

A Case Study: Chromium Concentration and its Species in a Calcareous Soil Affected by Leather Industries Effluents

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Abstract: Annually, a large amount of effluents is discharged from an industrial zone dedicated to leather industries into a dried seasonal waterway bed in Mashhad plain, Northeast of Iran. These soils are high in pH, CaCO₃ contents and have no naturally occurring chromium detectable in mg/kg range. Considering high concentration of chromium in the discharged leather industries effluents and their direct release into the soil with no further treatments the current research was performed to investigate the total chromium concentration and its trivalent and hexavalent species in contaminated soils. In order to obtain chromium distribution pattern among different soil fractions and evaluate its bioavailability, sequential extraction was carried out and chromium concentration was measured in exchangeable, organic, carbonated and residual fractions. As the mean of measured trivalent and hexavalent chromium in 0-45 cm depth of the contaminated soil were 193.64 mg/kg and 1.74 mg/kg, respectively, the experiment results showed that soil was polluted with chromium. Also considering high mobility and extreme toxicity of hexavalent chromium the threat of groundwater and other local water resources contamination is a major concern. Fractionation results indicated that more than 90% of the total chromium belonged to the residual fraction. However, because of its high concentration in polluted soil and specific characteristics of the contaminated area, as well as using plants growing in the vicinity of contaminated area for animal feeding, the potential risk of food chain toxicity is serious.

Key words: Chromium • leather industries • sequential extraction • soil pollution

INTRODUCTION

A substantial and unfortunate fact about industrialization and industrial production is generation and release of toxic waste products. Although these wastes can be treated, reused and recycled still thousands of chemicals are released and find their way into the environment. Unfortunately, the inadequate information regarding waste toxicity and post-disposal behavior, poor planning, improper disposal and poor management of disposal sites stimulates serious contamination problems at industrial and hazardous waste disposal sites. An example is several available reports about the genotoxicity of soils contaminated with chemicals originated from industrial sources [1,2]. Heavy metals are among these chemicals and constitute a main group of soil pollutants that their contamination in environment affects all

ecosystem components [3]. Chromium (Cr), as one of these heavy metals, can enter into the environment mainly because of human activities especially through the production of waste water in metal smelting, electroplating, tanning, metallurgy and dyestuff industries. However, it is the supreme additive, endowing alloys or materials with new properties, such as a resistance to corrosion, wear, temperature and decay, as well as strength, hardness, permanence, hygiene and color [4].

Nevertheless chromium is a toxic and carcinogenic element that its toxicity is very dependent on its chemical state. The most abundant species of Cr in environment is its trivalent and hexavalent form which their toxicity is significantly different. The same chemical properties that make chromium such an important component of so many industrial and consumer products are the important

factors controlling its environmental fate and toxicity. In all of its industrial applications the most important chemical property is that under typical environmental and biological conditions of pH and oxidation-reduction potential, the most stable form of chromium is the trivalent oxide [5]. Cr(III) and Cr(VI) display quite different properties. Cr(VI) is considered the most toxic form, whereas Cr(III) is essential for mammals, although it is considered a nonessential trace metal for microorganisms and plants [6]. Cr(VI) compounds are usually highly soluble, mobile and bio-available compared to Cr(III) compounds [5,7]. However, the toxicity of heavy metals as well as chromium in contaminated soils depends on their chemical state and bioavailability. Therefore, to obtain proper information on their potential environmental risks and their mobility, it is essential to determine their chemical species and distribution among different soil fractions [8].

In north east of Iran close to the city of Mashhad, there is a small industrialized zone which is dedicated to leather processing industries. The wastewater and effluents of this area is collected and transported via a main pipe to a discharge area a few kilometers away from that industrial zone. Although there is an industrial wastewater treatment facility under construction, unfortunately for about 5 years the leather industries effluents have been directly discharged to the environment and have caused serious soil contamination. As chromium is a necessary element in tanning and leather processing industries and in order to evaluate effects of these industries effluents on chromium concentration, the current research was carried out to determine amount Cr (III) and Cr (VI) species and also total Cr distribution in affected soil fractions.

MATERIALS AND METHODS

Soil samples were collected from an area which was directly under the wastewater influence. Shape of the chosen sampling area was close to a circle within the radius of approximately 300 m from the effluents discharge point. Composite sampling was performed in the sampling area from three depths; 0-15 cm, 15-30 cm and 30-45 cm in triplicates. For comparative studies and in order to obtain reference soil samples, the same sampling method and depths were used to collect samples from non effluents-affected soil in the vicinity of contaminated soil sampling area.

The soil samples were air dried and passed through a 2-mm sieve. Soil texture was determined by using

Bouyoucos or hydrometer method [9-11]. Soil pH and EC were obtained using a 1:1 soil: water ratio (by volume) suspension and a conductivity meter in a saturated soil-water paste. Soil CEC and organic matter content were measured by the Chapman [12] method based on ammonium acetate saturation at pH 7.0 and Walkley-Black [13] method. Equivalent calcium carbonate content was determined based on acid neutralization method [14]. Total chromium was extracted by aqua regia [15] and measured by flame-atomic absorption spectrometer, AAS (Shimadzu AA-670). In order to determine the concentration of total hexavalent chromium (soluble and insoluble), the method of [16] was applied, i.e. 50 ml of the solution of 0.28 M Na_2CO_3 and 0.50 M NaOH (pH 11.5-12.5) was added to a beaker containing 2.50 g of the soil sample. The beakers were shaken at 100 rpm for approximately 60 min and afterwards transferred to a preheated water bath and maintained at 90-95°C for another 60 min. All the beakers were swirled briefly every 10-15 min during heating. At the end of heating, samples were allowed to obtain the ambient temperature, approximately 25°C and then centrifuged for 10 min at 4000 rpm. After centrifugation, Cr(VI) was measured colorimetrically in the centrifuged by diphenylcarbazid (DPC) method at 540 nm wavelength. As this measurement is only accurate in acidic pH, it is essential to dilute the solution by adding distilled water to obtain at least 1:5 of original concentration [16]. A sequential extraction method was applied to evaluate total chromium distribution among four different soil fractions. For soluble and exchangeable fraction 0.50 M KNO_3 was added to the sample and shaken for 16 h, organic fraction was extracted by adding 0.50 M NaOH and 16 h shaking, carbonated was obtained by adding 0.05 M Na_2EDTA and shaking for 6 h and finally residual fraction was determined by adding 4 M HNO_3 and 16 h shaking at 80°C [17,18].

All chemicals were supplied from Merck (Germany) with appropriate purity grade, "for analysis" and de-ionized water was used through the experiments.

RESULTS AND DISCUSSION

The wastewater disposing area is part of a waterway that due to lack of enough precipitation has been dried for many years. In addition fluctuating in sedimentation may have caused some small changes in soil texture within relatively small distances. However in all samples, sand fraction was the dominant part of the soil particles resulting in low soil buffering capacity. As the discharged

Table 1: Some of leather industries effluents properties sampled from the discharging points

Effluents property	
Electrical conductivity (dS/m)	22.7
Total Cr (mg/L)	35.0
Cr (VI) (mg/L)	0.9
pH	8.7

effluents were collected from different leather processing units located at the industrial zone, the chemical compositions and their portions in released wastewater were not constant. However, some of the wastewater chemical properties that have been obtained immediately after sampling were shown in Table 1. Although the measured total Cr in effluents was considerably high it was nearly half of the theoretical expectations for Cr load in leather industries effluents in Iran [19].

As The World Bank report on pollution prevention states potential environmental impacts of tanning are significant. Composite untreated wastewater, amounting to 20–80 cubic meters per metric ton of hide or skin, is turbid, colored and foul smelling. It consists of acidic and alkaline liquors, including chromium, sulfide, nitrogen and high level of fats and many other decaying organic materials. It also contains a large volume of suspended solids [20].

Regarding the above mentioned facts and as it was expected and supported by the comparative results (Table 2) the discharged effluents have had major impacts on main properties of the affected soils. In all contaminated samples, an apparent increase of silt content was observed that could be attributed to the accumulation of the silt-size suspended particles or aggregates of deposited wastewater in soil profile. Measured EC in affected soils were approximately five times higher than the reference soil, however it is not very unexpected considering the electric conductivity of the discharged effluents. As it is predictable and supported by the data in Table 2, the amount of CEC and organic matter of the affected soil has increased. This is completely consistent with tannery effluents properties which include high quantity of organic matter and other compounds that participate in cation exchange reactions [21]. The change in calcium carbonate concentration and its distribution pattern may be due to the presence of such compounds in the leather processing wastewater and their eluviations from upper soil to lower depths [22].

The chromium concentration in reference soil samples was not detectable in the range of mg/kg. In Table 3, the total and hexavalent chromium measured in affected soils were mentioned. The average of the total chromium (including Cr(III) and Cr(VI)) regardless of

Table 2: Comparative results of some of the main properties of leather industries effluents affected and non-affected soils

Soil Property	Soil samples depth (cm)					
	0-15		15-30		30-45	
	Affected soil	Reference soil	Affected soil	Reference soil	Affected soil	Reference soil
Sand (%)	54.5	64.4	49.5	71.8	49.0	70.5
Silt (%)	32.8	23.8	37.0	15.5	37.0	18.3
Clay (%)	12.7	11.8	13.5	12.7	14.0	11.2
pH	8.0	8.1	8.3	8.2	8.0	8.2
EC (dS/m)	12.5	2.7	12.7	2.5	12.6	2.0
CEC (cmol _c /kg)	9.77	7.59	11.89	9.85	11.77	9.25
Organic matter (%)	1.35	0.27	1.42	0.33	1.20	0.25
Equivalent CaCO ₃ (%)	14.05	16.3	20.3	18.0	22.06	18.0

Table 3: Total and hexavalent chromium in contaminated samples (mean ± S.D.)

Measured chromium in under leather industries effluents soil samples	Soil samples depth (cm)		
	0-15	15-30	30-45
Mean total Cr concentration (mg/kg)	218.94±6.50	182.01±7.35	179.98±5.04
Mean total Cr(VI) concentration (mg/kg)	1.65±0.03	1.65±0.08	1.92±0.07

Table 4: Total chromium distribution among different soil fractions in percent (mean \pm S.D)

Soil samples depth (cm)	Chromium distribution (%)			
	Exchange	Organic	Carbonated	Residual
0-15	1.54 \pm 0.20	2.15 \pm 0.60	5.35 \pm 1.00	90.96 \pm 9.30
15-30	1.73 \pm 0.50	2.52 \pm 0.90	4.32 \pm 1.90	91.43 \pm 20.30
30-45	1.80 \pm 0.90	2.97 \pm 1.10	3.27 \pm 0.90	91.69 \pm 4.20

the sampling depths were 193.64 mg/kg and 1.74 mg/kg, respectively. These concentrations indicate that total chromium was nearly equal to Cr(III) concentration as it is expected under most environmental conditions [23]. It is apparent from provided data (Table 3) that the Cr(VI)/Cr(III) ratio in the discharged effluents is approximately 3 times more than this ratio for the contaminated soil. This can be attributed to the rapid conversion of Cr(VI) to Cr(III) in most environments specifically in the presence of a variety of electron donors [23,24]. The highest total chromium concentration was observed in 0-15 cm depth showing low mobility of trivalent chromium [25,15]. Hexavalent chromium concentrations were close in all sampling depths however, it was higher in 30-45 cm which can probably caused by better reduction conditions in upper soil layers e.g. more available decomposed organic matter, reducing agents and better soil aeration condition. Although chromium pollution in soil depends on specific soil properties, comparing these results with the suggested chromium range (100-150 mg/kg) confirms soil pollution [26]. This amount is even high enough to expose potential toxicity risk to food chain through entering the plants growing inside and close to the contaminated area [27]. This is especially the case when they are used for feeding local farm animals. Nevertheless, contamination and toxicity risks are much higher for the measured hexavalent chromium. Considering Cr(VI) as a very toxic and carcinogen pollutant and because of its high mobility in subsurface, restricted health protective levels have been set for this chromium species. According to some studies based on Cr(VI) carcinogenic effects, the maximum concentration of 0.2 μ g/L is allowed in drinking water [28]. Relatively high concentration of measured hexavalent chromium in affected soil and dynamic nature of contaminated area raise major concerns about fate of this pollutant species in soil and its possible entrance to groundwater.

Although the measured concentration of total chromium can be used as a general index for soil pollution, it doesn't provide enough information about the bioavailability, mobility and the exposed risk by this

heavy metal in contaminated soils [29]. As a result and to provide a comprehensive picture of chromium bioavailability and other potential risks, the chromium concentration in different soil fractions was determined by sequential extraction. Regarding the contaminated area soil properties as a semi arid region with high content of calcium carbonate, soil chromium distributions pattern in four fractions of; exchangeable, organic, carbonated and residual were obtained (Table 4). In all sampling depths, more than 90% of the measured chromium occurred in the residual fraction while less than 10% was shared by the others. The fractionation results of contaminated soil showed the following chromium distribution; Residual (~91.4%) > Carbonated (~4.4%) > Organic (~2.5%) > Exchangeable (~1.7%). These results are promising as they show more than 90% of the soil chromium has no or minimal participation in soil reactions and therefore provides less bioavailability and leaching [30]. However, as the distribution pattern indicates approximately 4.2% of the total chromium was in more accessible soil fractions. In other words, still close to 8.10 mg/kg of chromium exist in exchangeable and organic fractions which are considered readily available. Consequently the risk of chromium uptake by plant and its entrance into the food chain should not be neglected.

The results are comparable with the investigation of Walter and Cuevas [18] reporting that Cr was mainly found in the residual fraction in soils treated by sewage sludge for many years. It is also consistent with other previous studies indicating that most of the extractable chromium from sewage sludge treated soils belongs to residual fraction [31,32,33]. This pattern of chromium distribution among different soil fractions can be attributed to high sorption affinity of chromium to the solid phase as it is one of the most strongly adsorbed ions in soils [4].

CONCLUSION

The results of the current study indicated that leather industries effluents had contaminated the investigated soils and human activity is the only reason for trivalent

and hexavalent chromium pollution in the affected area. Although depths below 45 cm were not investigated yet, because of nearly permanent discharge of effluents for many years, probability of soil contamination in deeper soil layers is not negligible. This is especially the case for hexavalent chromium which because of its high mobility may enter local water resources and cause a great toxicity risk. There is no substantial difference between the measured chromium concentrations in the sampling depths, although its mean concentration was approximately 20% higher in 0-15 cm than 15-30 cm and 30-45 cm depths. This can be attributed to very low mobility of trivalent chromium in soil. This pattern was reverse for hexavalent chromium as its concentration in 30-45 cm depth was approximately 15% higher than 0-15 cm and 15-30 cm depths which probably can be caused by more availability of reducing agents in upper soil layers.

Based on the sequential extraction study results, chromium distribution pattern in soil fractions was; Residual > Carbonated > Organic > Exchangeable. In all sampling depths, more than 90% of the measured chromium was in residual fraction which has minimal possibility of leaching or plant uptake. However because of the high concentration of the total chromium in contaminated soil even small percentage of chromium distribution in exchangeable and organic fractions was still considerable. This is especially the case considering that some growing plants in the close vicinity of contaminated area are occasionally used for feeding local farm animals. Because of the dynamic nature of the polluted area and the great risk that it may expose to food chain, along with recommending monitoring plans for the study area, further studies are necessary to evaluate chromium species distribution in deeper soil profiles, local agricultural water sources and plants are growing in the vicinity of the contaminated area.

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