View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by AJOL - African Journals Online

S. Afr. J. Chem., 2005, **58**, 120–126,
<http://journals.sabinet.co.za/sajchem/>.

Comparative Studies of the Speciation Patterns of Nickel and Chromium in Surface-, Ground- and Wastewater Systems in Botswana

Jackson K. Kiptoo[a], J. Catherine Ngila[a*], Wellington R.L. Masamba[b] and Gerald M. Sawula[c]

[a]*Department of Chemistry, University of Botswana, Private Bag 00704, Gaborone, Botswana.*
[b]*Harry Oppenheimer Okavango Research Centre, University of Botswana, Private Bag 285, Maun, Botswana.*
[c]*NEMA, P.O. Box 22255, Kampala, Uganda.*

Received 31 January 2005; revised 6 July 2005; accepted 31 August 2005.

ABSTRACT

Results of speciation studies of nickel and chromium in wastewater, surface and groundwater systems using flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) are presented. Dimethylglyoxime (DMG) and diethylenetriaminepentaacetic acid (DTPA) were used as complexing agents for DPAdCSV determination of nickel and chromium, respectively, at a hanging mercury drop electrode (HMDE). Total nickel was in the range 3091–3201 mg L^{-1} in wastewater from an electroplating plant, 8.1–14.4 μg L^{-1} in surface water (freshwater) and 6.38–16.95 μg L^{-1} in groundwater. Total chromium was in the range 34.99–37.03 mg L^{-1} in electroplating wastewater and 15.8–571.0 mg L^{-1} in tannery effluents. Trace levels of chromium were detected in surface water (3.09–17.42 μg L^{-1}) and groundwater (18.01–36.39 μg L^{-1}). While most of the metal forms were found to be present in the CSV-labile fraction in the wastewater from the electroplating plant (mean of 67.9% for Ni and 79.8% for Cr), less than 5% of the total metal was present as CSV-labile fraction in tannery effluents, surface and groundwater samples. The tannery effluent was found to have very high complexation capacity (about 3 mg of Cr /L of effluent, i.e. 57.8 μM Cr). This complexing capacity of tannery effluent may have a potential application in environmental remediation.

KEYWORDS

Speciation, metals, complexation capacity, water systems, adsorptive cathodic stripping voltammetry.

1. Introduction

Most heavy metals are toxic to living organisms and have a tendency to accumulate in food chains. Nickel and chromium have been established as essential elements at trace concentrations but are toxic at high concentrations[1]. They both have wide industrial applications hence, their presence in various sectors of the environment is a public health concern and therefore requires strict control. Drinking water and wastewater guidelines for heavy metals are mostly limited to the control of total concentrations without regard to speciation. Studies have, however, shown that the toxicity, bioavailability, mobility[2–4] and geochemical reactivity[5] of trace metals are controlled by their free metal ion concentrations rather than by their total concentrations. For this reason, metal speciation has become of increasing relevance in environmental monitoring.

Trace heavy metals in water systems are present in various physico-chemical forms, which include simple hydrated ions, hydroxo complexes, inorganic and organic complexes and colloidal particulates[6]. Generally, the free metal ions and the simple complexes are more toxic than the strongly bound metal complexes and colloidal particles. Sometimes the degree of toxicity depends on the oxidation states of the elements present. For instance, chromium with oxidation state of +VI is relatively more toxic, shows higher water solubility and is more mobile in geochemical systems[7,8] than Cr(III). By contrast, Cr(III) is required at trace amounts for maintaining normal physiological functions of living organisms, although it is toxic at relatively higher concentrations.

The presence of natural and anthropogenic ligands in water has a profound effect on metal speciation and consequently their mobility and bioavailability. Humic substances (HS) are an important group of natural ligands occurring in abundance in freshwater systems. Their complexation reactions with metal cations and their role in environmental remediation has been documented[9]. The toxicity of most heavy metals to aquatic organisms is reduced upon complexation with humic materials. HS are also redox-active, and have been shown to reduce Cr(VI) to Cr(III) with beneficial effects in view of the toxic nature of the former[9]. Thus, knowledge of speciation is critical for proper interpretation of data and the definition of the quality of waters for legislative purposes. The objective of this study was therefore to determine the labile forms of nickel and chromium in both wastewater and freshwater systems containing varying concentrations of strongly binding ligands. We considered various water systems with contrasting types and levels of both metals and ligands. These were wastewater from an electroplating plant with elevated levels of nickel and chromium against a low ligand concentration, tannery effluents with both high chromium and high strong-ligand concentrations (protein-based materials) and finally surface- and groundwater systems with trace levels of both metals against high levels of HS. Our work on metal speciation patterns in wastewater from a nickel-chrome electroplating plant and a tanning factory (both located in the outskirts of Gaborone) is part of an environmental impact assess-

*To whom correspondence should be addressed. Tel: +267 355 2488; Fax: +267 355 2836; E-mail: ngilajc@mopipi.ub.bw

ment study of the operations of the rural industrial innovation centres (RIIC) in Botswana. There are concerns that the wastewaters may contain significant quantities of nickel and chromium and hence the need for compliance with safety guidelines for effluent discharges in Botswana[10].

Various analytical techniques and schemes[4,8,11–15] have been used to classify metal species into categories based on their physico-chemical properties. The simplest is distinction between particulate and dissolved metal fractions by filtration through a conventional 0.45-μm filter. Electrochemical techniques, especially stripping voltammetry which is used in the present study, in combination with other techniques, is considered one of the most powerful techniques for determining the labile metal fractions[4]. A metal complex is characterized as labile in the aqueous environment if it can dissociate to its free ion and then get reduced at the surface of the electrode within the time scale of measurement in stripping voltammetry, usually in the range of 2–10 ms[15,16]. This definition includes free metal ions and soluble complexes, which can dissociate fast enough in the diffusion layer. Non-labile fractions include strong metal-organic complexes and metal complexed with or adsorbed to colloidal matter. These species dissociate very slowly or not at all,[15] and cannot be detected voltammetrically. The advantage of using electrochemical methods, particularly anodic stripping voltammetry (ASV) is the high sensitivity and selectivity attainable. In addition, the labile fraction can correlate well with the toxic metal fraction obtained using bioassays[17,18]. Adsorptive stripping voltammetry is useful in the analysis of some metals such as nickel where ASV is not suitable[19]. It is also possible to distinguish between different oxidation states of an element using adsorptive techniques as in the case of chromium[20]. Our work employed differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) utilizing dimethyl glyoxime (DMG) and diethylenetriaminepentaacetic acid (DTPA) as the complexing agents for the determination of the labile forms for nickel and chromium, respectively, at a hanging mercury drop electrode (HMDE). With the DPAdCSV method it was possible to distinguish between Cr (III) and Cr (VI) because the former forms a complex with DTPA that is rendered electrochemically inactive after 30 minutes, leaving Cr (VI) in solution uncomplexed[20]. Flame atomic absorption spectrophotometer (FAAS) and graphite furnace atomic absorption spectrophotometer (GFAAS) were used to determine the total and dissolved forms of the metals. In this study, we demonstrate the role of natural and anthropogenic ligands occurring in fresh- and wastewaters in metal speciation and environmental remediation.

2. Experimental

2.1. Instrumentation

The determination of total metal and dissolved metal in wastewater samples was done with a Varian Spectra AA 220 FS atomic absorption spectrometer (Varian, Australia) using air-acetylene fuel system and equipped with a deuterium background correction. A graphite furnace atomic absorption spectrometer, SpectrAA 400 Plus (Varian, Australia) equipped with a graphite tube atomizer (GTA 96 Plus) was used for metal determination in freshwater. Sample solutions in GFAAS were delivered to the furnace in 20 μL volumes using a varian programmable autosampler. Integrated absorbance peaks computed with SpectrAA Quality Control Protocol version 3 (QCP-3) software was used exclusively for signal evaluation. Table 1 gives the graphite furnace temperature programmes for the determination of the two metals. In both FAAS and GFAAS, nickel and chromium were determined at 232.0 nm and 357.9 nm, respectively, with a spectral band width of 0.2 nm.

Table 1 Graphite furnace temperature programme for the determination of Ni and Cr using pyrolytic-graphite-coated tubes in GFAAS.

Stage	Temperature (°C)		Time (s)		Nitrogen gas flow (L min^{-1})
	Ni	Cr	Ni	Cr	
Drying	85	85	5	5	3.0
	95	95	40	40	3.0
	120	120	10	12	3.0
Pyrolysis	800	1000	5	5	3.0
	800	1000	1	1	0.0
Atomization	800	1000	2	3	0.0
	2400	2600	1.1	1.2	0.0
	2400	2600	2	2	3.0
Cleaning	2400	2600	2	2	3.0

An electrochemical analyser comprising an Autolab recorder (PGSTAT10, Ecochemie, Netherlands) and a voltammetric stand (663 VA, Metrohm, Switzerland) was used for determination of labile forms of both Ni and Cr. Software (757 VA Computrace, Metrohm, Switzerland) running on a Dell Dimension V400 computer was used for data acquisition and manipulation. The voltammetric cell with 150 mL capacity (Metrohm, Switzerland) consisting of the normal three electrodes, was employed. The working electrode was HMDE. A carbon rod and Ag/AgCl (saturated KCL_{aq}) auxiliary and reference electrodes were used.

2.2. Reagents

Ultrapure water was obtained by passing tap water through a reverse osmosis system (Milli-Q water system, millipore). Nitric, perchloric and hydrochloric acids used in the digestion process were of spectral purity (Fluka, Switzerland). Other reagents (analar grade) used were; dimethyl glyoxime (SAARCHEM, South Africa), diethylenetriaminepentaacetic acid (Aldrich, USA), methanol (Aldrich, USA), ammonia, sodium acetate and sodium nitrate (SAARCHEM, South Africa). Standard stock solution (1000 mg L^{-1}) of Ni and Cr were purchased from SAARCHEM, South Africa.

2.3. Sample Collection

Wastewater samples were collected from the settling tank of a nickel-chrome electroplating plant. Tannery effluents were collected from three sites namely, the *receiving, settling* and *final disposal* tanks (TR, TS and TF, respectively). Surface water was sampled from five sites along the main channel of Boro River in the Okavango Delta located in northern Botswana. Groundwater samples were obtained from boreholes located in various parts of Botswana. In all cases, samples were collected in plastic containers, rinsed at least three times with the water in question before the sample was taken.

2.4. FAAS/GFAAS Determination of Total Metal and Dissolved Metal

An aliquot of the sample (10 mL for wastewaters and 50 mL for each of surface- and groundwater) was put into a 250 mL conical flask and digested with a 5 mL mixture of concentrated nitric acid (65%) and perchloric acid (70%). When digestion was complete, 10 mL of 0.5 M HCl was added to redissolve the residue and the resultant solution filtered into a 50 mL volumetric flask. Ultrapure water was used to bring the volume to the mark. Total

dissolved Ni and Cr were determined by FAAS (in wastewater) and GFAAS (in surface water and groundwater).

Water samples were filtered through a 0.45 μm cellulose acetate membrane filter. Each time, the collection flask was rinsed with the first portion of the filtrate and discarded before retaining the sample filtrate (about 50 mL). The samples were then acidified to pH 2.0–3.0 by addition of minimum amounts of conc. nitric acid before being stored in plastic sample bottles for later FAAS/GFAAS measurements.

2.5. DPAdCSV Determination of Labile Metal Fraction

Ammonia buffer was prepared by mixing 26 mL of conc. HCl (32%) and 44 mL of ammonia (25%) in a 100 mL volumetric flask. It was then made to the mark with ultrapure water. The water sample (20 mL) was placed in a voltammetric cell followed by the addition of 50 μL of ammonia buffer and 10 μl of 0.1 M DMG in 95% methanol. The pH was adjusted to 9.2 ± 0.1 by addition of either NH_3 or HCl depending on the pH of the initial solution. In the case of wastewater from an electroplating plant, 50 μL of the sample (diluted 500 times with ultrapure water) was placed in the voltammetric cell containing 20 mL of ultrapure water. After purging with nitrogen for 5 min, the DPAdCSV determination of Ni was carried out under the following instrumental conditions: adsorption potential –0.700 V, step height 0.004 V, pulse amplitude 0.050 V, starting potential –0.700 V, end potential –1.250 V, adsorption time, 30 s for wastewaters and 120 s for both surface water and groundwater.

For Cr determination, a mixture containing sodium acetate (0.2 M), DTPA (0.05 M) and sodium nitrite (2.5 M) was used as the background electrolyte. The sample (20 mL) was put in the cell followed by 2.5 mL of the background electrolyte. For wastewater from the electroplating plant, 20 mL of ultrapure water was put in the cell followed by 100 μL of the sample (diluted 10 times with ultrapure water) and 5 mL of the background electrolyte. The pH of the resulting solution was adjusted to 6.2 ± 0.1 by the addition of a minimum amount of sodium hydroxide solution (30%). The solution was purged with N_2 for 5 min and then Cr was determined by the DPAdCSV method. Total labile Cr was determined immediately after the addition of DTPA. Chromium(VI) was determined by delaying the analysis for 30 min after purging N_2, to allow the Cr (III) complex to be converted into its electrochemically inactive form[20]. The instrumental settings were; pulse amplitude –0.050 V, voltage step time 0.3 s, adsorption potential –1.000 V, starting potential –1.000 V and end potential –1.450 V, adsorption time of 30 s for wastewater and 120 s for both surface and groundwater samples.

Effect of Dilution on Peak Potential

The wastewater from the electroplating plant was diluted appropriately with ultrapure water to achieve dilution factors of 1 to 2000. Aliquots of the diluted samples (20 mL) were placed in the voltammetric cell and the peak potentials of nickel and chromium were then measured using the procedures described in section 2.5 above.

2.6. Statistical Tests

For all samples, accuracy and precision of the experimental data were ensured by taking the average of three replicate measurements per sample for at least duplicate samples. The data obtained is presented as mean ± standard deviation (one sigma, n = 3). Statistical tests, namely analysis of variance (ANOVA), F-tests and t-tests, were performed using Microsoft Excel, to establish whether the variations in the data were due to speciation or simply random errors.

Table 2 Mean concentrations (n = 3) of nickel for total, dissolved and CSV-labile forms in wastewater from an electroplating plant (EW, mg L^{-1}), freshwater (FW, μg L^{-1}) and groundwater (GW, μg L^{-1}) samples.

Sample identity	Total Ni (mg L^{-1})	Total dissolved Ni (mg L^{-1})	CSV-labile Ni (mg L^{-1})
EW1	3091 ± 62	2906 ± 38	2089 ± 6
EW2	3112 ± 46	3053 ± 39	2148 ± 61
EW3	3198 ± 92	3141 ± 79	2100 ± 102
EW4	3187 ± 49	3117 ± 89	2121 ± 63
EW5	3201 ± 102	3098 ± 65	1976 ± 76
EW6	3192 ± 81	3088 ± 60	2052 ± 109
	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})
FW1	14.40 ± 1.30	1.86 ± 0.44	0.15 ± 0.02
FW2	10.40 ± 1.60	0.81 ± 0.15	0.19 ± 0.07
FW3	12.33 ± 1.36	0.74 ± 0.08	0.15 ± 0.01
FW4	13.73 ± 0.36	0.69 ± 0.05	0.11 ± 0.02
FW5	11.48 ± 1.0	1.170 ± 0.08	0.12 ± 0.03
FW6	8.11 ± 0.25	0.42 ± 0.06	0.14 ± 0.06
	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})
GW1	13.92 ± 1.56	3.37 ± 0.49	2.41 ± 0.33
GW2	6.47 ± 0.67	1.22 ± 0.38	0.90 ± 0.06
GW3	6.38 ± 0.77	1.24 ± 0.35	0.96 ± 0.09
GW4	7.04 ± 0.93	1.03 ± 0.13	0.41 ± 0.02
GW5	12.23 ± 2.00	2.20 ± 0.24	0.64 ± 0.06
GW6	16.95 ± 2.84	3.59 ± 0.37	1.51 ± 0.08

3. Results and Discussion

3.1. Speciation of Nickel

The concentrations of total, dissolved and CSV-labile forms of nickel are summarized in Table 2.

3.1.1. Total and Dissolved Nickel

As expected, values obtained from FAAS/GFAAS are higher than those from AdCSV (Table 2). Although voltammetry is fundamentally a more sensitive technique, it can only detect 'free' and weakly bound metal species. The difference between values obtained by the AAS and AdCSV techniques therefore gives an estimate of strongly bound metal species (inert fraction). Based on ANOVA, at P = 0.05 the three sets of data for each type of water system were significantly different. Thus the differences between total, dissolved and CSV-labile levels can be attributed to speciation of the metal.

Total and dissolved nickel in the wastewater from the electroplating plant were in the range 3091–3201 mg L^{-1} and 2906–3141 mg L^{-1}, respectively. These levels compare well with other studies on similar effluents[21]. Values for total and dissolved nickel are close, with a mean ratio of 1.03 (n = 3). Statistical tests namely, ANOVA and F-tests performed on the data for total and dissolved metal, showed a significant difference at P = 0.05 (F_{exptal} 5.88 > $F_{critical}$, 4.96). Thus, there is only a small fraction of the metal in the particulate phase, suggesting that simple inorganic and organic ligands are predominant in the wastewater system. In view of the relatively high nickel concentrations reported, the effluent is a potential environmental pollutant and therefore requires safe disposal methods. The plant has, however, complied with the guidelines for effluent discharges in Botswana[10] by constructing underground settling tanks lined with poly(vinylchloride) (PVC) material to ensure there is no

seepage of the wastewater. Trace levels of total and dissolved nickel were observed in both freshwater (range 0.42–14.44 μg L^{-1}) and groundwater (1.03–16.95 μg L^{-1}). These levels are typical of non-polluted natural waters. Since there are no industrial activities close to the areas where the surface and groundwater samples were collected, trace metal sources are principally geochemical. In contrast to the situation with regard to wastewater, total concentrations of nickel in groundwater and surface-water samples were respectively 8–20 times and 4–7 times higher than the dissolved concentrations. Thus most of the nickel is present as particulate or colloidal forms retained by the 0.45 μm membrane filter used in the study. These forms mainly consist of nickel bound to humic materials and iron-manganese oxides as they are ubiquitous in surface as well as underground water systems.

3.1.2. CSV-labile Nickel

The AdCSV technique used to determine labile metal species in this study involves competing ligand exchange reactions. The DMG and DTPA displace other ligands and the Ni-DMG and Cr-DTPA complexes, respectively, formed are preferentially adsorbed on mercury electrode surface where the metals are reduced. Thus the AdCSV values reported in this work represents the free hydrated metal ions as well as weakly bound metal complexes that undergo fast ligand exchange kinetics. The uptake of nickel by DMG is sufficiently fast to complex all 'free' nickel in solution and enable its voltammetric detection[22], especially in the presence of a large excess of DMG as was the case in this study. Results for AdCSV-labile nickel fractions were in the range 1976–2147 mg L^{-1} (EW), 0.11–0.19 μg L^{-1} (FW) and 0.41–2.41 μg L^{-1} (GW), with peak potentials observed for the different water samples being in agreement within –0.97 ± 0.005 V in each water system.

A greater proportion of the nickel in the wastewater exists in the labile fraction (64–74%), implying that strongly binding ligands are not abundant in the wastewater. The nickel-chrome plating plant utilizes nickel ($NiCl_2$, $NiSO_4$) salts and chromium salts ($CrCl_3$) as well as chromic acid (H_2CrO_4), boric acid (H_3BO_3) and ammonia as plating agents. These compounds, together with organic detergents used to clean the electroplating plant structures, are the major constituents in the effluent. The expected dominant nickel species within the labile fraction are the aqua forms as well as simple inorganic and organic complexes. The pale-green nature of the wastewater confirms that the aqua ion $[Ni(H_2O)_6]^{2+}$ and its derivatives dominate the chemistry of nickel in the wastewater. Stabilization of the free metal ions can also be attributed to the acidic conditions in the samples (pH 5.1–5.3), arising from the use of acids in the plating process.

AdCSV being essentially a trace analysis technique, there was concern that the dilution of the wastewater samples could significantly affect the speciation of the metals. To allay these fears, the peak potentials observed for the metals in wastewater samples from the electroplating plant were measured at different dilution factors. The results are plotted in Fig. 1. The peak potentials for both nickel and chromium were shifted in the cathodic (negative) direction, with dilution. However, the respective peak potentials were in agreement to within ±0.005 mV beyond a dilution factor of 100 at fairly constant peak current intensities. Generally, the observation of only small peak shifts in potentials (3.7% for Ni and 7.2% for Cr) and minimal changes of peak current intensities suggest that there is insignificant change in the overall percentage lability due to dilution effects. Furthermore, these potential shifts could be attributed to changes in the

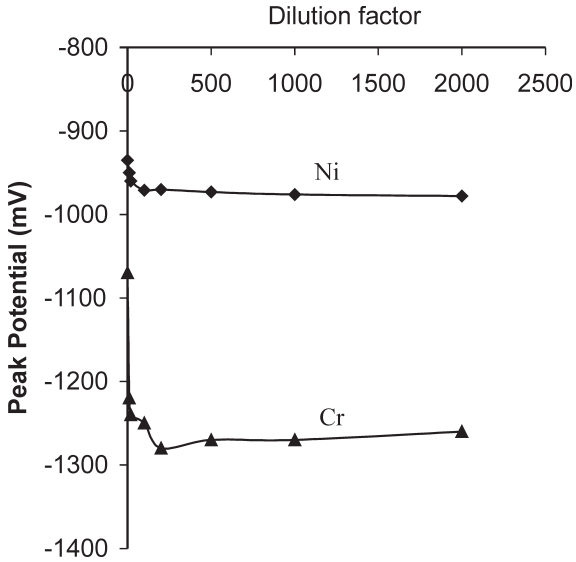

Figure 1 A plot of peak potentials (mV) for Ni and Cr versus dilution factor of electroplating wastewater sample, determined by DPAdCSV.

ratio of concentration of background electrolyte to that of the analyte, with the result that electromigration becomes an important mode of mass transport to the electrode surface.[27] However, it is expected that, overall, the changes in speciation as a result of sample dilution, would be minimal.

The labile fraction of nickel in the surface and groundwater, on the other hand, was found to be less than 5% of the total concentrations. The implication is that possibly the metal is present in strongly complexed and organically and/or inorganically adsorbed forms, mainly nickel-humic complexes which cannot be displaced by DMG fast enough to allow its measurement. The formation of 'inert' metal-humic complexes is well documented in the literature[9,23] and up to 99.9% of dissolved nickel in freshwater systems has been reported to be present in this form. In more recent studies[24], the dissociation of Ni(II)-humic acid and Ni(II)-fulvic acid complexes has been shown to be much slower than the uptake of DMG by Ni(II). This may partly explain why only a small fraction of dissolved nickel was found to be labile in this study.

3.2. Speciation of Chromium

The concentrations of total, dissolved and CSV-labile forms of chromium are summarized in Table 3.

3.2.1. Total and Dissolved Chromium

Similar to the case of nickel, CSV-labile values for chromium were observed to be consistently lower than those by FAAS/GFAAS, for total- and dissolved Cr (Table 3). This was confirmed by ANOVA and *F*-tests for all the water systems. The concentrations of total and dissolved chromium in the wastewater from the electroplating plant were observed to be close, with 83% Cr being in dissolved form. It is, however, interesting to note that over 97% of the chromium in tannery effluents was present in the undissolved (particulate) form. Total chromium concentration in the tannery effluents was highest in the settling tank (TS), followed by recycling tank (TR) and final tank (TF). Chromium(III) salts are used in the leather tanning process[25]. When chromium discharged from this process is mixed with tannery effluents containing protein compounds, it reacts very rapidly with these compounds to form precipitates, mainly protein-chrome complexes adding to sludge generation[26]. The chromium in sludge is highly stabilized and hence immobilized in

Table 3 Mean concentrations ($n = 3$) of chromium in total, dissolved and CSV-labile forms in wastewater from an electroplating plant (EW, mg L^{-1}), tannery effluents (TF, TR, TS, mg L^{-1}), freshwater (FW, μg L^{-1}) and groundwater (GW, μg L^{-1}) samples.

Sample identity	Total Cr	Total dissolved Cr	CSV-labile Cr	CSV-labile Cr(VI)
Electropl. wastewater	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
EW1	36.5 ± 1.5	30.7 ± 1.2	24.7 ± 1.7	20.7 ± 0.9
EW2	36.2 ± 1.1	31.2 ± 1.5	24.0 ± 1.1	18.3 ± 1.5
EW3	37.0 ± 2.1	31.0 ± 1.1	26.4 ± 2.3	21.2 ± 1.1
EW4	35.7 ± 1.6	31.7 ± 1.8	23.5 ± 1.1	16.1 ± 0.4
EW5	34.9 ± 1.8	30.8 ± 2.0	24.3 ± 1.4	21.3 ± 1.3
EW6	36.7 ± 2.2	31.1 ± 1.4	25.8 ± 1.6	18.1 ± 0.8
Tannery wastewater	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
TF1	16.1 ± 0.2	0.38 ± 0.02	ND	ND
TF2	15.8 ± 0.3	0.46 ± 0.02	ND	ND
TR1	75.5 ± 1.4	0.52 ± 0.03	ND	ND
TR2	75.6 ± 1.4	0.53 ± 0.01	ND	ND
TS1	547 ± 23	1.02 ± 0.04	ND	ND
TS2	571 ± 26	1.15 ± 0.02	ND	ND
Freshwater	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})
FW1	17.42 ± 1.02	1.15 ± 0.07	ND	ND
FW2	11.08 ± 0.41	1.52 ± 0.32	ND	ND
FW3	3.09 ± 0.18	0.57 ± 0.06	ND	ND
FW4	5.50 ± 0.13	0.54 ± 0.12	ND	ND
FW5	3.56 ± 1.05	0.58 ± 0.14	ND	ND
FW6	4.04 ± 0.18	0.57 ± 0.32	ND	ND
Groundwater	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})	(μg L^{-1})
GW1	36.39 ± 4.12	5.13 ± 0.32	0.55 ± 0.06	0.50 ± 0.11
GW2	22.39 ± 1.16	3.21 ± 0.42	0.34 ± 0.08	0.30 ± 0.09
GW3	23.09 ± 1.20	2.80 ± 0.30	0.25 ± 0.05	0.27 ± 0.06
GW4	18.01 ± 0.91	0.81 ± 0.18	1.03 ± 0.14	1.31 ± 0.14
GW5	26.74 ± 2.11	3.22 ± 0.30	0.51 ± 0.07	0.42 ± 0.12
GW6	18.73 ± 0.67	2.26 ± 0.46	0.61 ± 0.12	0.48 ± 0.09

ND = not detectable.

the environment. However, in cases where excessive chromium is discharged, it may exist in soluble forms with possible deleterious effects to aquatic organisms.

Although results from our study show that the total chromium in tannery effluent is in excess of Botswana[10] and other countries'[26] pollution guideline limits for discharge of effluents into water bodies and sewers, it is important to note, however, that the levels of dissolved chromium is within the limits. We therefore recommend that the effluents be subjected to proper pre-treatment, such as recovery of chromium from the sludge as well as insolubilization of chromium using suitable compounds in order to arrest chromium mobility in the environment.

Chromium concentrations in both groundwater and surface water were in the parts per billion range, suggesting that metal loading from anthropogenic sources in these sampling localities is not significant. The distribution between the dissolved and particulate forms follows a similar trend as that of nickel (section 3.1), with most of the chromium being transported principally in the particulate phase (over 97% in freshwater and over 85% in groundwater).

3.2.2. CSV-labile Chromium

CSV-labile forms determinations show that 76.8–96.5% of Cr in the wastewater from the electroplating plant exists in the labile fraction, again attributable to the absence of strongly binding ligands. It is of concern that a greater proportion of the CSV-labile chromium exists as Cr(VI), which is an environmentally undesirable species owing to its greater mobility and toxicity. Considering the pH of the wastewater samples (5.1–5.3), the chromium species expected to dominate the speciation distribution are the aquo Cr(III) and its hydrolysis products such as $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, whereas those for Cr(VI) are CrO_4^{2-} and $Cr_2O_7^{2-}$. No CSV-labile chromium fraction was detected in the tannery effluents, showing the strong complexing capacity of the constituents in the sample matrix. Tannery wastewater is usually characterized by high amounts of inorganic ligands such as chlorides, ammonia, sulphides and sulphates as well as organic ligands, including proteins, amino acids and organic acids[25]. The fact that labile fractions were not detected in the samples shows that the organic ligands, particularly proteins, dictate the chromium speciation since proteins form non-CSV-labile compounds. This may be due to the fact that chromium forms stable inert complexes with the various side-chain amino acid groups in the protein structure, being the basis of the tanning process.[26]

In freshwater samples, no CSV-labile Cr was detected, while a small amount (1.1–7.3%) was detected in groundwater, most of which was Cr^{6+} (79–91%). The concentration of HS in freshwater is generally higher than in groundwater systems[9] and given their strong complexing property towards metal ions, the

Table 4 Overall mean percentage distribution of nickel and chromium in wastewater from an electroplating plant (EW), tannery wastewater (TW), freshwater (FW) and groundwater (GW) samples.

Water system	Metal	% Dissolved	% Labile	% Particulate
EW	Ni	96.94	65.81	3.06
	Cr	85.98	68.51	14.02
TW	Ni	ND	ND	ND
	Cr	1.17	ND	98.82
FW	Ni	7.85	1.28	92.15
	Cr	13.16	ND	86.84
GW	Ni	19.38	11.04	80.62
	Cr	11.53	2.55	88.47

ND = not detectable.

absence of labile forms in freshwater is expected. The fact that the form of Cr mostly detected in groundwater samples was Cr(VI), suggests the greater mobility of this species in geochemical systems.

Table 4 gives a summary of mean distribution of metal species in the dissolved, CSV-labile and particulate forms calculated as a percentage of the total metal. The data reflect the nature of ligands in each water system and hence metal speciation patterns. The implications of metal complexation on bioavailability and toxicity are important since strong complexation can render toxic metal fraction innocuous[1].

3.3. Complexation Capacity of Tannery Effluents

Based on the results obtained for tannery effluent, which appeared to contain a high content of organic complexants, an attempt was made to estimate the complexation capacity of the soluble effluent fraction by titrating 20 μg L^{-1} model Cr(VI) solution with the filtered (through 0.45 μm filter paper) tannery effluent. Figure 2 shows a decrease in percentage lability of chromium with effluent additions. Percentage lability is expressed as a ratio of the peak current values $\acute{\imath}_k$ obtained for mixtures of various amounts of tannery effluent and a constant amount of standard metal solution, to that of the same metal concentration in the absence of the effluent, $\acute{\imath}_o$. In the titration curve (Fig. 2), the lability initially falls slowly (0–30 μL) then falls rapidly at the middle segment (30–110 μL), again falls slowly (110–150 μL) and finally no change in lability (>150 μL). This can be explained with reference to the existence of different types of ligands in the effluent, each with different metal binding abilities. At the initial portion of the curve, the ligand concentration is low. Subsequently, the strong and weaker binding sites are occupied.

Binding to weaker sites contributes to some degree of lability

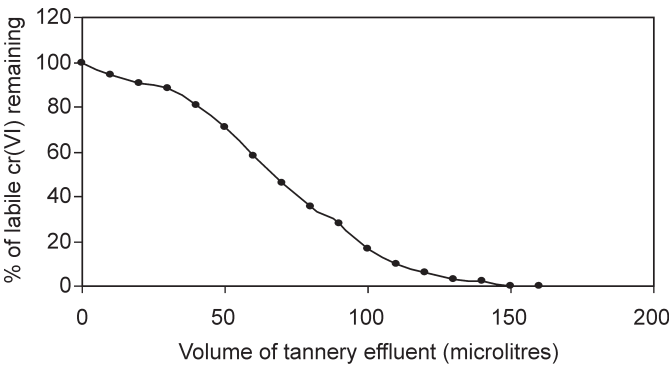

Figure 2 Variation of % labile Cr(VI) concentration (20 μg L^{-1}) in model solutions upon spiking different volumes (0–160 μL) of tannery effluent.

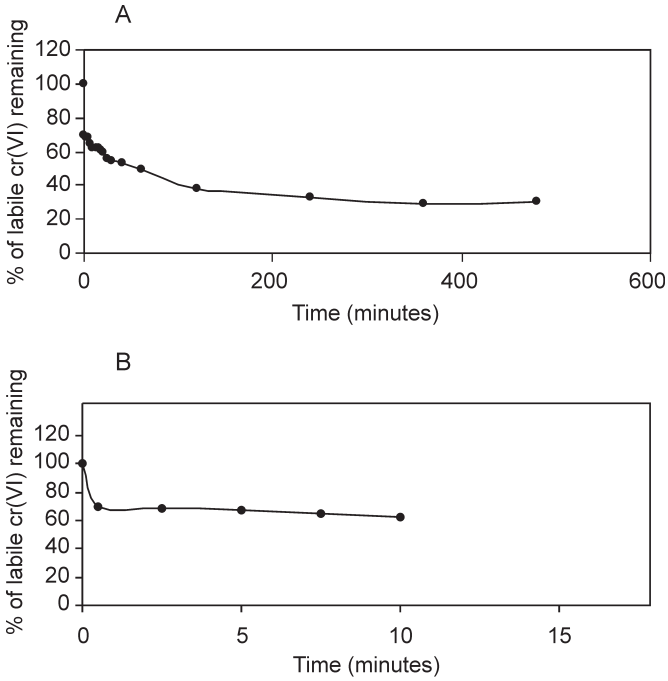

Figure 3 The effect of reaction time for a mixture of 20 μg L^{-1} Cr(VI) model solution and spiked (50 μL) tannery effluent; (**A**) 0–500 minutes and (**B**) 0–10 minutes.

due to dissociation hence the slow fall in the curve (Fig. 2). As the concentration of the ligand increases with addition of more effluent, lability rapidly decreases because the Cr(VI) ions are binding preferentially to the strong binding sites, forming inert complexes. The final portion of the curve (Fig. 2), where lability falls slowly, may be interpreted to represent labile species as well as contributions from 'residual' lability (result of slow dissociation of otherwise inert complexes). It should be noted that 'residual' lability could also be present at the other sections of the curve, but its contribution may be negligible relative to the overall lability. Labile chromium was undetectable after addition of >150 μL of the effluent, which corresponds to a complexation capacity of about 57.8 μM Cr. This value is about 10 times higher than the value reported[28] for Cu (II) in HS-rich freshwater, determined by ion selective electrode method. Within the pH range of the samples (8.7–11.3), acidic groups in the binding sites of the effluent components are deprotonated, hence the enhanced complexation capacity.

The complexation kinetics of Cr(VI) in the effluent was further studied by observing changes in Cr(VI) lability as a function of time using a volume of 20 mL containing 20 μg L^{-1} of model solutions of Cr(VI) spiked with 50 μL of the effluent. Figure 3 gives a time profile of the Cr(VI) lability. The results show fast complexation kinetics with about 40% of the 'inert'complexes being formed within 30 seconds, leading to a decrease in concentration of CSV-labile fraction. The curves (Fig. 3a,b) can be divided into two portions representing two kinetically distinguishable components. The portion showing fast rate of decrease (0–1 min in Fig. 3b) can be interpreted to represent the fast formation of strong chromium complexes, presumably protein-chrome complexes. The portion showing a slow (>2 min, Fig. 3b) rate of decrease could be ascribed to the relatively slower complexation reactions of chromium that yield strong complexes, mainly complexes of free amino acids and organic acids that bind to weaker binding sites of the protein molecules.

Complexation is further slowed by competition for binding

sites between the Cr(VI) ions and the major cations, mainly Na^+ ions released by NaCl used in the tanning process[25]. Thus the complexation kinetics reveals a situation where chromium associates with a polyfunctional complexant or with different ligands of different complexing abilities. No significant change (t-test, $P = 0.05$) in CSV-labile concentration of Cr was observed after 10 minutes. Compared to the binding time of 48 hours[9] for most trace metals with humic substances, we report much faster complexation kinetics of chromium with tannery effluents. It is, however, possible that the very high complexation capacity of the effluents is specific to chromium and similar cations.

4. Conclusions

The results obtained in this study clearly demonstrate the role of complexation abilities in metal speciation with the mean labile metal fraction decreasing in the order: electroplating plant wastewater (65.81% Ni, 65.81% Cr) > groundwater (11.04% Ni, 2.55% Cr) > freshwater (1.28% Ni, Cr not detectable) > tannery wastewater (Cr – not detectable). Furthermore, these findings emphasize the need to take into account metal speciation when evaluating the potential toxicity of metals as well as in the formulation of pollution control guidelines for industrial effluents. The complexation ability of tannery wastewater towards chromium was found to be particularly high where complexation studies revealed fast kinetics with two kinetically distinquishable components. A study on complexation capacities towards other trace metal ions is currently going on in our laboratory.

References

1 T.M. Florence, *Talanta,* 1982, **29**, 345–364.
2 International Programme on Chemical Safety (IPCS), Environmental Health Criteria 61: Chromium, WHO, Geneva, 1988.
3 D. Oktavec, J. Lehotay and E. Hornackova, *At. Spectrosc.,* 1995, **16**, 92–96.
4 T.M. Florence, *Analyst,* 1986, **111**, 489–505.
5 F.L.L. Muller and D.R. Kester, *Mar. Chem.,* 1991, **33**, 71–79.
6 M. Hiraide, *Anal. Sci.,* 1992, **8**, 453–459.
7 O. Domínguez and M.J. Arcos, *Anal. Chim. Acta,* 2002, **470**, 241–252.
8 D.T. Gjerde, D.R. Wiederin, F.G. Smith and B.M. Mahson, *J. Chromatogr. A.*, 1993, **640**, 73–78.
9 J.F. Gaffney, N.A. Marley and S.B. Clark, in *Humic and Fulvic Acids: Isolation, Structure and Environmental Role,* (J.F. Gaffney, ed.), ACS symposium series, 1996, pp. 2–10.
10 *Guidelines for Effluent Discharges,* Department of Water Affairs, Botswana, 1992.
11 M. Hiraide, T. Ueda and A. Mizuike, *Anal. Chim. Acta.,* 1989, **227**, 421–424.
12 M. Soylak and L. Elci, *Intern. J. Environ. Anal. Chem.,* 1997, **66**, 51–59.
13 S. Tokalioglu, S. Kartal and L. Elci, *Anal. Sci.,* 2000, **16**, 1169–1174.
14 T.M. Florence and G.E. Batley, *CRC Crit. Rev. Anal. Chem.,* 1980, **9**, 219–237.
15 M. Scoullos and A. Pavlidou, *Croat. Chim. Acta,* 1997, **70**, 229–307.
16 W. Davison, *J. Electroanal. Chem. Interface Electrochem.,* 1978, **87**, 395–404.
17 T.M. Florence, B.G. Lumsden and J.J. Fardy, *Anal. Chim. Acta,* 1983, **151**, 281–295.
18 J.S. Young, J.M.Gurtisen, C.W. Apts and E.A. Crecelius, *Mar. Environ. Res.,* 1979, **2**, 265–273.
19 A.W. Bott. *Current Separations,* 1995, **14**(1) 24–30.
20 J. Golimowski, P. Valenta and H.W. Nürnberg, *Fresenius J. Anal. Chem.,* 1985, **322**, 315–322.
21 H.D. Revanasiddappa and T.N.K. Kumar. *J. Anal. Chem.,* 2001, **56**(12), 1084–1088.
22 M. Lam, J. Murimboh, N.M. Hassan and C.L. Chakrabarti, *Anal. Chim. Acta,* 1999, **402**, 195–210.
23 H.B. Xue, S. Jansen, A. Prash and L. Sigg. *Environ. Sci. Technol.,* 2001, **35**, 539–546.
24 J.W. Guthrie, R. Mandal, M.S.A. Salam, N.M. Hassan, J. Murimboh C.L. Chakrabarti, M.H. Back and D.C. Grégoire, *Anal. Chim. Acta,* 2003, **480**, 157–169.
25 E. Ates, D. Orhon and O. Tünay, *Wat. Sci. Tech.,* 1997, **36**, 217–223.
26 M. Bosnic, J. Buljan and R.P. Daniels, United Nations Industrial Development Organization (UNIDO), report on Pollutants in Tannery Effluents, US/RAS/92/120.
27 J.C. Myland and K.B. Oldham, *J. Electroanal. Chem.,* 1993, **347**, 49–91.
28 J.C. Rocha, É. Sargentini, I.A.S. Toscano, A.H Rosa and P Burba, *J. Braz. Chem. Soc.,* 1999, **10**(3), 169–175.