Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7125-7130

Chromium Speciation and Removal of Chromium(III) by Complexation in Nilüfer Stream, Turkey

M. SUAT AKSOY

Department of Chemistry, Faculty of Arts and Sciences, Uludag University, 16059 Bursa, Turkey
Fax: (90)(224)4428136; Tel: (90)(224)4429256/1316; E-mail: msaksoy@uludag.edu.tr

Nilufer stream (Bursa, Turkey) receives domestic and industrial discharges containing heavy metals as well as organic pollutants. The speciation profiles of discharge waters were built up for chromium(III) and chromium(VI) ions in samples those were collected on a monthly basis from two stations in September 1996-August 1998 period. They indicate that chromium(III) contents of samples from station I that was in leather tanneries region were higher than of samples from station II that was in automotive and textile industries region. In order to remove Cr(III) ion from discharge waters by complexometry, the removing tendencies of some ligands such as salicylic acid and salicylic acid derivatives were ordered by means of the speciation diagrams of Cr(III):ligand systems, the working pH values and reduced concentrations of Cr(III).

Key Words: Chromium(III) removal, Speciation, Nilüfer stream.

INTRODUCTION

The second biggest industrial area of Turkey is located at the South Marmara region, in Bursa plain that is 20 km far from Marmara Sea. The wastewaters of the Bursa Organized Industrial Zone that has both small and large industrial enterprises with domestic discharges, cause high level of pollution in Nilufer stream because the industrial and the domestic discharges were not treated to make them acceptable for release into Nilufer stream. Therefore, Nilufer stream was the main receiving body for heavy metals as well as chromium compounds. Leather tanning facilities use Cr(VI) salts as tanning agents, the main environmental problem of leather tanneries is the disposals in liquid and solid form containing substantial quantities of chromium especially rich in Cr(III) and Cr(VI), along with organic matter, lime and sulfide[1,2]. The US Environmental Protection Agency designated Cr (and its compounds) as one of 17 chemicals posing the greatest threats to human health[3]; Cr(III) is less toxic than Cr(VI) and virtually immobile[4-6]. Chromium(III) can be chelated by naturally occurring organic material[7-9]. The humic substances are effective chelating agents of inorganic compounds in natural waters, while phenols are major constituents of natural organic and humic matters[4].

The first stage of present study was carried out to determine only the levels of heavy metals and polyaromatic hydrocarbons in Nilufer stream for 1991-1994 period[10-12]. Current measurements at sample sites in defined period revealed that total chromium concentrations steadily increased and were significantly above the national criteria. Therefore these waters were included in polluted class of waters according to Water Pollution Control Regulation of Turkey[13].

Our second stage study originating from interest in the speciation profiles of discharge water samples. Since we should improve effective procedure that can be applied to remove Cr(III) from discharge water treatment units. Those would be constructed in Bursa leather organized industry zone. Moreover the work reported on speciation of chromium in tannery sludges is scanty[2]. Therefore we performed chromium speciation studies as a part of the project in September 1996-August 1998 period. Although the coordination ability of Cr(III) towards several phenolic ligands were investigated by Ozer *et al.*[14-16], the speciation studies were not performed in these complex formation equilibria of Cr(III). Such that the Cr(III) forms very stable complexes with hydroxysalicylic acids (2,x-DHBA, x = 4-6)[14]; salicylic acid[15] and hydroxy naphthoic acids [(1,2-hydroxy naphthoic acid (1,2-HNA) and 3,2-hydroxy naphthoic acid (3,2-HNA)][16] and 2,3-dihydroxynaphthalene-6-sulfonic acid and 4,5-dihydroxynaphthalene-2,7-disulfonic acid[17]. Therefore, it would be possible to solubilize chromium compounds from deposits of leather industry by phenolic complexing agents and to remove chelated chromium in chemical waste treatment.

EXPERIMENTAL

All the chemicals of this study were of analytical reagent grade; $Cr(NO_3)_3{\cdot}9H_2O$, $K_2Cr_2O_7$, HNO_3 (100 % purity, d = 1.52), H_3PO_4 (85 %, d = 1.71); 1,5-diphenylcarbohydrazide (DPCI), salicylic acid and disodium salt of dihydrate of EDTA were purchased from Merck. 2,x-DHBA ligands from Aldrich and HNA ligands from Sigma companies. All chemicals were used without further purification, the molecular weights of ligands were periodically checked by Gran titrations[15].

In order to avoid hydrolysis, the Cr(III) stock solution (1000 μg cm^{-3}) was prepared in 10^{-2} M HNO_3. It was standardized by EDTA titration by the method of Schwarzenbach[18,19]. For standard Cr(VI) stock solution (1000 μg cm^{-3}) appropriate amounts of $K_2Cr_2O_7$ was dissolved with double distilled water.

Sampling: The discharge water samples of leather industry zone were collected on a monthly basis from two stations on Nilufer stream for 2 years (September 1996-August 1998); seasonal variations of all other inorganic parameters defined in our cited references[14-17]. The samples were obtained using a precleaned 1 L glass bottle with Teflon-lined cap. All samples were filtered within 5 min of collection through 0.4 μm Nuclepore membrane filters and then acidified to $pH \leq 2$ by HNO_3 immediately after sampling.

In order to built up chromium speciation profiles of discharge waters total chromium concentration was measured after repeated digestions in HNO_3 followed by assay flame atomic absorption spectrometer (AAS-ATI Unicam 929) using airacetylene flame with a gas flow of 1.4 L/min. AAS was used in the absorption mode at 324.8 nm with. The approximate absorption sensitivity of 0.05 mg/L, the lamp current was 10 mA and a slit width of 0.5 nm was used. Calibration graph for AAS was constructed using the standard solutions. All the standards used for AAS were prepared in reagents noted in references[19,20].

In order to determine Cr(VI) concentration, 1,5-diphenylcarbohydrazide (DPCI) was used as an indicator which was dissolved in H_3PO_4. The spectrum of Cr(VI) ion showed the absorption maximum at 540 nm. This procedure offered a ten-fold increase in sensitivity, approximating to 1.2 µg/L over the direct spectrophotometric methods[21-23]. Cr(VI) concentration was determined by Shimadzu UV-2100 (Kyoto, Japan) spectrophotometer; then Cr(III) concentration was found by calculation.

pH measurements were performed with a Schott-pH meter (Hofheim, Germany) to determine pH of the polluted water of Nilufer Stream by Cr(III) and to define pH of solutions those contain Cr(III) and ligands in different mole ratios. It had an accuracy ± 0.05 and calibrated by the procedure as described[14].

RESULTS AND DISCUSSION

The results of chromium contents in discharge water samples as mg/L in September 1996-August 1998 period were given Table-1. The speciation results indicate that total chromium contents of discharge waters of leather tanneries (station I) were higher than automotive and textile industries region (station II) during autumn, winter and early spring; while Cr(III) fraction of samples of station II dominates in summer. Although high chromium concentrations were related with low level of water especially in summer and partly autumn in Nilufer stream that was effected inversly, but there was another reason for these results that all the leather tanneries increased their production capacities in spring and summer terms.

According to the Water Pollution Control Regulation of Turkey, chromium concentration at surface waters should not exceed 0.1 mg/L[13] on the other hand, the acceptable level as a chromium standard for industrial wastewaters should not exceed 2 mg/L for 2 h and 1 mg/L for 24 h in composite sample; but as a result of chromium discharges directly into the Nilufer stream could be considered highly polluted water.

The second part of this research was carried out to determine equilibrium concentrations of Cr(III) ion in various media involving either 5-nitrosalicylic acid (5-NSA), 2,6-dihydroxybenzoic acid (2,6-DHBA), 5-sulphosalicylic acid (5-SSA), 3,2-hydroxynaphthoic acid (3,2-HNA), 1,2-hydroxynaphthoic acid (1,2-HNA), 2,5-dihydroxybenzoic acid (2,5-DHBA), 2,4-dihydroxybenzoic acid (2,4-DHBA) and salicylic acid either in 1:1 or 1:2 mol ratios. The equilibrium concentrations of Cr(III) and Cr(III) complex species were calculated by means of formation constant of each complex[14-16]. Then, the speciation diagram was drawn for each Cr(III):H_2L (H_2L stands for SA, 5-SSA and 5-NSA) or Cr(III): H_3L (H_3L stands for 2,x-DHBA, x = 4-6) ligand systems (Fig. 1, only speciation diagram for Cr(III):salicylic acid

TABLE-1
RESULTS OF CHROMIUM CONTENTS IN DISCHARGE WATER SAMPLES (mg/L) IN SEPTEMBER 1996-AUGUST 1998 PERIOD; WHERE STATION I: DISCHARGE POINT OF LEATHER TANNERY INDUSTRIES, STATION II: DISCHARGE POINT OF GENERAL INDUSTRY AREA

Mon and Year	Total chromium		Cr(III)		Cr(VI)	
	Station I	Station II	Station I	Station II	Station I	Station II
September 1996	0.696±0.020	0.061±0.010	0.040	0.057	0.656	0.003
October 1996	0.443±0.020	-	0.041	-	0.402	-
November 1996	0.187±0.080	0.106±0.060	-	0.102	0.187	0.004
December 1996	0.027±0.004	0.104±0.010	-	0.101	0.027	0.003
January 1997	0.075±0.010	0.245±0.030	0.059	0.243	0.016	0.002
February 1997	1.217±0.060	0.744±0.080	0.596	0.732	0.621	0.012
March 1997	0.679±0.130	0.536±0.080	0.569	0.520	0.110	0.016
April 1997	0.626±0.130	0.392±0.040	0.082	0.358	0.544	0.034
8 May 1997	0.515±0.170	1.094±0.090	0.048	1.068	0.467	0.026
26 May 1997	1.148±0.220	1.329±0.200	0.022	1.329	1.125	-
13 June 1997	1.391±0.550	2.480±0.070	0.025	2.480	1.366	-
30 June 1997	1.948±0.010	2.489±0.480	0.002	2.489	1.954	-
8 July 1997	2.366±0.230	2.751±0.560	0.034	2.735	2.332	0.016
29 July 1997	0.094±0.020	0.402±0.040	-	0.382	0.094	0.020
8 August 1997	0.280±0.030	0.378±0.090	0.013	0.354	0.267	0.024
26 August 1997	0.615±0.040	0.462±0.020	0.042	0.434	0.573	0.028
5 September 1997	0.394±0.060	0.552±0.070	0.019	0.528	0.375	0.024
25 September 1997	0.557±0.090	0.469±0.010	0.034	0.449	0.523	0.020
October 1997	0.308±0.030	0.515±0.070	0.016	0.467	0.292	0.048
November 1997	3.502±0.160	0.480±0.040	0.038	0.468	3.464	0.012
December 1997	0.790±0.100	0.524±0.060	0.034	0.518	0.756	0.006
January 1998	0.023±0.008	0.009±0.001	-	0.009	0.023	-
February 1998	0.039±0.009	0.060±0.009	-	0.060	0.039	-
March 1998	0.024±0.005	0.053±0.010	-	0.053	0.024	-
April 1998	0.233±0.020	0.402±0.009	0.020	0.344	0.213	0.058
May 1998	0.013±0.004	0.071±0.010	-	0.055	0.013	0.016
June 1998	0.032±0.060	0.085±0.020	-	0.072	0.032	0.013
July 1998	0.584±0.070	0.061±0.010	0.121	0.470	0.463	0.032
August 1998	0.463±0.050	-	0.099	0.271	0.364	0.024

system in 1:2 mole ratio is given). Thus the removing tendency of each ligand and its working pH range were established for each Cr(III):H_2L or Cr(III):H_3L systems. The formation constants of formed complexes reflect their removing tendencies of the used ligands increase in the order 5-NSA < 2,6-DHBA < 5-SSA < 3,2-HNA < 1,2-HNA < 2,5-DHBA < 2,4-DHBA < SA. For instance, Cr(III) concentration could be decreased from 1.148 mol/L to 4.17×10^{-11} mol/L if salicylic acid is added in 1:2 mole ratio to discharge water of leather tanneries in May 26, 1997; Thus pH of polluted water by Cr(III) would be adjusted above pH higher than 4.00 to clean it by complexometry (Fig. 2). Since main species that are mainly [Cr(HL)L] and [Cr(HL)L(OH)] type complexes.

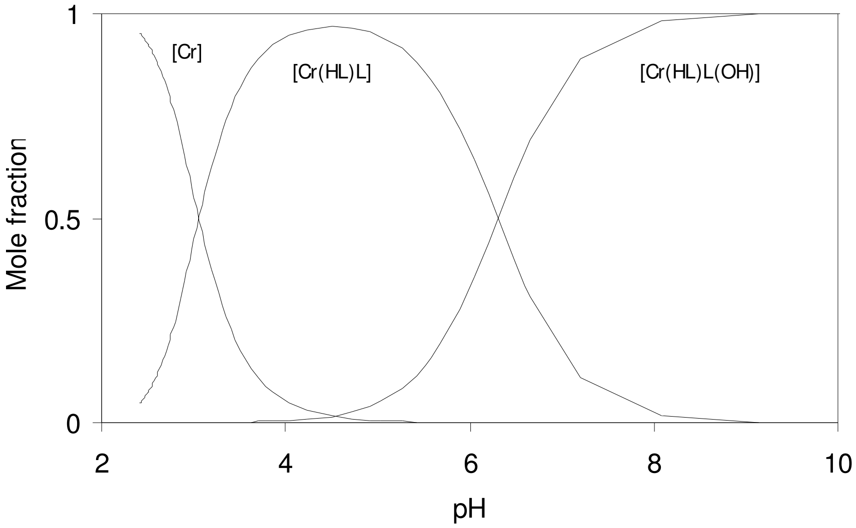

Fig. 1. Species distribution curves of the Cr(III):salicylic acid system as a function of log [H^+], for a solution initially containing 3.94 × 10^{-4} mol L^{-1} salicylic acid and 1.97 × 10^{-3} mol L^{-1} Cr(III) ion. T = 25 °C and I = 0.1 mol L^{-1} KNO_3

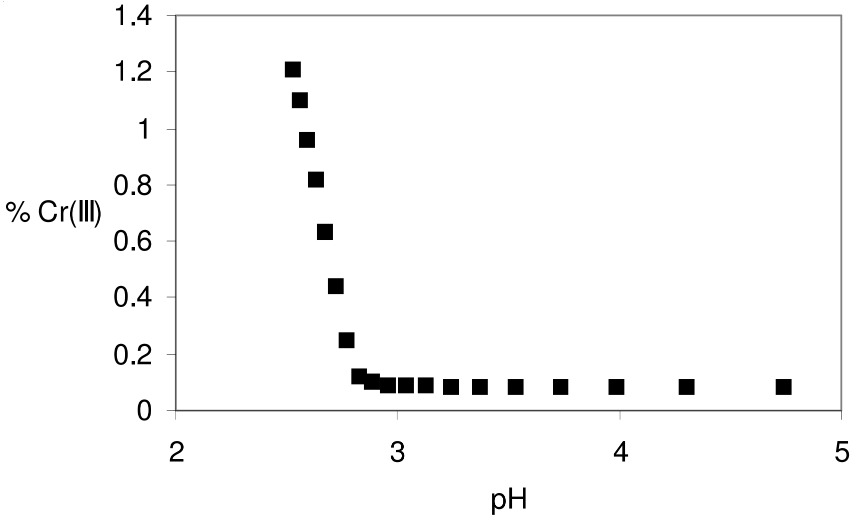

Fig. 2. Variations of Cr(III) ion concentrations in 1:2 Cr(III):salicylic acid system as a function of pH

Conclusion

The formation constants of formed complexes reflect their removing tendencies of the used ligands increase in the order 5-NSA < 2,6-DHBA < 5-SSA < 3,2-HNA < 1,2-HNA < 2,5-DHBA < 2,4-DHBA < SA.

REFERENCES

1. J.O. Nriagu and E. Nieboer, Chromium in The Natural and Human Environments, John Wiley and Sons, New York, Vol. 20 (1988).
2. M. Raju and S.N. Tandon, *Chem. Speciat. Bioavail.*, **11**, 67 (1999).
3. P.H. Masscheleyn, J.H. Pardue, R.D. Delaune and W.H. Patrick, *Environ. Sci. Technol.*, **26**, 1217 (1992).
4. S.E. Manahan, Environmental Chemistry, Lewis Publishers, Chelsea, Michigan, edn. 5, pp. 145-182 (1991).
5. V. Bianchi, A. Zantadeschi, A. Montaldi and F. Majone, *Toxicol. Lett.*, **23**, 51 (1984).
6. M. Vanweerelt, W.C. Pfeiffer and M. Fiszman, *Mar. Environ. Res.*, **11**, 201 (1984).
7. B.R. James and R.J. Bartlett, *J. Environ. Qual.*, **12**, 169 (1983).
8. B.R. James and R.J. Bartlett, *J. Environ. Qual.*, **12**, 173 (1983).
9. S.E. Kaczynski and R.J. Kieber, *Environ. Sci. Technol.*, **28**, 799 (1994).
10. U. Özer, A. Yilmaz, T. Torunoglu and S. Aksoy, Evaluation of Heavy Metal Contents and Some Inorganic Pollutants in South Marmara Streams, Turkey, 34th IUPAC Congress, 15-20 August 1993, Beijing, China (1993).
11. A. Yilmaz, U. Özer, T. Torunoglu and S. Aksoy, Evaluation of Heavy Metals and Some Inorganic Pollutants the South Marmara Streams(II), Turkey, 35th IUPAC Congress, 14-19 August 1995, Istanbul (1995).
12. A. Yilmaz, U. Ozer, S. Yemenicioglu, S. Aksoy and T. Torunoglu, *Fresenius Environ. Bull.*, **7**, 269 (1998).
13. Offical Gazette, 04.09.1988, 19919 (1988).
14. M.S. Aksoy and U. Özer, *Turk. J. Chem.*, **27**, 667 (2003).
15. M.S. Aksoy and U. Özer, *Chem. Pharm. Bull.*, **52**, 1280 (2004).
16. M.S. Aksoy, R. Aydin, N. Türkel and U. Özer, *Chem. Pharm. Bull.*, **53**, 471 (2005).
17. M.S. Aksoy, *Chem. Pharm. Bull.*, **56**, 771 (2008).
18. M.T. Beck and I. Nagypal, Chemistry of Complex Equilibria, John Wiley, New York (1990).
19. G. Schwarzenbach and H. Flaschka, Complexometric Titrations, Interscience Publishers, New York (1969).
20. R. Rubio, A. Sahuquillo and G. Rauret, *Int. J. Environ. Anal. Chem.*, **47**, 99 (1992).
21. M. Sperling, S.K. Xu and B. Welz, *Anal. Chem.*, **64**, 3101 (1992).
22. O. Nygren and J.E. Wahlberg, *Analyst*, **123**, 935 (1998).
23. K. Tirez, W. Brusten, A. Cluyts, J. Patyn and N.D. Brucker, *J. Anal. Atom Spectrom.*, **18**, 922 (2003).

(*Received*: 5 January 2009; *Accepted*: 10 August 2009) AJC-7740