Equilibrium and Kinetic Studies for Extracting Cu, Mn, and Fe From Pulp Wastewater onto a C-18 Column with Acetylacetone Complexing Ligand

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EQUILIBRIUM AND KINETIC STUDIES FOR EXTRACTING Cu, Mn, AND Fe FROM PULP WASTEWATER ONTO A C-18 COLUMN WITH ACETYLACETONE COMPLEXING LIGAND

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A preconcentration procedure using solid phase extraction of heavy metals in pulp wastewater is reported. The procedure was optimized by using model solutions of selected heavy metals to investigate the effect of matrix constituents. Equilibrium studies highlighted the bonding and adsorption characteristics. The metal recoveries after spiking pulp waste filtrate with Cu, Ni, and Pb each at 0.1 and 0.2 ppm was 120, 91, and 93%, respectively. The Freundlich adsorption isotherms with correlation coefficients (R^2) 0.612, 0.810, and 0.750, showed a better fit compared to Langmuir isotherm values of 0.277, 0.389, and 0.272 for Cu, Mn, and Fe, respectively.

INTRODUCTION

The direct and accurate determination of trace elements in complex liquid matrices with most instrumental techniques is difficult due to the low concentration

of analytes as well as interferences caused by sample matrices. Analysis of trace metal ions in saline matrices using inductively coupled plasma-atomic emission spectrometry (ICP-AES) has several problems because the aspiration of solutions with high salt concentrations into plasma systems leads to nebulizer blockage, considerable background emission, transport and chemical interferences, with a consequent drop in sensitivity and precision (Boumans 1987; Bekjarov, Kmetov, and Futekov 1989; Montaser and Golightly 1990; Budic and Hudrick 1994).

In order to solve the problem of matrix interference and trace metal levels, sample clean-up and preconcentration is inevitable. Solid phase extraction is one of the most effective multi-element analyte-matrix separation and preconcentration methods because of its simplicity, rapidity, and ability to attain a high concentration factor (Dogan et al. 1997; Seren et al. 2001; Soylak 2001; Killian and Pryznska 2002). The method's ability to eliminate sample matrix makes it attractive for the analysis of liquid samples with complex matrices.

In the present work, a novel analytical procedure for the SPE extraction/ preconcentration of metals in pulp wastewater matrices and saline environmental water samples prior to their determination by inductively coupled plasma-atomic emission spectrometry (ICP-OES) was developed. The extraction/preconcentration is based on the chelation of metals with acetylacetone prior to adsorption onto a C-18 column. Though acetylacetone is known to form stable metal complexes, it has not been employed as a complexing agent in solid phase extraction systems (Schaefer and Mathisen 1965).

EXPERIMENT

Reagents

All solutions were prepared in Milli-Q water of resistivity $18.2\,\Omega\,cm^{-1}$; the reagents were of analytical grade, unless otherwise specified. Calibration standards were prepared from Fluka TraceCert 10 ppm multi-element stock standard. Nitric acid was TraceSelect ICP grade >69% supplied by Fluka. Solid phase extraction (SPE) materials employed in the study were XAD-1180, XAD-2, and Supelclean LC-18 cartridges (1.0 g), all supplied by Supelco, Bellefonte, USA. The SPE material specifications included: C-18 surface area $496\,m^2/g$ (BET Method), average particle size $56.2\,\mu m$, and average pore diameter of 71 angstroms; XAD-1180 with surface area $500\,m^2/g$, mesh size 20–60 μm and average pore diameter 300 angstroms; and XAD-2 with surface area of $300\,m^2g^{-1}$, mesh size 20–60 μm and average pore diameter 90 angstroms. Sea water reference material NASS-5 obtained from the National Research Council of Canada was used to test the method accuracy.

Preconcentration Procedure

The proposed analytical method was tested on 0.2 ppm model solutions comprising either a mixture of metals or just Cu, depending on the parameter being investigated. Five milliliters of appropriate buffer solution (pH 2 to 10) was added to 30–40 mL of model solution containing 6–36 μg of metal ions. Acetylacetone (0.4 mL of 1.0 mM) was added to the buffered model solution and allowed to stand for ten

minutes. The solid phase extraction column was conditioned with 5 mL of methanol flushed with 5 mL Milli-Q water. This was followed by washing with 5 mL of 0.5 M HNO_3 in acetone and flushed with 20 mL Milli-Q water, followed by 5 mL of 1 M NaOH, again flushed with 20 mL Milli-Q water, and finally conditioned with 10 mL of appropriate buffer. The conditioning process introduced a thin film of water-miscible solvent on the packing, which promotes better contact between an aqueous sample matrix and the hydrophobic solid phase. The process also removes possible impurities initially contained in the sorbent or the packaging and removes the air pockets present in the column, filling the void volume with solvent. The model solution was then run through the preconditioned solid phase column under vacuum (in a VacMaster vacuum manifold) at a flow rate of 3 mL min^{-1}. Thereafter the metal ions were eluted with 5 mL of 0.5 M HNO_3 (TraceSelect ICP grade >69% supplied by Fluka) and the retained solutes collected for analysis by ICP-OES. All preconcentrations and extractions were performed in a "clean room."

Influences of pH on Sorption

Solid phase materials namely XAD-1180, XAD-7, and C-18 were employed in the experiment to determine the optimum extraction pH. The C-18 cartridges were factory packed in quantities of 1.0 g in 6 mL polyethylene tubes. While XAD-1180 and XAD-7 were packed in the laboratory, the resin material (600 mg) was weighed in a beaker and suspended in methanol for about 10 minutes. The methanol was decanted and thereafter water added onto the resin and the contents poured into 6 mL polyethylene tubes and allowed to settle. Two frits were inserted, one before pouring the resin and the other after the resin had settled. Metal impurities were removed by flushing through the column with 5 mL of 0.5 M HNO_3 in acetone and then rinsing with 20 mL of Milli-Q water, followed by 5 mL of 1 M NaOH. The system was then rinsed with 20 mL of Milli-Q water and flushed with the appropriate buffer.

A model solution comprising 0.2 ppm of Cd, Cu, Cr, Fe Mn, Pb, and Si was prepared in Milli-Q water. Portions of 30 mL metal solution were dispensed into 100 mL polyethylene sample bottles and then 0.4 mL of 1.0 mM acetylacetone was added. The solution was then adjusted to the appropriate pH range 2–10, using various buffer systems. Phosphate buffer solution was prepared by mixing 0.1 M sodium dihydrogen phosphate (Sigma-Aldrich) solution with an appropriate amount of phosphoric acid to make up pH 2 and adding an appropriate amount of 1 M NaOH solution to obtain pH 7. Acetate buffer solutions were prepared by mixing 0.1 M sodium acetate solution with an appropriate amount of acetic acid to achieve either pH 4, 5, or 6. Ammonium chloride buffer was prepared by mixing 0.1 M ammonium chloride with an appropriate amount of NH_4OH to obtain pH 8, 9, or 10.

The buffer solution (10 mL at the appropriate pH) was passed through the column and, thereafter, 30 mL of the model metal solution loaded in the column at a flow rate of about 3 mL per minute. The column was then washed with the appropriate buffer and the adsorbed metal eluted with 5 mL of 0.5 M HNO_3 at a flow rate of about 3 mL per minute. The column was reactivated by washing with 20 mL of Mill-Q water and 10 mL of the appropriate buffer solution and was ready for reuse. Care was taken not to allow the solid sorbent to dry in between the

conditioning and the sample treatment steps. If this happened, it would induce channeling phenomena due to expansion and contraction of the stationary phase.

Influence of Acetylacetone on Metal Recovery

Acetylacetone (1.0 mM) was added in varying volumes (Figure 1) to 30 mL of 0.2 ppm Cu model solution at pH 6. After shaking, the mixture was allowed to stand for 10 minutes and thereafter run through a C-18 column at a flow rate of 3 mL min^{-1}. The retained Cu was stripped by passing 5 mL of 0.5 M HNO$_3$ (TraceSelect ICP grade >69% supplied by Fluka) through the column and eluent collected in 15 mL polyethylene vials for analysis by ICP-OES.

Effect of Sample Volume

Acetylacetone (0.5 mL of 1.0 mM) was added to 30 mL of 0.2 ppm model solution at pH 6. The volumes of the model solutions were varied from 10 mL to
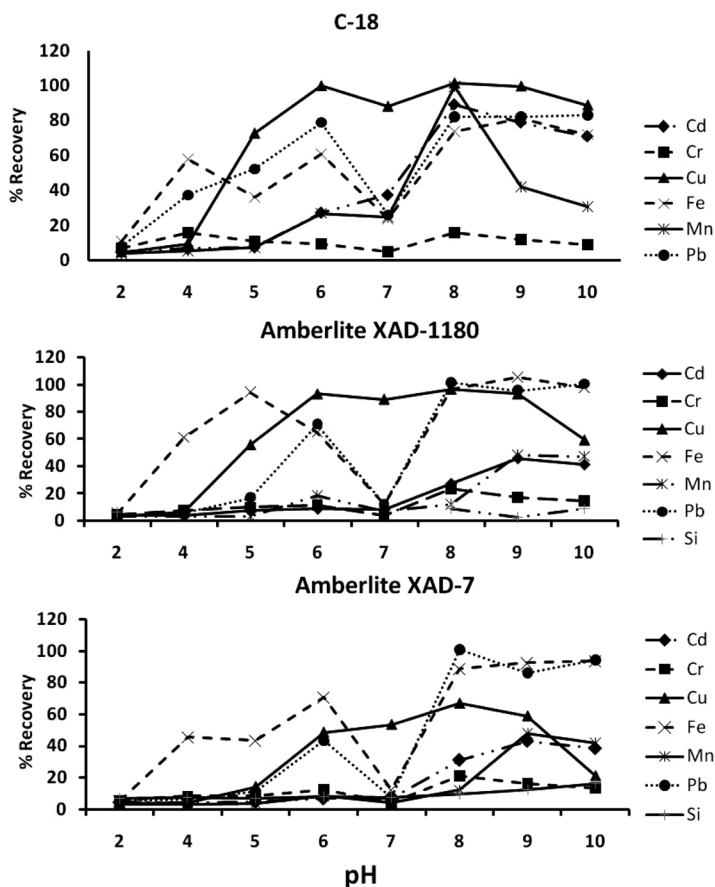
Figure 1. Effect of pH on % recovery of metal (Cd, Cr, Cu, Fe, Mn, and Pb) as acetylacetone complexes, adsorbed onto different SPE material (C-18, XAD-1180, and XAD-7).

150 mL and run through solid phase extraction column at a rate of $3\,mL\,min^{-1}$. The retained Cu^{2+} was stripped by passing 5 mL of 0.5 M HNO_3 through the column and collected in 15 mL polyethylene vials for analysis by ICP-OES.

Effect of Sample Matrix

The recovery of analyte ions in the presence of selected alkaline and alkaline earth metals was investigated by adding known concentrations of either Ca^{2+}, Mg^{2+}, or Na^+ ions to a model solution containing 0.2 ppm of both Cu^{2+} and Fe^{3+}. The mixture was adjusted to pH 8 with an ammonium buffer and ran through a C-18 solid phase extraction column after the addition of 0.4 mL acetylacetone.

Procedure for Standard Reference Material

Sea water reference material NASS-5 (60 mL), from the National Research Council of Canada was spiked with 0.5 mL of acetylacetone and ran through a C-18 SPE column. The sample and sea water reference material were preconcentrated without adjusting their pH. The SPE column was, however, conditioned with 10 mL of 0.1 M pH 8 ammonium buffer before loading and thereafter cleaned with 5 mL of the ammonium buffer before stripping.

Application of Proposed Method on Pulp Waste

The pulp waste filtrate (2 mL) was made up to 40 mL with Milli-Q water and dispensed into a 100 mL polyethelene bottle. The metals in the sample were then extracted/preconcentrated and analyzed as discussed under the "Preconcentration Procedure."

Equilibrium Isotherm Models

Background theory. An isotherm describes the relationship between the amount of metal adsorbed and metal ion concentration remaining in the solution as the metal concentration in the two phases influences the kinetics of metal adsorption. Langmuir and Freundlich are among the most common isotherms describing this type of adsorption system. Langmuir (first studied in 1918) is the most important model for a monolayer adsorption. It is based on the assumption that adsorption can only occur at a fixed number of definite localized sites whereby each site can hold only one adsorbate molecule (monolayer); all sites being equivalent with no interaction between adsorbed molecules, even on adjacent sites. The Langmuir isotherm can be derived from the Gibbs approach (Yang 1987) according to Ng, Cheung, and McKay (2003) as shown in Eq. (1):

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e is the amount of metal adsorbed on a gram of adsorbent and C_e is the metal concentration of the solution at equilibrium. The constants K_L and a_L are the

characteristics of the Langmuir equation and can be determined from a linearized form of the previous equation, represented by Eq. (2):

$$\frac{C_e}{q_e} = \frac{a_L}{K_L} C_e + \frac{1}{K_L} \qquad (2)$$

A plot of C_e/q_e vs. C_e gives a straight line with a slope of a_L/K_L and an intercept of $1/K_L$. The constant K_L is the equilibrium constant and the ratio a_L/K_L gives the theoretical monolayer saturation capacity (Ng et al. 2003)

Freundlich isotherm (Freundlich 1906) is the most important multi-site adsorption isotherm, widely applied in heterogeneous systems especially of organic compounds and highly interactive species on activated carbon and molecular sieves. However, it does not obey Henry's Law, Eq. (3), at low concentrations (Ng et al. 2003):

$$q_e = K_F C_e^{bF} \qquad (3)$$

The linearized form of Eq. (3) is obtained by taking logarithms where the parameters K_F and b_F can then be obtained from a plot of $\ln q_e$ vs. $\ln C_e$ [Eq. (4)]:

$$\ln q_e = b_F \ln C_e + \ln K_F \qquad (4)$$

where q_e and C_e have the same meaning as in Eq. (1); K_F and b_F stand for Freundlich isotherm constant, $(dm^3\,g^{-1})$ and Freundlich isotherm exponent constant, respectively.

Procedure for adsorption studies. Dynamic flow adsorption experiments were conducted at 25°C on factory packed C-18 solid phase columns (1.0 g). The equilibration was considered to occur at a loading flow rate of 3 mL min^{-1}, determined by monitoring flow rate and the point of maximum adsorption. Model solutions (30 mL) adjusted to pH 8, comprising Cu, Fe, and Mn acetylacetone (1.0 mM) complexes of varying concentrations (0.2 ppm to 3.2 ppm), were loaded onto C-18 columns. The adsorbed metal in the acetylacetone complex was stripped from the C-18 column by eluting with 5 mL of 0.5 M HNO$_3$ and, thereafter, analyzed by ICP-OES.

The amount of the metal adsorbed (mg) per unit mass of adsorbent, q_e, was obtained by using Eq. (5):

$$q_e = \frac{C_a V}{m} \qquad (5)$$

where C_a in μM is the concentration of the retained metal after acid stripping, m is the dry mass of biosorbent in grams, and V is volume of solution in liters.

RESULTS AND DISCUSSION

### pH Influence on Acetylacetone Metal Complex Formation

In solid phase extraction studies of heavy metal ions based on chelation, the pH of aqueous solutions is one of the main factors influencing the quantitative recoveries of the analytes (Korn et al. 2006; de Castro, de Alâcantara, and dos

Santos Roldan 2004; Gilli et al. 1989; Yoon, Choi, and Kim 1999; Tateki, Fumio, and Shigeki 1999; Xu et al. 2004; Pearson and Anderson 1970). Environmental samples are comprised of complex matrixes depending on the sample type and sediment biogeochemistry. Physicochemical parameters influence the speciation and mobility of metal ions; a change in solution pH would influence the speciation of a metal ion. For pollution and speciation studies, it is important that the physico-chemical parameters are maintained to simulate in-situ conditions.

The results obtained in the investigation of the influence of pH on metal preconcentration showed Cu to be quantitatively recovered over a wide pH range 6–10 (see Figure 1) as opposed to the other metals under study. The solid phase material is shown to have an influence on the recovery of metal ions; the less polar the solid phase, the more efficient the retention (see Figure 1). Amberlite XAD-7 is a polyacrylic acid ester polymer resin having hydrophilic sites of intermediate polarity (Horwitz et al. 1992; Compano et al. 1994; Lin et al. 2007; Tewari and Singh 2000; Korn et al. 2004). Amberlite XAD-1180 is a polystyrene divinylbenzene copolymer and is a nonionic polymeric adsorbent (Soylak et al. 2003a). The C-18 column used in this work is an octadecyl chain bonded monomerically onto a silica gel base material, with strong hydrophobicity used to adsorb analytes of even weak hydro-phobicity from aqueous solutions.

Acetylacetone abbreviated as Hacac, exists in three forms in aqueous solution: the tautomeric keto (I) and enol (11) forms, and the anionic form (111) as shown in Scheme 1. The latter scheme is the common product of dissociation of either proto-nated tautomer (Fay et al. 1971; Pearson and Anderson 1970). The enol form is characterized by an internal hydrogen bond that forms a stable six-membered ring and is the predominant species at room temperature (Fay et al. 1971; Pearson and Anderson 1970). Hydrogen bonding in the enol reduces the steric repulsion between the carbonyl groups.

It has been proposed that the first step in the reaction between copper (II) and the keto tautomer of acetylacetone in an acidic media involves the formation of a symmetrical precursor complex in which the metal ion is bonded to both keto groups similar to that shown in (IV), Scheme 2 (Pearson and Anderson 1970). In this mech-anism the cupric ion acts as an electron sink and the rate determining step involves a slow, metal ion catalyzed proton release (Pearson and Anderson 1970). This rate determining step is influenced by the electronegativity of the metal ion. A higher value enhances its ability to act as an electron sink. The electronegativities (EN) and electronegativity differences, ΔEN of the metals under study, are listed in
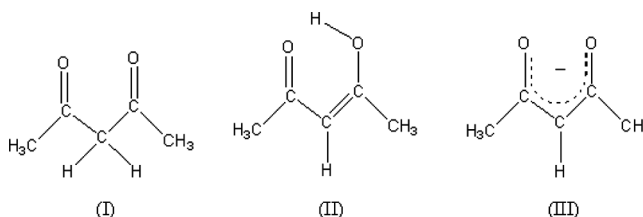
Scheme 1. The forms of acetylacetone that exist in solution; (I) the keto-form, (II) the enol-form, and (III) the acetonato ion.
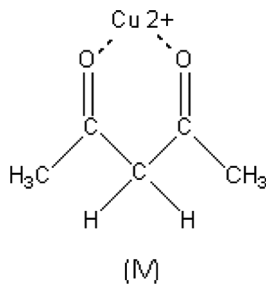
Scheme 2. Structure of copper acetylacetone complex in acidic medium.

Table 1. A higher % analyte recovery corresponded with a low ΔEN of analyte and oxygen. Oxygen donor atoms have a weaker effect on the ligand field stabilization resulting in less electron transfer capability from the ligand to the metal, and a weaker covalent bond as reported by Imura and Suzuki (1985) and Sohn and Lee (2000) indicated that cations of higher polarizing power are able to interact more effectively with the oxygen of the carbonyl group in the acetylacetone molecule. Acetylacetone pK_a is 8.95 (Pearson and Dillon 1953) and thus at higher pH the solvent abstracts the acidic proton and the resonance stabilized structure (III) is formed that readily combines with the metals in solution (Scheme 1).

Influence of Acetylacetone on Recovery

The amount of acetylacetone required to optimally extract metal ions in solution was determined by varying the volume of 1.0 mM acetylacetone that was added to 30 mL of 0.2 ppm Cu model solution. The acetylacetone sample mixture was preconcentrated onto a C-18 column and analyzed by ICP-OES. From the results reported in Figure 2, 0.4 mL of 1.0×10^{-3} M acetylacetone was chosen as the appropriate volume for a 30 mL model solution. There was no significant difference (based on ANOVA statistical test, n = 3; p = 0.05) in the extraction efficiency between addition of 0.1 mL and 2 mL acetylacetone.

Table 1. The metal electronegativities (EN), electronegativity difference (ΔEN) of the metal and oxygen and % recovery; recovery performed at pH 6 (slightly acidic)

Metal	Electronegativity	% Recovery $x \pm s/\sqrt{N}$	Δ Electronegativity (EN) ΔEN=O-metal
Cu	1.90	100 ± 0.02	1.54
Fe	1.83	61 ± 12.0	1.61
Pb	2.33	79 ± 0.4	1.11
Mn	1.55	27 ± 0.5	1.89
Cr	1.66	9 ± 1.4	1.78
Cd	1.69	27 ± 0.3	1.75

Electronegativity values quoted from Roymech 2008 website. http://www.roymech.co.uk/Related/Chemistry/Chem_Electronegativity.html assessed 7/10/2009.
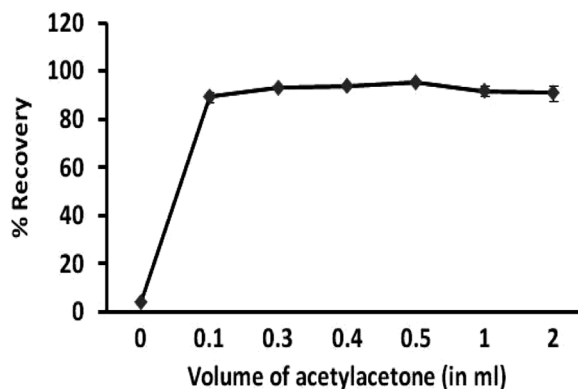
Figure 2. The % recovery of 0.2 M Cu model solution (pH 6) adsorbed onto C-18 columns under varying volumes (0 to 2 mL) of 1.0 mM acetylacetone.

Effect of Sample Volume

The effect of the sample volume on Cu recovery was studied by loading 10–150 mL of 0.2 ppm Cu model solutions adjusted to pH 6, through C-18 SPE column at a flow rate of 3 mL min^{-1}. The results are given in Figure 3, the method is quite sensitive even on sample volumes as low as 10 mL, the extraction efficiency remained consistent over a wide range of sample volumes (10–150 mL). For samples with low analyte concentration, the detection limit (see Table 2) can be improved by increasing the sample volume and still maintain the extraction efficiency.

Effect of Sample Matrix

The effect of sample matrix due to alkaline and alkaline earth metals on Cu recovery was investigated by adding the matrix ions into a 30 mL model solution and loading
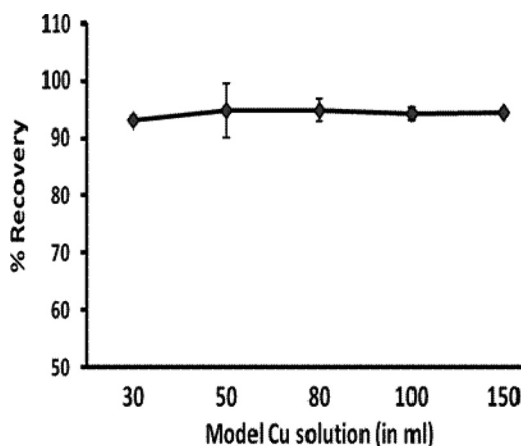
Figure 3. The % recovery under varying volumes (10 to 150 mL) of 0.2 M Cu model solution (pH 6).

Table 2. Effect of matrix ions on the recovery of Cu and Fe (pH 8; sample volume: 30 mL, n = 3)

Ion	[Matrix] in ppm Added	[Cu] in ppm x ± S.D	[Fe] in ppm x ± S.D
Na^+	500	94 ± 2.4	92 ± 0.5
	1000	94 ± 2.5	80 ± 5.2
	2000	94 ± 4.1	57 ± 1.3
	8000	97 ± 3.2	48 ± 8.7
	10,000	88 ± 0.8	28 ± 4.2
	15,000	89 ± 3.8	38 ± 9.1
Ca^{2+}	500	87 ± 0.8	87 ± 3.7
	1000	84 ± 1.9	84 ± 1.8
	2000	82 ± 0.9	84 ± 0.5
	4000	85 ± 4.6	85 ± 6.0
	8000		84 ± 4.2
	10,000	84 ± 3.1	87 ± 7.6
	15,000	80 ± 0.9	71 ± 4.0
Mg^{2+}	500	84 ± 1.0	93 ± 5.9
	1000	83 ± 0.2	
	2000	76 ± 3.0	91 ± 3.0
	4000	86 ± 4.4	94 ± 12.0
	8000	82 ± 0.9	101 ± 0.5
	10,000	80 ± 4.7	90 ± 2.5
	15,000	85 ± 3.5	96 ± 1.2

onto a C-18 column. From the results reported in Table 2, it was observed that the proposed preconcentration method can be applied on saline samples. The extraction was quantitative in model solutions containing a matrix of up to 8000 ppm Na^+.

Detection Limit and Standard Reference Material

The detection limits of the analytes based on three times the standard deviations of the blank divided by the slope of the calibration graph (3 s/b, n = 20, where s is the standard deviation of the blank and b is the slope of calibration curve) are reported (Vandecasteele and Block 1997) in Table 3. The proposed method is sensitive to concentrations in ppb levels (Table 4) and compares favorably with other preconcentration methods as reported in the literature (see Table 5 for references). The method was tested on seawater standard reference material NASS-5 and the results obtained, which gave a pre-concentration factor of 12, was in agreement with those reported for the seawater standard reference material NASS-5.

Application of Proposed Method on Dissolving Pulp Wastewater

The method was applied on dissolving pulp waste filtrate obtained from the alkaline bleaching stage. The pulp waste filtrate matrix comprises mainly of lignin, organic extractives, as well as alkaline and alkaline earth metals. A sample was first analyzed, as stated previously, to obtain its original Cu concentration and thereafter spiked with Cu solutions to constitute sample concentrations of 0.1 and 0.2 ppm. The metal recovery values after spiking pulp waste filtrate with a mixture of Cu, Ni, and

Table 3. Detection limits of metal ions (Cd, Cu, Fe, Pb) at different sample volumes and the analysis of 60 mL NASS-5 Seawater reference material

			NASS-5 Seawater Reference Material	
Metal	PF	Detection limit/ ppb	Certified value	Our value
Cd	4	0.15		
	12	0.05	0.023 ± 0.003	BDL
	20	0.03		
Cu	4	0.40		
	12	0.14	0.297 ± 0.046	0.31 ± 0.12
	20	0.08		
Fe	4	8.40		
	12	2.80	0.207 ± 0.035	BDL
	20	1.70		
Pb	4	15.70		
	12	5.20	0.008 ± 0.005	BDL
	20	3.10		

BDL=Below Detection Limit; PF=Preconcentration Factor.

Table 4. Heavy metal (Cu, Ni, Pb) analysis in pulp waste filtrate after acetylacetone complexation and preconcentration on C-18 SPE

Metal in pulp filtrate	PF	Spike ppm	Concentration ppm $(x \pm s/\sqrt{N})$	% Recovery
Cu	8	0	0.0061 ± 0.0004	
Ni	8	0	0.0062 ± 0.0050	
Pb	8	0	0.0034 ± 0.0008	
Cu	8	0.1	0.1163 ± 0.0150	110
Ni	8	0.1	0.0910 ± 0.0080	84
Pb	8	0.1	0.1084 ± 0.0016	104
Cu	8	0.2	0.2721 ± 0.0060	133
Ni	8	0.2	0.2050 ± 0.0690	99
Pb	8	0.2	0.1662 ± 0.0500	81

PF = preconcentration factor.

Table 5. Comparative data from literature reports on solid phase extraction

Analyte	Complexing Media	Adsorbent	PF	Detection Limit ppb	Reference
Fe, Pb & Cr	*p*-xylenol	Amberlite XAD-7	6	3.07–18.6	Divrikli et al. 2007
Cu, Fe, Ni & Co	calmagite	Chromosorb-102	10	6–113	Soylak et al. 2003b
Cd & Pb	1-(2-pyridylazo) 2-naphthol (PAN)	Chromosorb-106	250	0.19–0.32	Tuzen, Parlar, and Soylak 2005
Cd, Cu, Cr Co, Fe, Mn, Pb	alpha-benzoin oxime	Diaion SP-850	50	0.28–0.73	Soylak & Tuzen 2006
Cu, Cr Co, Fe, Pb	calmagite	cellulose nitrate membrane filter	50	0.06–2.5	Soylak et al. 2002
Cu, Mn, Fe	Acetylacetone	C-18	8	0.03–1.7	This work

Pb to obtain two model solutions of concentration 0.1 and 0.2 ppm, were 120%, 91%, and 93%, respectively (Table 4). This method is highly sensitive for the determination of Cu, Ni, and Pb in complex liquid matrixes and can be applied in the pulp and paper industry to monitor metal levels in wastewater. At elevated levels, Cu is especially toxic to invertebrates which can also lead to growth inhibition and repro-duction disturbances in marine invertebrates (Nimmo and Hamaker 1982). The toxicity of Cu is mainly from the bioavailable fraction and has been shown to be depen-dent on the concentration of the free copper ion, Cu^{2+} (Sunda and Guillard 1976).

Adsorption Isotherms

Sorption and isotherm studies were performed on selected metals (Cu^{2+}, Fe^{2+}, and Mn^{2+}) and results are reported in Figure 4 and Table 6. The choice of the three metals was based on their relative abundance to those of the other metals in the pulp.

The C-18/acetylacetone dynamic flow system showed a high affinity for Cu and the binding sites were not saturated even after passing 30 mL of 3.2 ppm model solution (Figure 4). The system had a low affinity for Fe with the adsorption capacity $q_e \approx 2.0$ ($\mu mol\, g^{-1}$). Acetylacetone exists in solution in keto and enol forms and at higher pH, the ionized form is also present. The existence of acetylacetone in various forms affects the bonding/binding characteristics of Hacac complexed metal species onto the C-18 and, therefore, it is not a homogeneous solution. Sohn and Lee (2000), reported the linking of acetylacetone to an exchangeable metal cation through a water bridge bonding as $>C=O-H-O(H)-M^{n+}$. The size of the cation and orien-tation of water molecules around the cation is controlled by the coordinating power of the cation and the space around it should also be an important factor (Sohn and
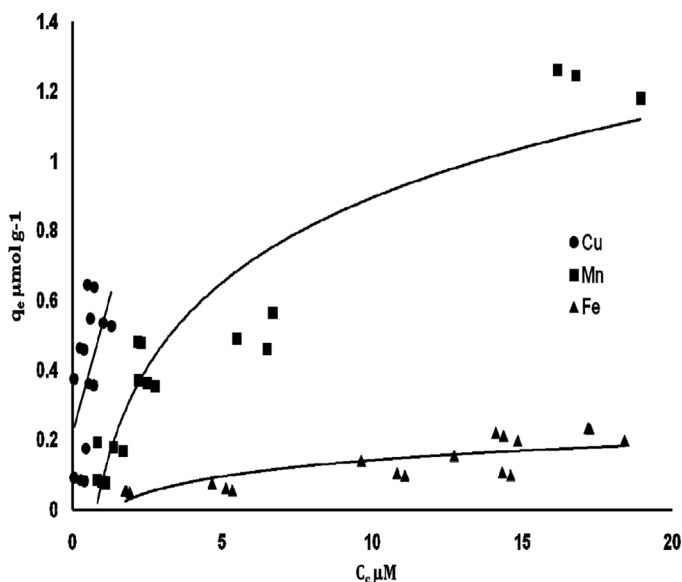

Figure 4. Adsorption isotherm for Cu, Fe, and Mn acetylacetone complexes on C-18 SPE column.

Table 6. Langmuir and Freundlich adsorption isotherm parameters for Cu, Fe and Mn acetylacetone complexes on C-18 SPE. Showing regression line characteristics R^2, a_L/k_L, $1/k_L$, b_F, and lnK_F

	Langmuir Isotherm			Freundlich Isotherm		
	R^2	a_L/K_L	$1/K_L$	R^2	b_F	lnK_F
Cu	0.277	0.959	1.687	0.612	0.618	−0.963
Mn	0.389	0.407	7.515	0.810	0.779	−1.931
Fe	0.272	2.892	49.660	0.750	0.606	−3.469

Lee 2000). The results obtained in this work are in agreement with those reported on non-homogeneous existence of acetylacetone. The experimental adsorption isotherm system did not fit the Langmuir model, which assumes a homogeneous system with no interaction between adsorbed molecules, even on adjacent sites. Thus, the linear Langmuir correlation coefficients (R^2) for Cu^{2+}, Mn^{2+}, and Fe^{3+} were 0.277, 0.389, and 0.272, respectively (Table. 6). The system, however, correlated well with the Freundlich adsorption isotherm model which assumes a heterogeneous system especially for organic compounds and highly interactive species on activated carbon (Ng et al. 2003). Linear regression for Freundlich plots gave correlation coefficients (R^2) for Cu, Mn, and Fe of 0.612, 0.810, and 0.750, respectively (Table 6). These values are much better than the coefficients obtained for Langmuir plots. These results (Freundlich) imply that the Hacac ligand provides multiple binding sites for metal ions.

CONCLUSIONS

The proposed analytical method was found to be effective in the analysis of pulp waste and salt matrices for trace metals. It is suitable for the analysis of seawater and wastewater systems with high content of organic matrices. The method is however best suited for the analysis of Cu (up to $0.2\,M \sim 12,600\,ppm$) over a wide pH range (2–10). The advantage of using this method for the analysis of Cu in environmental waters is that there is no need to adjust the sample pH. Analyzing the samples without prior adjustment of the pH is important so as to avoid over- or under-estimation of Cu levels due to precipitation or leaching during sample pH adjustment.

Acetylacetone complexes of Cu, Mn, and Fe fitted the Freundlich adsorption model implying that they were retained on the solid phase material via physical adsorption due to weak attractive forces; generally Van der Waals forces (Perez et al. 2007). The Freundlich model principally represents a physical adsorption phenomenon, whereas the Langmuir model represents a chemical adsorption process (Perez et al. 2007).

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