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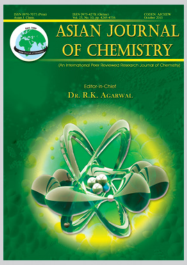

Assessment of Trace Total Chromium Together with Other Pollutants in the Sewages of Electroplating Industries

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One of the prominent and unavoidable cases in environmental sciences is the contamination problem. The present project is a part of a research proposal which was fundamentally defined for evaluation the type and quantity of the main pollutants present in the waste water of electroplating, dye, drug industries and repairing plants located in the eastern regions of Tehran. After sampling and pretreatment step, the samples were analyzed by flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) using external calibration graphs. The experimental results revealed that the main constituent component of the wastes involves chromium. Furthermore, the other trace metals are Pb, Cd, Fe, Cu and Mn.

Key Words: Pollutants, Sampling, Flame atomic absorption spectrometry, Inductively coupled plasma atomic emission spectrometry.

INTRODUCTION

Pollution is a challenging task forever due its critical and vital importance for all living things. A tremendous trend of industrialization has caused numerous noxious difficulties which has been predominately originated from their poisonous effluents. Therefore, measurement of heavy metal traces has a significant influence on our life. Tehran as one of the most crowded metropolises together with its eastern suburbs are the centre of different electroplating industries. Unfortunately, the wastes of these plants pollute the surface and underground water, directly. Ultimately, these polluted waters may contaminate drinking water sources of the city. This probability as a warning for respective organizations necessitates determination of chromium and other probable metallic species in the collected waste water samples by using FAAS and ICP-AES.

Contamination of soil and ground water due to the use of chromium in various anthropomorphic activities like leather, steel plating and dyeing industries have become a serious source of concern to plant and animal scientists over the past decades. Chromium in contrast to most trace metals like cadmium, lead, mercury and aluminum with no known function in plants has got relatively less attention from plant scientists. The complex electronic chemistry of Cr has been a major hurdle in unraveling its physiological interaction in plants. Chromium has an electronic configuration of [Ar] $3d^5$ $4s^1$ and forms of biologically active Cr are the trivalent (Cr(III)) and the hexavalent (Cr(VI)) species. Differential toxicity of Cr speciation to plants is well documented[1,2].

Chromium speciation has a prime importance in different branches of natural sciences. The importance of chromium speciation originates from widespread participation of this element in various environmental and biological samples. The speciation of Cr determines not only its ecological impact, but also its mobility and transport behaviour in the environment. Hence, new investigations have been oriented in this field. The major sources of entrance of chromium to the environment are steel, electroplating, tanning, chemical industries, oxidative dyeing, cooling water towers, corrosion inhibitors used in water pipes and containers as well as sanitary landfill leaching[3,4].

Chromium occurs essentially only in two thermodynamically stable oxidation states in nature which are Cr(III) (trivalent) and Cr(VI) (hexavalent). It has been proved that the traces amounts of Cr(III) are necessary for mammals health as mineral supplement and micronutrient in order to maintain glucose, lipid and perform protein metabolism. However, Cr(VI) is an inhaled carcinogen which exerts an extremely toxic effect on human organisms. This property is attributed to high oxidation potential and relatively small size of this ion. Accumulation and inhalation of hexavalent chromium bearing substances, lead to bronchitis, pneumonitis, asthma, nasal septum and inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Meanwhile, direct contact with these materials may cause dermatitis, dermal necrosis, skin allergies and dermal corrosion[5-8]. Studies related to reduction and migration of Cr(VI), distribution of Cr(III) between inorganic and organic compounds and remediation of contaminated environment are currently underway. Accurate and precise analyses of chromium speciation in environment samples are therefore required[9,10].

Chromium(VI) exhibits relatively simple hydrolysis behaviour. The hydrolysis products are $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$. Chromium(III), however, has more complicated reactions in the natural environment. The hydrolysis reactions produce mononuclear species $CrOH_2^+$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$ and polynuclear species $Cr_2(OH)_2^{4+}$,$Cr_3(OH)_4^{5+}$ even though they form very slowly at room temperature[11]. In the presence of natural or anthropogenic organic substances, organic complexes of Cr(III) are slowly produced as well[12,13]. The complicated forms and very slow kinetics of Cr(III) lead to difficulty in understanding its behaviour.

In previous reports, novel modifiers were introduced for monitoring of trace chromium[14,15] and lead[16-18] by using solid phase extraction followed by flame atomic absorption spectrometric detection. Nonetheless, the main goal of the present work as a complementary investigation from environmental standpoint is comparison the amounts of chromium and other pollutants released from the electroplating industries waste waters over the seasons of 2007.

EXPERIMENTAL

All chemicals were of analytical grade and used as received without any further purification. The chemicals obtained from E.Merck, Darmstadt, Germany. The nylon filters (45 µm) used for filtration of water samples were obtained from S&S Company. Deionized water was prepared by passing of double distilled water through Nano-pure ultrapure water system from Barnstead Company (U.S.A.) and was used throughout the experiments.

Determinations of chromium and other heavy metal contents in working samples were carried out on a commercial available Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp (HI-HCL) as a light source and main acquisition parameters were as follows: slit width = 0.2 nm, operation current of HI-HCL = 7.0 mA, resonance fine = 357.9 nm, length of air-acetylene burner = 13/50 mm, air flow = 13/50 L min^{-1} and acetylene flow = 2.90 L min^{-1} under a deuterium lamp background correction. An ICP-AES JY 138 Ultrace was used for the determination of sub ppm levels according to the recommendations of the manufacturers.

Sampling map: Sewage water samples were gathered in Tehranpars, Bumehen up and down, Roodehen and Jajrood as presented in Fig. 1. The samples were collected from 1 m depth of the waste water containers.

Sampling methods: The common methods for sampling in literature are as follows:

(a) Manual sampling: This comprises minimal equipment but may be unduly costly and time consuming for routine or large scale sampling programs. It requires trained field technicians and is often necessary for regulatory and research investigations for which critical appraisal of field conditions and complex sample collection techniques are essential.

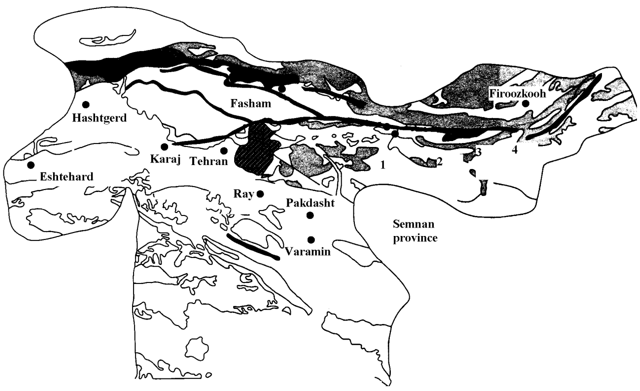

Fig. 1. Geographical map of sampling stations

(b) Automatic sampling: This eliminates human errors in manual sampling, reduces labor costs and may provide the means for frequent sampling[19]. An automatic sampler should be programmed in accordance with sampling needs. Pump speeds and tubing sizes must be carefully matched to the type of sample to be taken.

(c) Sorbent sampling: Solid sorbents particularly membrane type disks are frequently used for sorbent sampling. These methods offer advantages of rapid, inexpensive sampling if the analytes of interest can be adsorbed and desorbed efficiently and the water matrix is free of particulates that plug the sample.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes. This implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled and the sample will be handled in such a way that no significant changes in composition occur before the tests are made. Frequently, the objective of sampling and testing is to demonstrate whether continuing compliance with specific regulatory requirements has been achieved. Real water samples were predominately as one of the following ones:

(a) Grab samples: Which were single samples collected at a specific spot at a site over a short period of time and represent a snapshot in both space and time of a sampling area.

(b) Composite samples: Which provide a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary with time. Composite samples can be obtained by combining portions of multiple grab samples[20].

Sample containers: The type of sample container is of utmost importance. Assurance from non existence of analytes of interest on the sample containers is essential specially when very low levels of analyte is treated. Collection was achieved with narrow-necked polyethylene bottles provided with 30 cm diameter polyethylene funnels. The containers were completely clean, free of contaminants and quality assured. To avoid the probable adsorption of the pollutants onto the container walls, before the sampling the vessels were cleaned vigorously and afterwards washed with a proper detergent followed by 500 mL of doubly distilled water and 10 mL of concentrated hydrochloric acid. Then, sampling vessels soaked in 1 mol L^{-1} HNO_3 overnight, rinsed twice with deionized water and dried in a dust-free environment. The simple designs of the employed containers have been depicted in Fig. 2. These devices are proper for sampling at various depths. The vessels were wrapped in a proper aluminum foil and stored under 4 ºC at commercial ice substitutes mainly to slow down or retard the potential for volatilization, biodegradation and any chemical or biological change.

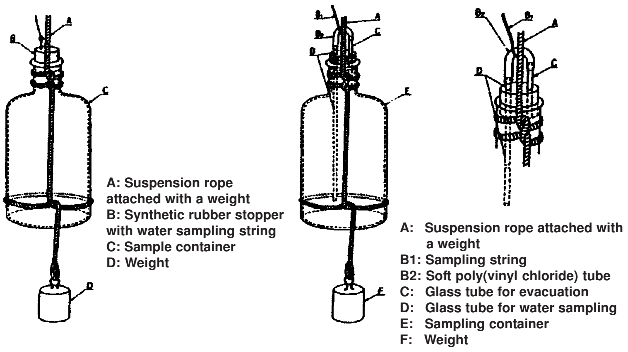

Fig. 2. Typical structure of sample containers

Sample pre-treatment: Sample handling was performed with adequate precautions to avoid of deterioration or change of composition. The real samples were dark or turbid and in some cases with a pungent smell. The pH of the samples varied between 4 to 6.

After sampling, the samples were immediately acidified with nitric acid at pH below 2 to minimize precipitation and adsorption on container walls. In order to eliminate small suspended materials, turbid water samples were filtered through 45 μm nylon filters. This process was repeated sequentially to approach to a white clear status prior to determination. The acidified samples were analyzed for different heavy metals, particularly total chromium, within at the most 10 days after collection.

Stock and standard solution preparation and regression equation: The standard stock solutions of Cr(III) and Cr(VI) (1000 ppm) were prepared by dissolving 0.4868 g of $CrCl_3{\cdot}6H_2O$ (95 %) and 0.2828 g of $K_2Cr_2O_7$ (99.9 %) in deionized water in 100 mL volumetric flasks, respectively. Standard solutions of chromium were obtained by appropriate stepwise dilution of standard stock solutions. The external calibration graph for total chromium obtained by FAAS is shown in Fig. 3.

RESULTS AND DISCUSSION

Analytical results of aqueous samples of chromium by using FAAS and ICP-AES in different seasons as a function of distance from the pollution source has been shown in Fig. 4. Accordingly, the maximum and minimum amounts of chromium pollution occur in autumn and spring. Moreover, as it is expected, the total chromium content decreases as the distance from the dye plants increases.

On the other hand, the distribution profile of all other heavy metals in the electroplating waste water in the seasons of spring, summer, autumn and winter have been presented in Figs. 5 -8. In these samples the most abundant pollutants

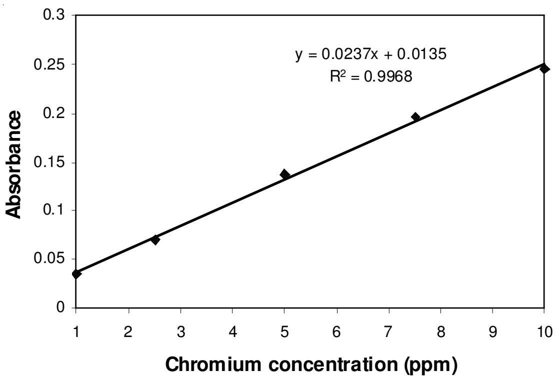

Fig. 3. External calibration curve of total chromium

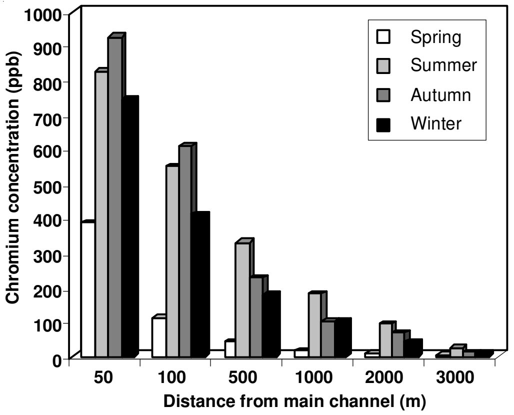

Fig. 4. Distribution profile of chromium in all seasons

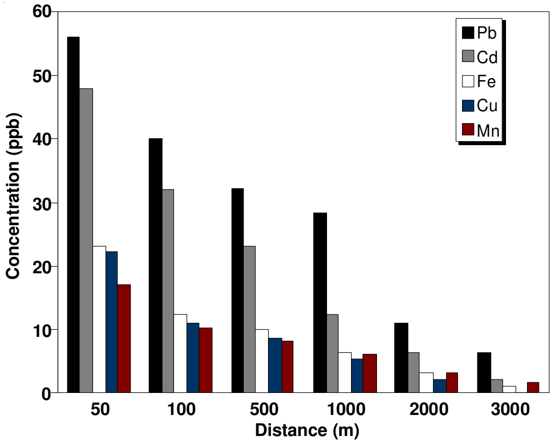

Fig. 5. Distribution profile of Pb, Cd, Fe, Cu and Mn in spring

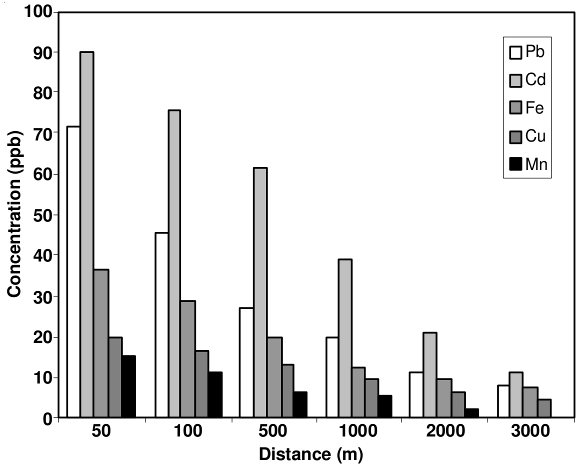

Fig. 6. Distribution profile of Pb, Cd, Fe, Cu and Mn in summer

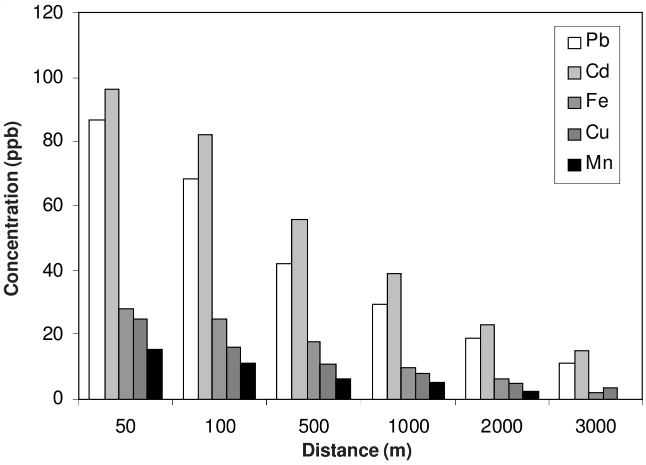

Fig. 7. Distribution profile of Pb, Cd, Fe, Cu and Mn in autumn

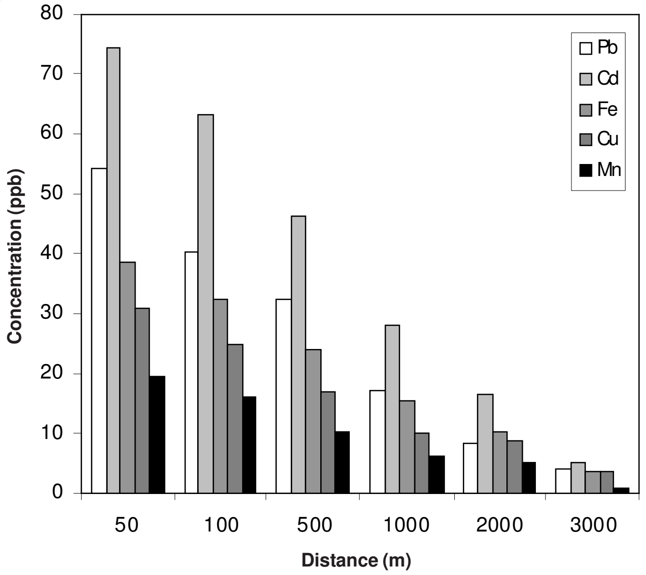

Fig. 8. Distribution profile of Pb, Cd, Fe, Cu and Mn in winter

after chromium are lead and cadmium which are most probably due to the dye manufacturing plants and anthropogenic activities in neighborhood of electroplating industries.

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