lead, cadmium and manganese were not detected in the leachate.

Effect of pH on metal sorption

The effect of pH on the distribution ratio of each metal ion between the sorbent phase and the solution phase, D, is plotted in Fig. 1. It is evident from the plotted data that metal sorption on hair is a function of the nature of the metal and the pH of the aqueous medium in contact with the sorbent. At the optimum pH (for each element), selectivity of metals follows the order Cd=Pb>Fe (pH 6)>Cr (pH 7.5)>Cu (pH 5.5)>Ni >Mn. Copper is the only element for which the optimum pH is acidic (<6.75). On the other hand, the optimum sorption of Cd, Ni and Mn is in the basic region. Lead, iron and chromium are best sorbed from nearly neutral solutions.

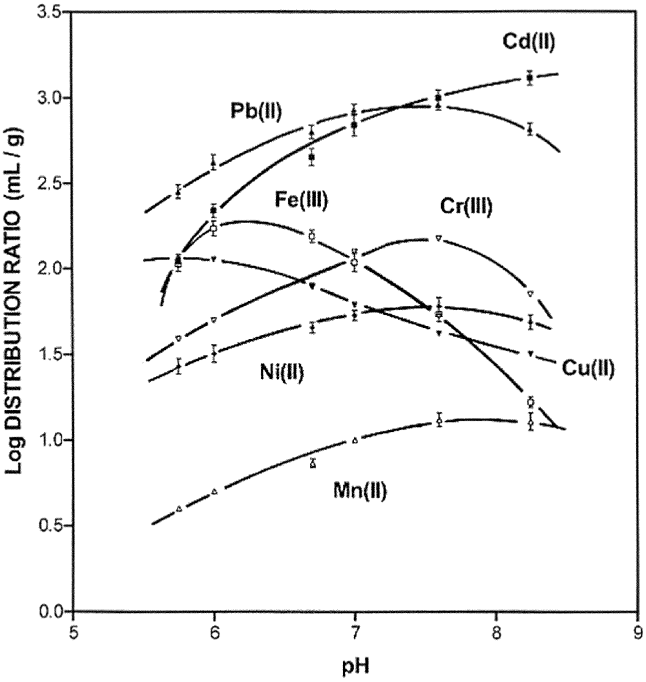

Fig. 1 The effect of pH on the distribution ratio of metals between hair sorbent and aqueous solution. Error bars are standard deviations for triplicate runs

The order of decreasing distribution ratio of metal ions approximately follows the order of their decreasing softness of acidic character [25]. This indicates a potential role of the sulfhydryl group of cysteine (a soft base) in metal ion complexation. This reasoning is supported by observations by other workers [12, 13] The lower general trend of distribution ratio at high pH values is probably due to competition of hydroxide ion for the metal ions.

The distribution ratios for lead and cadmium are the highest among tested metals, exceeding 1000 mL g^{-1} at pH 7. Therefore, this work is focused on pre-concentration of lead and cadmium using hair shavings as adsorbent.

Kineties of sorption and desorption

Figure 2 is a graphical representation of the sorption data for the tested elements. Metal sorption is rather slow indicating a lack of accessibility of binding sites of a firm fibrous protein-based sorbent. Breakthrough condition was reached in 0.5 to 2 h for Pb, Cd and Cu. On the other hand, chromium reached a plateau in 4 h while nickel is the slowest and a plateau was hardly reached after 4 h. The slow equilibration means that this sorbent cannot he used for fast flow-through column methods.

Desorption rates are much faster than sorption rates. Desorption of Pb and Cd with 0.5 mol L^{-1} HNO_3 is fast

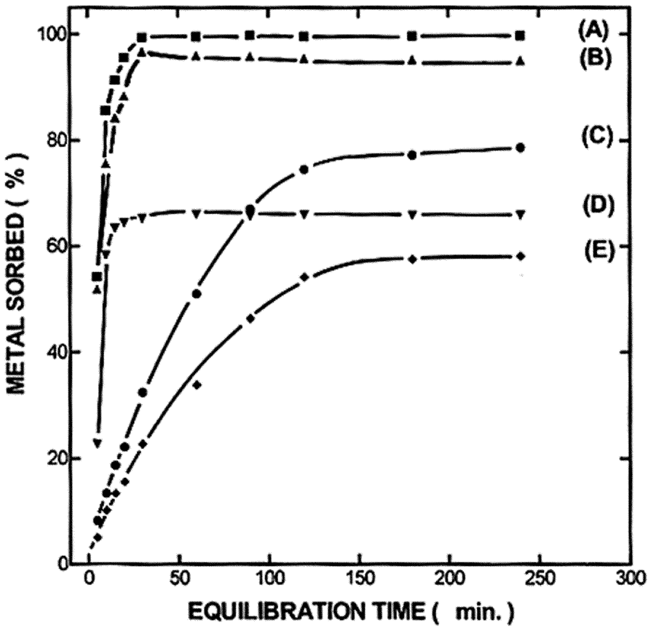

Fig. 2 Effect of equilibration time on sorption of metal ions on hair sorbent at pH 7.0 (*A*) Cd^{2+}, (*B*) Pb^{2+}, (*C*) Cr^{3+}, (*D*) Cu^{2+}, (*E*) Ni^{2+}

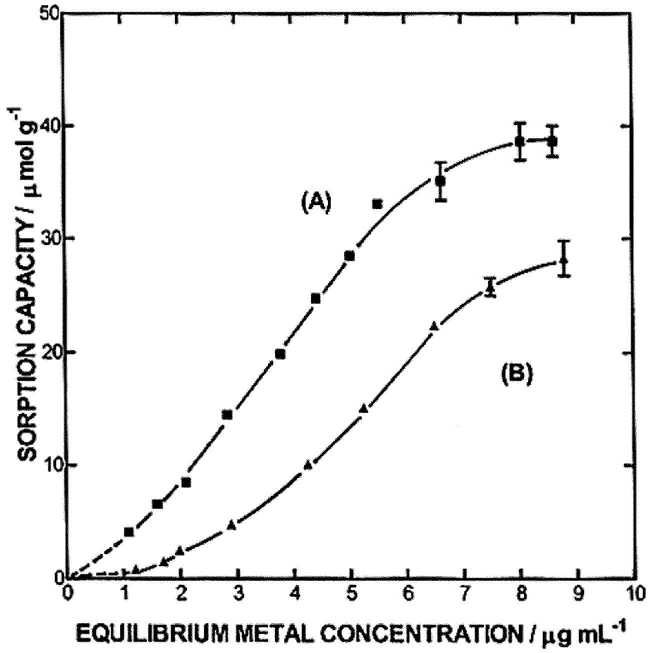

Fig. 3 Sorption isotherm for cadmium (*A*) and lead (*B*) at pH 7.0 using the variable sorbent mass method

and almost complete in 5 min. Desorption of copper is also fast but only 80% complete after 5 min agitation. Desorption of Ni and Cr are even slower and less quantitative with 0.5 mol L^{-1} HNO_3. Desorption with 0.5 mol L^{-1} HCl was as efficient as HNO_3 and has no distinct advantage. On the other hand, desorption with 0.1 mol L^{-1} EDTA (pH 8) was both quantitative and efficient in desorbing all metals from the sorbent. Recycling the sorption desorption process several times showed no memory effect. However, for trace work it is advisable to use a fresh sorbent sample for each test.

The sorption isotherm

The effect of equilibrium metal ion concentration (µg mL^{-1}) on the sorption capacity in µmol g^{-1} for Pb and Cd (breakthrough curves) is shown in Fig. 3. The higher uncertainty for the data near the plateau region is due to the use of a low mass of sorbent. In initial tests a fixed mass (0.1000 g) of sorbent and variable initial metal concentration (5 to 50 µg mL^{-1}) was used. However, in these tests a plateau was not reached because of the turbid solutions formed above about 18 µg mL^{-1} of metal concentration. Figure 3 shows that the sorption capacity for Cd and Pb are 39 and 26 µmol g^{-1}, respectively. These sorption capacity values are similar to or higher than those obtained by grafting special ligands on some inorganic matrixes [26, 27] and resins [28].

Effect of diverse ions

The effect of diverse ions commonly present in water samples on the recovery of Pb and Cd was studied at appropriate levels of the diverse ions (Table 2). It is evident from Table 2 that recovery of both Pb and Cd is not compromised to any significant extent by any of the major anions and cations likely to be present in natural water. Furthermore, recovery is acceptable for metal concentrations as low as 25 µg L^{-1}. High level of phosphate may lead to precipitation of metal ions. However, this is not viewed as interference in the method since precipitates are settled or filtered prior to analysis. The presence of strongly complexing anions such as EDTA and cyanide will definitely lead to lower metal recoveries if their metal complexes did not sorb as strongly as the free metal ion, and other kinetically labile complexes.

Analytical figures of merit

The calibration curve for lead is linear up to 220 µg L^{-1} with a slope of 0.0016 absorbance units (AU) per µg L^{-1} and a y-intercept of +0.0006 AU. For cadmium the calibration curve is linear to a sample concentration of 75 µg L^{-1} with a slope of 0.0062 AU per µg L^{-1}, and a y-intercept of 0.0008 AU.

The limit of detection was calculated (5 replicate blank runs) from the average absorbance plus 3 times the standard deviation of the average absorbance. The obtained limits of detection for lead and cadmium were 3.4 and 4.6 µg L^{-1}, respectively. At 50 µg L^{-1} level, reproducibility of the proposed analytical method for lead (estimated

Table 2 Recovery of trace metals in the presence of common ions

Element*	Concentration (μg mL^{-1})	Recovery (%)**					
		Pb			Cd		
		25	50	100	25	50	100
-	-	96.8	97.2	98.0	99.0	99.2	99.4
Zn(II)	0.50	97.0	97.1	98.1	98.8	99.4	99.5
Cu(II)	0.050	96.9	97.3	97.5	98.9	99.2	99.3
Fe(III)	0.50	96.9	97.2	97.2	98.8	99.2	99.4
Ca(II)	50	97.2	97.5	97.5	99.0	99.1	99.1
	200	97.0	97.1	97.3	98.3	99.0	99.0
Mg(II)	20	97.4	97.6	97.9	98.6	99.2	99.3
Na(I)	20	96.6	97.4	98.0	99.2	99.2	99.4
	100	96.5	97.0	97.5	98.3	98.6	99.0
K(I)	10	97.8	98.1	98.1	98.6	99.2	99.5
HCO_3^-	100	95.8	96.6	98.2	98.2	98.7	99.4
SO_4^{2-}	100	93.6	94.4	94.8	96.3	97.5	98.1
Cl^-	100	97.1	98.0	98.2	99.2	99.3	99.4

*Cations were added as their nitrate or chloride salts while anions were added as their sodium salts. Results are averages from duplicate samples.

from the data tabulated above) ranged between 3.2% to 7% relative standard deviation (RSD), while that of cadmium ranged between 7% and 10.3% RSD.

Application to treated wastewater

Grab samples were collected in polyethylene bottles between January and June 2001 at the discharge point from abu-Nakhla pond that receives treated wastewater from two sewage treatment plants in the area [29]. The filtered sample was analysed for Pb and Cd by GFAAS. The sample was also analysed after spiking with 50 μg L^{-1} of both lead and cadmium by GFAAS and by pre-concentration-FAAS according to the proposed procedure. Results from this test are collected in Table 3. Analytical precision of the two methods is comparable, as is evident from the standard deviation next to each value (n=3). However, recovery of both elements ranged between 79 and 86%. The treated wastewater probably contains some ligands that form stronger and/or less labile complexes with metal ions than those available on hair sorbent. This result means that the treated wastewater has a low buffering capacity for metal ions [30] and could be vulnerable to contamination by heavy metal ions.

Conclusions

Human hair shavings could be used for pre-concentration work especially for lead and cadmium with a pre-concentration ratio of about 40. Other transition elements sorb on this sorbent as well but their recovery is less than quantitative. The optimum concentration efficiency varies from one element to another. The sorption of toxic heavy metals on hair could have a negative impact on human health, for example, during swimming in polluted rivers and lakes.

It is interesting to study the sorption of other metals ions and semi-metals such as mercury and arsenic which is known to accumulate in hair. Other fibrous proteins such as wool, animal hooves, and fish scales may show similar sorption characteristics. Such material may find applications in treatment and decontamination of wastewater. Work in this direction is under investigation in this laboratory.

Table 3 Determination of lead and cadmium concentration in treated wastewater samples from Abu-Nakhla pond in Qatar

Sample ID	Cd Concentration (μg L^{-1})*			Pb Concentration (μg L^{-1})*		
	As is GFAAS	Spiked (50 μg L^{-1})		As is GFAAS	Spiked (50 μg L^{-1})	
		GFAAS	FAAS		GFAAS	FAAS
JAN 01	ND	50.0±3.1	41.2±1.5	D	51.2±4.1	40.4±3.7
FEB 01	1.8±0.6	52.1±2.7	44.5±2.3	ND	50.2±4.3	40.7±3.2
MAR 01	3.5±0.1	54.6±4.7	47.0±3.2	1.9±0.3	52.2±2.2	42.8±3.0
APR 01	ND	49.2±3.1	39.4±1.3	7.5±1.3	56.3±3.6	46.7±4.4
MAY 01	0.5±0.2	50.3±1.0	42.8±3.1	1.7±0.4	51.2±2.8	42.5±3.3
JUN 01	ND	49.4±2.5	40.0±2.6	2.0±0.3	50.1±5.0	41.1±4.2

*ND=not detected (below the limit of detection), D=detected (below the limit of quantification). The uncertainty is the standard deviation for triplicate runs.

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