

Four-Stage Sequential Extraction of Heavy Metals from Zayandeh-Rud River Sediments

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The fractionation and release of seven heavy metals *e.g.*, lead, copper, chromium, nickel, manganese, zinc and iron from river sediments under the different conditions was investigated by performing a four-stage sequential extraction. The results showed the potential mobility of heavy metals in river sediments. Considerable amounts of chromium and iron were extracted at 4th stage and indicate lower potential mobility for these two elements. The concentrations of heavy metals extracted with total extraction procedure were compared with those extracted with the sequential extraction procedure and showed that the proposed method is quite capable to remove whole of the elements from river sediments in different stages. The concentration of heavy metals in 10 different points along the river was also studied and showed that as the river pass the city the concentration of heavy metals increased in the sediments.

Key Words: Zayandeh-Rud, Heavy metals, Extraction.

INTRODUCTION

The major sources responsible for releasing heavy metals into the environment are manmade processes include metallurgical processes, power plants, garbage incineration, combustion of fossil fuels in automobile engines, and industrial wastewaters¹. The toxic effects of heavy metals are now well recognized and determination of their concentrations in the environmental samples is of great interest. During the last decade an extensive database has been published providing a direct link between the exposure to low concentrations of heavy metals and different diseases².

Zayandeh-Rud is one of the most famous rivers in the central part of Iran. Considerable amounts of the wet depositions in the Zagross mountains is discharged into the Isfahan province and finally into the Gavkhooni wetland by means of Zayandeh-Rud. The length of the river is 350 Km. Many industries and agricultural areas have been developed around the river Zayandeh-Rud and close to the city of Isfahan. The river receives the

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agricultural wastewater and also the effluents of the industrial wastewater treatment plants. Because of these reasons, the continuous control of the quality of the river water is required^{3,4}.

The pollution of sediments with heavy metals has become a question of considerable public and scientific concern in the light of evidence of their toxicity for human health and to biological systems^{5,6}. The determination of total concentration of heavy metals in river sediments does not give sufficient information about the mobility of these elements^{7,8}. The ability to determine the chemical characterization of heavy metals in river sediments is becoming important. It is necessary to assess the potential of the sediments for releasing of heavy metals in river aquatic environment. Methods for the determining of the different forms of metals in sediments including sequential extraction are based on using different reagents for extraction of metals from different phases in a defined sequence. The principle of the method is based on the fractionation of a material into different fractions which can be selectively destroyed by using specific extractions. The fractions which are most frequently studied are:

Fraction 1: Exchangeable, in which elements are easily extracted with solution contains electrolytes at pH=7.

Fraction 2: The elements associated with carbonates are extracted under the acidic condition.

Fraction 3: The iron and manganese oxides are reduced and the elements associated with them are released.

Fraction 4: The elements combined with different organic matter. The elements in this fraction are released under the strong acidic and oxidizing condition.

Fraction 5: The residue contains elements associated with silicates and other minerals. The residue can be released by digestion with a mixture of hydrofluoric and nitric acids.

The aim of this work was to develop a four-stage sequential extraction procedure to investigate the potential of the river sediments for releasing of heavy metals into the river aquatic environment.

EXPERIMENTAL

All chemicals were of analytical grade. Commercial standard solutions of 1000 $\mu\text{g mL}^{-1}$ of metals for atomic absorption spectrometry were used as stock standard solutions. Working standard solutions were diluted from the stock standard solutions with a 0.1 M nitric acid solution. Solutions of 2 mol/L nitric acid, 0.11 mol/L acetic acid, 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ (pH = 2 adjusted with 2 M nitric acid) were prepared in distilled deionized water. Polyethylene vessels were used for the storage of standard solutions. All glasswares were cleaned before use by soaking overnight in 1.5 M nitric

acid and triple rinsed with distilled deionized water and allowed to be dried.

The determinations of heavy metals concentrations were carried out on a Varian, Model AA-220 atomic absorption spectrometer equipped a GTA-110 graphite furnace system. A Deuterium lamp was used as background corrector. Varian standard hollow cathode lamps were used for the determination of heavy metals. The wavelengths used for the absorption measurements were 283 for Pb, 357 for Cr, 324 for Cu, 232 for Ni, 279 for Mn, 213 for Zn and 248 nm for Fe. An atomizer with air-acetylene burner was used for determining of all elements.

Collection of samples: The sediment samples were collected by a stainless steel dredge from 10 different points along the river in the province of Isfahan. The samples were prepared by air drying grinding and particles less than about 50 μm were separated and used for the extraction and determination of heavy metals.

Sequential extraction procedure

Step 1: exchangeable and acid soluble fraction: 2 g of the sediment sample was placed in a glass container and 40 mL of acetic acid (0.11 mol/L) was added on that. The mixture was shaken for 16 h by a shaker at speed of 40 rpm at room temperature. The extract was separated from the solid residue by centrifuge at 3000 rpm for 20 min. The supernatant was transferred into a 50 mL volumetric flask and diluted to 50 mL with 0.1 M nitric acid.

Step 2: The residue from the first step was leached at room temperature with 40 mL of hydroxyl ammonium chloride (0.1 mol/L) adjusted to pH = 2 with nitric acid. The following operations were exactly the same as that mentioned in step 1.

Step 3: The residue from step 2 was digested with 10 mL of hydrogen peroxide (8.8 mol/L) and the mixture was left still for 1 h and occasionally shaken. The mixture was then heated at 80°C to near dryness. Then 50 mL ammonium acetate (1 mol/L) adjusted to pH = 2 with nitric acid. The following operations were exactly the same as that mentioned in step 1.

Step 4: The residue from step 3 was digested with a mixture of nitric hydrofluoric acids and a procedure same as that mentioned for total extraction of heavy metals was followed.

Extraction of total elements: The sediment sample was placed in a PTFE beaker and moisturized with a few mL of de-ionized distilled water, and then 10 mL of Aristar nitric acid was added. The lid of the beaker was replaced and the beaker was heated on a hot plate and refluxed for 8 h until all organic material be oxidized. The PTFE lid was then removed and the beaker heated at 90°C. When the volume was reduced to a half, 5 mL of nitric acid and 3 mL of hydrofluoric acid were added. The mixture was refluxed again to dissolve the material completely. The lid was then

removed and the mixture was evaporated to near dryness. After removing the remainder of HF (by adding HNO₃ and heating) the digest was extracted in nitric acid, transferred into a 50 mL volumetric flask and made to the volume by de-ionized distilled water.

RESULTS AND DISCUSSION

The calibration curves of the elements in extracts were compared with those obtained for the elements in nitric acid matrix and an excellent correlation was found between them. It can be concluded that there was no interferences from the reagents used for sequential extraction.

The concentrations of heavy metals released by the sequential extraction in different stages showed that the potential mobility of Mn, Ni, and Pb are more than the other elements. The results obtained from the fractionation of heavy metals by the sequential extraction are summarized in Table-1.

TABLE-1
MEAN CONCENTRATIONS OF HEAVY METALS EXTRACTED BY
SEQUENTIAL PROCEDURE FROM RIVER SEDIMENTS ($\mu\text{g/g}$)

Element	Sequential extraction			
	Step 1	Step 2	Step 3	Step 4
Pb	0.64 ± 0.42	1.62 ± 0.38	7.92 ± 3.69	8.46 ± 3.56
Cr	-	-	0.64 ± 0.42	8.58 ± 4.51
Cu	0.37 ± 0.21	1.47 ± 0.32	8.82 ± 3.12	7.72 ± 3.21
Ni	1.87 ± 0.35	3.22 ± 0.38	23.21 ± 4.52	17.94 ± 4.98
Mn	17.98 ± 4.52	10.21 ± 4.56	34.21 ± 5.11	6.82 ± 3.12
Zn	2.35 ± 2.23	11.72 ± 4.23	16.45 ± 8.43	6.45 ± 4.16
Fe	-	389 ± 92	1743 ± 520	3237 ± 709

TABLE-2
COMPARISON OF TOTAL AND SEQUENTIAL EXTRACTION
PROCEDURE FOR RELEASING OF HEAVY METALS
FROM RIVER SEDIMENTS

Element	Total metal extraction ($\mu\text{g/g}$)	Sequential extraction ($\mu\text{g/g}$)	Recovery (%)
Pb	20.3 ± 3.1	19.5 ± 4.2	105
Cr	15.1 ± 3.2	14.6 ± 3.7	96.7
Cu	18.4 ± 2.9	18.7 ± 3.3	102
Ni	48.1 ± 2.5	48.8 ± 2.7	101
Mn	70.7 ± 3.7	71.6 ± 6.9	101
Zn	48.8 ± 5.7	52.1 ± 4.2	106
Fe	4811 ± 821	4870 ± 7.06	101

Several sediment samples were subjected to both total extraction of heavy metals and also sequential extraction. The results of this investiga-

tion are summarized in Table-2 and showed that sequential extraction is quite capable to release whole of the heavy metal content from the sediments in different steps.

The total cocentrations of heavy metals in the sediment samples collected from 10 different points are shown in Fig. 1.

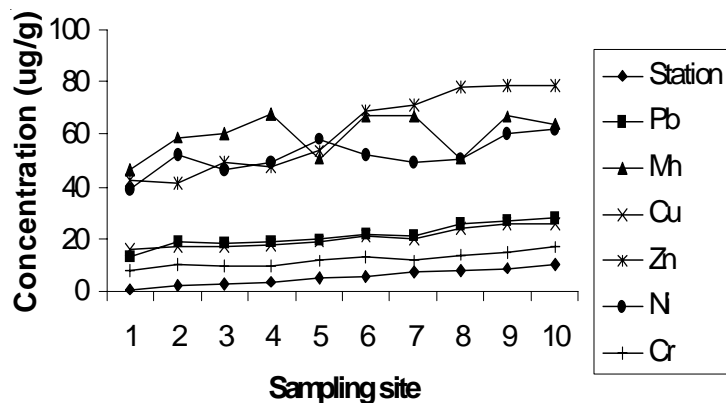


Fig. 1. Concentration of heavy metals associated with river sediments at different points

The concentrations of heavy metals in the river sediments are continuously increased as the river passes through the Isfahan province. At the points where the industrial and agricultural wastes were discharged into the river higher concentrations were observed.

The percentages of heavy metals extracted in the different fractions of the sequential extraction is shown in Fig.2. The results show not only the potential mobility of the heavy metals in the river sediments but also the source of the heavy metals. The elements which are mostly released in the step 4 of sequential extraction are mostly have a natural sources while those released in steps 1 and 2 can come from the anthropogenic sources.

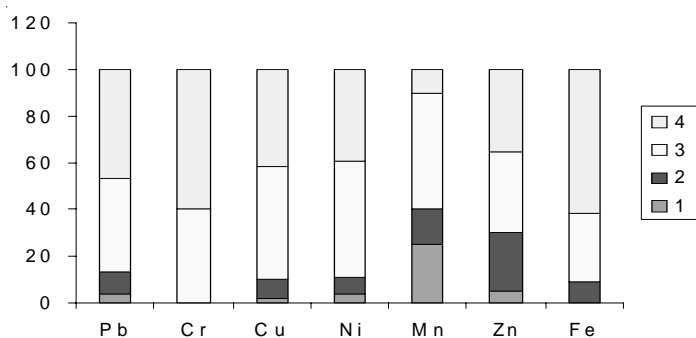


Fig. 2. Percentages of heavy metals released in different stages of the sequential extraction

The four-stage sequential extraction is relatively rapid and easy and offers valuable information about the mobility of heavy metals in the river sediments. Concerning to the percentages of the elements released in different stages it can be concluded that fortunately most of the elements come from the natural sources and the river aquatic environment can easily be controlled by proper programming.

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