Quantification Of Lead And Other Metallic Pollutants In The Waste Water Of Dye Manufacturing Industries

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ABSTRACT

Monitoring of heavy metal traces has a vital influence and is of prime importance for all living things. Tehran as one of the most crowded metropolises together with its eastern suburbs are the centre of different industries involving dye manufacturing ones. 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 encouraged us to determine lead and other probable metallic species contents in the collected waste water samples of dye factories using flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).
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INTRODUCTION

Delirious progress of industrialization has caused numerous defects and emerging problems in human health. In fact, the lack of frequent inspection on the industrial wastes by authorities creates the serious jeopardizes.

Various industries utilize considerable amounts of poisonous chemicals and their effluent sewages could yield wide contaminations in weather, soil and environment. The adjacency of dye manufacturing industries with other bearing ones such as electro- plating, results in deliverance a series of harmful pollutants. For instance, dye industries use lead as major constituent component in the dye pigments. Unfortunately, the amount of this toxic metal in the waste waters is much higher than the allowed level. The typical level of Pb^{2+} in natural water lies between 2 and 10ng mL^{-1}, whereas, the upper limit recommended by world health organization (WHO) is less than 10ng mL^{-1}. Lead is considered as one of the metals of prime environmental concern and is tabulated among 129 priority pollutants and one of the 25 hazardous species for human health. It has

been classified as a class B2 pollutant by environmental protection agency (EPA)[1].

One of the attractive aspects of lead is its cumulative toxicity which yields harmful influences on animals and human health. It has long been recognized that cumulative poisoning effect of lead causes hematological damage, anemia, kidney malfunctioning, brain damage, muscles sore, fatigue, irritation, and distributions in central nervous system[2].

On the other hand, inorganic lead is attached with thiol group(-SH) in proteins or enzymes and hence considered as an inhibitor. This element disturbs calcium metabolism and deposits in the bone. Meanwhile, the organic derivatives of lead are highly toxic because the easiness of their absorption by the body through skin and mucus membranes[3,4]. The toxicological treatment of lead may be attributed to its ability for uncoupling oxidative phosphorilation, modification of ion transport in mitochondria, and inhibition of the metabolisms of enzymes containing thiol (-SH) group in hem synthesis and mitochondria energetic processes[5].

The most common procedures and techniques for the determination of lead involve spectrophotometry[6], flame atomic absorption spectrometry[7], electrothermal atomic absorption spectrometry (ETAAS)[8], inductively coupled plasma atomic emission spectrometry (ICP-AES)[9], inductively coupled plasma-mass spectrometry (ICP-MS)[10], and non-dispersive atomic fluorescence spectrometry (ND-AFS)[11].

In our previous reports, we introduced novel modifiers for assessment of trace lead by using solid phase extraction followed by flame atomic absorption spectrometric detection[12-14]. However, the main goal of the present work is comparison the amounts of lead and other pollutants released from the dye industries waste waters over the seasons of 2006 year.

EXPERIMENTAL

Reagents and materials

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 (45μm) 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.

Apparatus

Determinations of lead and other heavy metals in working samples were carried out on a commercial available Varian spectra A. 200model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCL) as a light source.

TABLE 1 : The operational characteristics of flame

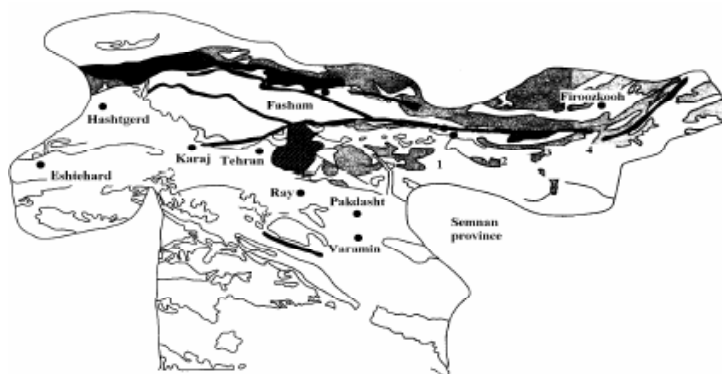| Type of background correction	Deuterium lamp
Length of air -acetylene burner	13.0mm
Operation current of HI-HCL	10.0mA
Resonance fine	217.0nm
Slit width	1.0nm
Type of flame	air/ acetylene
Air flow	13.50L min⁻¹
Acetylene flow	2.0L min⁻¹

Figure 1 : The geographical map of sampling stations

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The main acquisition parameters are summarized in TABLE 1. 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 figure 1. The samples were collected from 1m depth of the waste water containers.

Definition the types of water samples

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[15]. 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.

Sample containers

The type of sample container is of utmost importance. Collection was achieved manually with narrow-necked polyethylene bottles provided with 30cm diameter polyethylene funnels. The containers were completely clean, free of contaminants and quality assured. To avoid the probable adsorption or cross contamination of the pollutants onto the container walls, before the sampling the vessels were cleaned vigorously and afterwards washed with a proper detergent followed by 500mL of doubly distilled water and 10mL of concentrated hydrochloric acid and enough amounts of 2M nitric acid. Then,
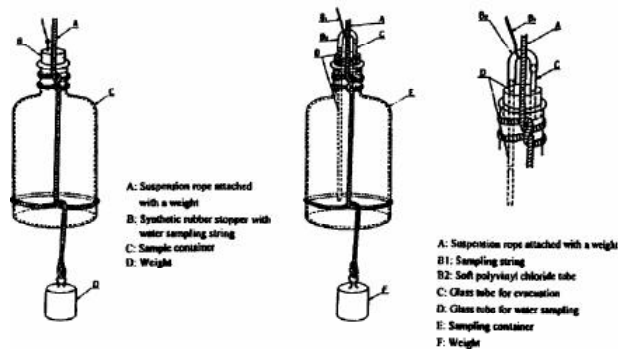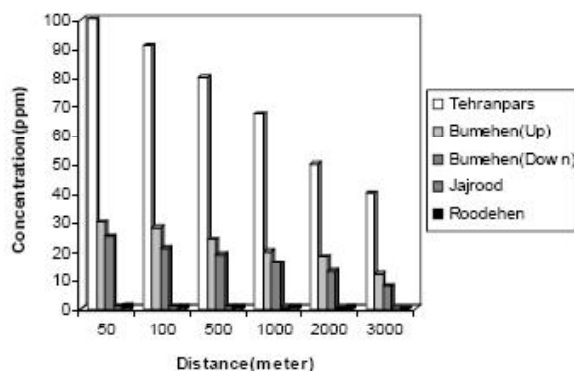

Figure 2 : The typical structure of sample containers

Figure 3: Distribution profile of lead in spring

Sampling vessels soaked in 1 molL^{-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 figure 2. These devices are proper for sampling at various depths. The vessels were wrapped in a proper aluminum foil and stored under 4^{0}C at commercial ice substitutes mainly to slow down or retard the potential for volatilization, biodegradation and any chemical or biological change.

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 10mL of high purity nitric acid at pH below 2.0 to minimize precipitation and adsorption onto container walls. In order to eliminate small suspended materials, turbid water samples were filtered through 45μm nylon filters. This process was repeated sequentially
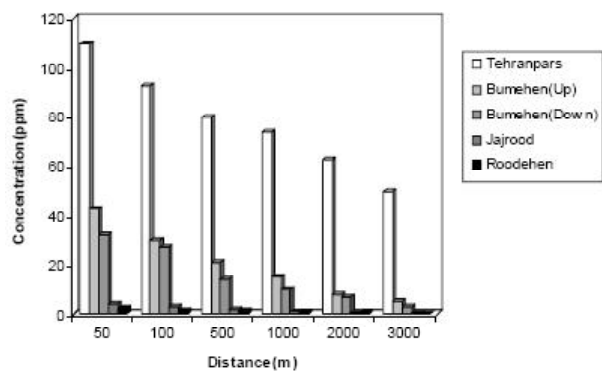
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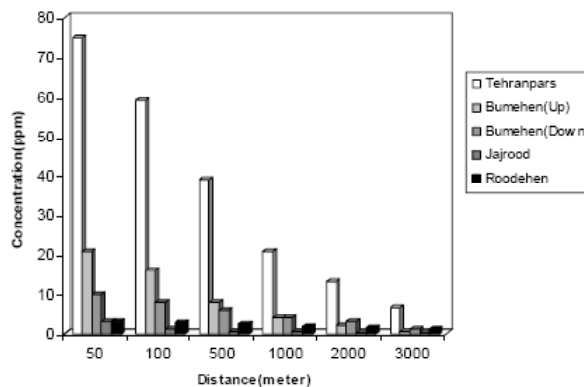Figure 4 : Distribution profile of lead in summer

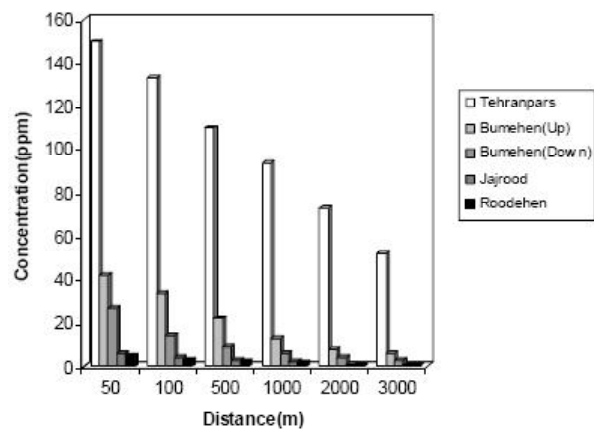Figure 6 : Distribution profile of lead in winter

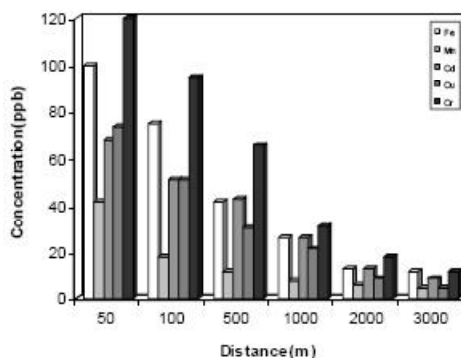Figure 5 : Distribution profile of lead in autumn

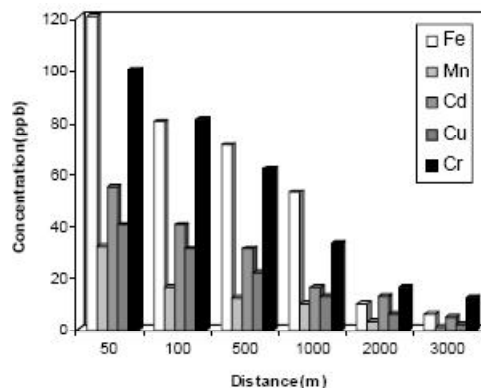Figure 7 : Distribution profile of other pollutants in spring

Figure 8 : Distribution profile of other pollutants in summer

to approach to a white clear status prior to determination. The acidified samples were analyzed for different heavy metals, particularly lead, within at the most 10 days after collection.

Stock and standard solution preparation and regression equation

The stock solution of lead(II) was prepared by dissolving a proper amount of analytical grade lead(II) nitrate (159.8mg) in 100mL of deionized water. One mL of dilute nitric acid was added to this solution. This is mainly for preventing the hydrolysis of lead ions, decreasing or stopping the biological changes[16]. The working solutions of lead were prepared by accurate stepwise dilution of the stock solution with double distilled deionized water. The linear regression equation of lead(II) standard solutions was as $A = 0.016C + 0.0032$ with a correlation coefficient of $r^2 = 0.9997$ using an external calibration curve. The linearity of the graph was in the range of 2.5-30μg.mL^{-1}.

RESULTS AND DISCUSSION

Analytical results of aqueous samples of lead by using FAAS in different seasons as a function of distance from the pollution source are shown in figure 3 to figure 6. Accordingly, the maximum and minimum amounts of lead pollution occur in autumn and winter. Moreover, as it was expected, the lead concentration decreases as the distance from the dye
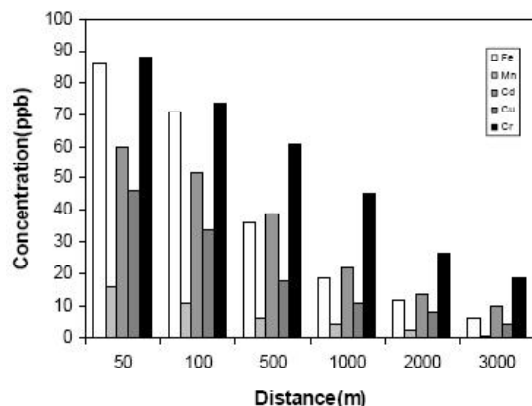
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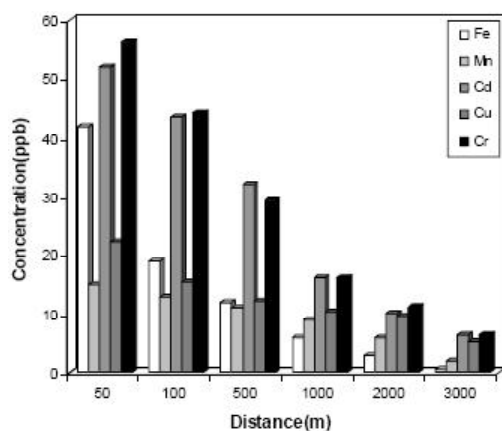Figure 9 : Distribution profile of other pollutants in autumn

Figure 10 : Distribution profile of other pollutants in winter

plants increases.

On the other hand, the distribution profile of all other heavy metals in the dyes waste water in the seasons of spring, summer, autumn and winter have been presented in figure 7 to figure 10. In these samples the most abundant pollutant one after lead is chromium which is most probably due to the electroplating plants in neighborhood of dye manufacturing ones.

ACKNOWLEDGMENT

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