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THE REMOVAL OF HEAVY METAL IONS FROM FERROCHROME WASTES BY ELAZIG SOILS

Rüstem GÜL*, Sücaattin KIRIMHAN**, and Bekir SOLMAZ**

* Atatürk University, Engineering Faculty, Erzurum
** Fırat University Department of Environmental Engineering, Elazığ,

Key Words : Environmental, wastwater, soil, adsorption, removal

ABSTRACT: The heavy metal pollution potential of Elazığ Ferrochrome Plant (EFP) slag, its variation with water application rate and time, the capacity of Elazığ-Region soil to adsorp these metal ions, and the dispersion of these metal ions in the soil were investigated by column and extraction tests. Statistical models were developed by using the relationship between distribution of heavy metals in the soil, depending upon the thickness of the soil and the heavy metal concentration changing with respect to the amount of applied water. To reduce the metal ions to almost zero in the EFP slag the necessary period of time, and thickness of the soil to adsorp these metal ions were found as 21 years and 90 cm, respectively.

ELAZIĞ YÖRESİNDEKİ TOPRAKLA AĞIR METAL İYONLARININ FERROKROM ATIKLARDAN UZAKLAŞTIRILMASI

ÖZET : Elazığ Ferrokrom Fabrikası (EFF) curufunun ağır metal sızdırma potansiyeli, bunun tatbik edilen su mikları ve zamanla değişimi, Elazığ yöresindeki toprağın bu metalleri tutma kapasitesi ve bu metallerin toprak içerisindeki dağılımı kolon ve ekstraksiyon testleri ile incelendi. Curufa tatbik edilen su miktarına göre metal konsantrasyonları arasındaki ilişki ile, ağır metal iyonlarının toprak kalınlığına bağlı olarak dağılımı ilişkisinden istatistiksel modeller geliştirildi. EFF curufundaki metal iyonları derişimlerinin sıfıra yaklaşması için gerekli süre ve bu metalleri tutan toprak tabakası kalınlığı sıra ile 21 yıl ve 90 cm olarak bulundu.

1. INTRODUCTION

Heavy metals resulting from industrial wastes play a major role in environmental pollution. Treatment of these metals, which are toxic for living things, with an economical method is very important. A number of studies have shown that land treatment is an economical method for this purpose. However, U.S. Environmental Protection Agency (EPA),U.K. Department of Environment (DoE) and some other investigations have suggested that maxsimum heavy metal loadings should not exceed a given amount in soil matrix. This amount is determined based on cation exchange capacity (CEC) and other properties. When CEC of a soil is between 5-15 meq/100 g soil and pH of soil greater than 6.5, maximum cadmium application to land should be 10 kg/ha For Cr, Co, Cu, Zn, Ni, and Mn, this amount should be 100-1,000 kg/ha, 90-220 kg/ha, 250-280 kg/ha, 560 kg/ha, 70 kg/ha, and 100 kg/ha, respectively It has been reported that these amounts can be applied to land for 30 years [1, 2].

It has been observed that intensive use of solid fertilizer may result in a certain accumulation of nutrient elements in soil. However, this type of contamination is less important than soil and plant pollution with external sources of trace element [3].

It has been claimed that an enrichment of trace elements from sewage sludge fertilizer takes place in soil and particularly in plants for elements which are micro nutrients [4]. The results of another study revealed that plant uptake of heavy metals decreases when organic particles or clay colloids are present in soil to bind heavy metals [5].

Adsorption on colloidal surfaces plays an important role in the retention of heavy metal ions in a soil matrix. When heavy metal ions exist at very low concentrations in the soil solution, adsorptions of metal ions to clay minerals shows a very low reversibility because of preferential adsorption by chemical bond [6].

Another prevention process in the soil below a landfill is precipitation with sulphides and possibly carbonates. Concentrations of these anions are strongly dependent on pH and redoxpotential of soil solution [7] . Elazığ Ferrochrome Plant (EFP) was built at the bank of the Fırat river, Elazığ, Turkey. Its slag (solid waste) has been collected and left on the field near the river without any control. It is very important to know heavy metal pollution potential of this slag and develop a solution to remove the metal ions from the slag. In this research, the heavy metal potential of EFP slag, its variation with water application rate and time, the capacity of Elazığ soil to prevent heavy metal ions, from leaching into groundwater and the dispersion of these metal ions in the soil were investigated.

2. MATERIALS AND METHODS

Experimental Set-up

Six experimental columns of PVC pipe with a length of 75 cm and an inside diameter of 14 cm were constructed. The experimental set up is schematiged in Figure 1. The soil collected from different locations of Elazığ were used as sample material. Prior to the experiments, the material was air-dried at room temperature, homogenized and passed through a standard sieve which has 2 mm openings.

The slag samples was obtained from the EFP The raw slag used in the experiments had no prior contact with water. It was ground and passed through a standard sieve which had 2 mm openings. Some properties of the soil and slag sample are given in Table I.

In the column tests, deionized water was used to represent rain and snow waters. All experiments were carried out at room temperature, in thelaboratory of Fırat University, Elazıg, Turkey.

Table I. Some Properties of the Soil and EFP Slag Samples Used In Column Experiments.

Chemical and Mineralogical Analyses of Soil (%)

SiO_2	46.97	MgO	5.56
Al_2O_3	14.64	K_2O	0.87
Fe_2O_3	8.21	Na_2O	2.00
TiO_2	1.00	Ni	0.007
CaO	10.30	Mn	0.15
Cr	0.015	Cu	0.010
V	0.010	LOI*	10.02
Montmorillonite			45
Chlorite			40
İllite, Quartz, Felspath and Calcite			15

pH : 8.25 CEC** : 8.90 meq/100 g soil

Density of Soil : 1.40 g/cm^3

Chemical Analysis of EFP Slag (%)

SiO_2 : 32.00 Cr_2O_3 : 5.89 MgO : 31.58

Fe_2O : 1.98 Al_2O_3 : 30.60 CaO : 0.98

* : Loss On Ignition

** : Cation Exchange Capacity.

Preparation of Exprimental Columns

The test columns were filled with glass wool and soil from bottom to the top. The soil sample was left on the glass wool into the columns 1-6 to 40 cm thickness. All soil samples were placed into the columns in four steps and compressed by vibrator. About 10 cm (2.5 kg) slag sample was set on the top of soil for each of columns 4-6. The columns 1-3 were kept without slag sample in order to compare with columns 4-6. Water was applied to all columns from below up to give a depth of 13 cm over the soil or slag levels, and the taps on the columns were kept closed for 24 hours in order to get a saturated soil. This water level was kept during the column test by float for all columns. At the end 24 hours, the taps were opened, and deionized water was applied for 120 days. The filtrate water were collected in the glass containers. The experimental apparatus is shown in the Figure 2.

Extraction Test (EPA Test)

One thousand and six hundred ml of deionized water was added to 100 g slag samples, and mixed by mechanical mixer for 24 hours. During this time, the pH was adjusted to 5 ± 0.2 by adding acetic acid. At the end of 24 the hours, the sample was filtered and metal concentrations in the solution determined [8].

Initially, the extraction test of the Environmental Protection Agency (EPA) was applied to the original slag sample and as well as column samples at the end of 15th, 30th, 60th, and 120th days after water application so as to determine the pollution potential of metal ions leaching from EFP slag into the water, and its variation with time and unt of deionized water applied. This test was also applied to soil

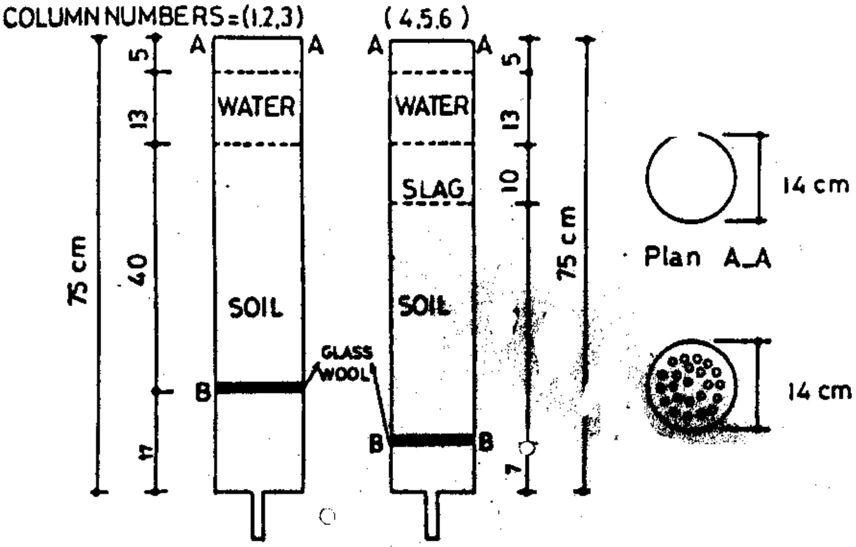


Figure 1. Experimental Columns

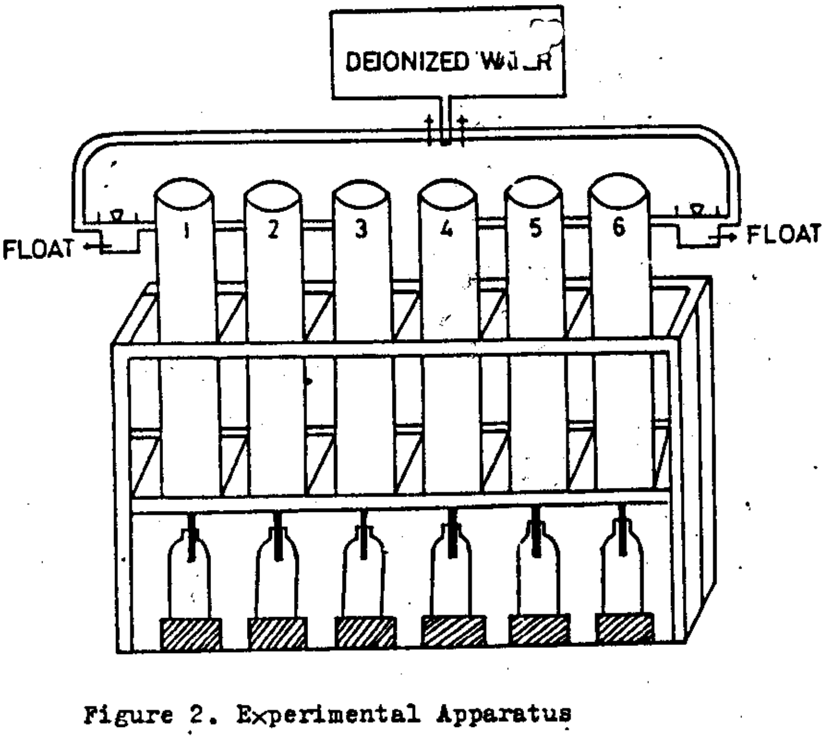


Figure 2. Experimental Apparatus

samples taken from 2.5, 7.5, 15, 25 and 35 cm depths of soil in the columns in order to investigate distribution of metal ions in the soil depending upon the amount of water applied to the columns and thickness of soil, at the end of the column experiment.

Sampling and Method of Analysis

The liquid were taken from under the columns once a day and composite leachates were prepared to be able to show all properties of this liquid. The composite leachates were refrigerated after HNO_3 addition before metal analyses. pH and electrical conductivity were determined in the first day leakage water of every composite leachates. The metal ion concentration in the leachates obtained columns experiment and extraction tests were determined for Cu,Fe,Zn,Cr,Mn, Co, Ni, and Cd by atomic absorption methods. Because these metal ions were found in the EFP slag by extraction test at the begining of this study.

3. RESULTS AND DISCUSSION

Heavy metal potential of the EFP slag, its variation with amount of applied water and time, total amounts of metal ions from 2.5 kg EFP slag, and average amounts of applied water are given in Table II, and shown in Figure 3.

In the leachates obtained from EFP slag by exration tests, the amount of Cr was the higher than those of the other metal ions. Fe, Zn, Cu, Mn, Ni, Co, and Cd were appeared in the leachates less than Cr, respectively.

These data indicated that the leaching metal ions from EFP slag into the water gradually decreased with time and water applied from initially. In the first 15 days, 7.872 liters of deionized water were applied to the EFP slag and 36 percent metal ions passed into the water. From 1th day up to 30th day 15.815 liters and from 1th till 60th day 26.280 liters and from 1th to 120th day 35.000 liters water were applied to the EFP slag but only 18 percent, 10 percent and 8 percent metal ions leaked into the water from EFP slag, in turn. After 60th day, the concentration of Ni, Co, Cd, ions reached zero, and concentrations of Cr, Fe, Zn, Cu and Mn became 0.88, 0.52, 0.30, 0.45 and 0.21 mg/l, respectively. At the 120th day, the value of Cr, Fe, Zn, Cu and Mn were found 0.70, 0.43, 0.30, 0.40 and 0.15 mg/l, in turn. In the leachates obtained from the orijinal EFP slag the amount of Cr (8.61 mg/l) is highger than the criteria of EPA. The amounts of other metals are high than that given in the guideline of drinking and using water. That means heavy metal ions have to be treated before given to environment.

In the leachates obtained from column tests, metal icns were disappeared. That means all the metal ions were prevented by soil column has 40 cm thichness. This result can be explained high amount of soil in the test columns, the presence of clay minerals in soil, low hydraulic conductivity of the soil columns, more than 7.0 pH value of environment in columns, and behaviour of metal ions in soil [9, 10, 11].

Hydraulic and electrical conductivities showed gradual decrease with time and the water application, in the leachates. The values of electrical conductivity obtained from soil and soil + EFP slag columns ranging from 1,000 - 552 µmhos/cm and 648 - 318 µmhos/cm were found, respectively. The pH values generally appeared higher than 7.0 in the leachates.

The capacity of Elazığ-Region soil to prevent heavy metal ions from passing into ground water, and the dispersion of these metal ions in the soil are given in Table III, and shown in Figure 4.

These data showed that the metal ion concentrations obtained from soil columns were lower than those of soil + slag columns. This situation indicated that the heavy metal ions leaching from EFP slag were adsorbed by soil.

The dispersion of the metal ions in the soil showed a decrease from the surface to down. The considerable amounts of Cu and Cr were prevented by soil layer near the surface. In the soil sample taken from 7.5 cm depth, all the metal ions were reached the highest values, except Cr. There were small amounts of Ni and Co in the samples. Very low amounts of Zn, Fe and Cr ions were appeared, and Mn, Ni, Co, and Cu ions disappeared between 30 and 40 cm depths of soil layer. Cu and Co ions were reached zero at the 25 cm depth of soil. Cd ions were disappeared in all samples because the motion and behavior of metal ions are different in the different type of soil and environmet [6,12,13,14].

Table II. The Amounts Of Metal Ion Leaking To The Environment From EFP Slag Depending Upon Applied Water (mg/l)

Metal	Original EFP Slag	Time (Day) 15	30	60	120	Amount of Metal Ions From 2.5 kg EFP Slag (mg)
Cr	8.61	2.30	1.11	0.88	0.70	200
Fe	5.50	2.61	0.98	0.52	0.43	181
Zn	5.00	1.94	0.82	0.30	0.30	134
Cu	2.30	0.72	0.46	0.5	0.40	81
Mn	1.50	0.48	0.53	0.21	0.15	55
Ni	1.15	0.50	0.45	0.00	0.00	38
Co	0.80	0.43	0.20	0.00	0.00	25
Cd	0.04	0.02	0.01	0.00	0.00	1.2
Total Metal Ions From EFP Slag	24.90	9.00	4.56	2.36	1.98	
Amounts of Water Applied to EFP Slag (liters).		7.872	15.815	26.280	35.000	

In the leachates, the concentration of the Cr ions was higher than that of the other metals. The amounts of Fe, Zn, Cu, Mn, Ni and Co were high after Cr, respectively. This results can be explained by the different initial concentration of metals from EFP slag, and behaviour of them in the soil matrix [15, 16].

Table III. The Dispersion Of Metal Ions In the Soil Depending Upon Its Depth (mg/l)

Metal	Column Number	Depth (cm)				
		0-5	5-10	10-20	20-30	30-40
	A*	0.65	0.75	0.75	0.65	0.67
Cr	B**	2.44	2.45	1.73	0.97	0.82
	(B-A)***	1.79	1.70	0.98	0.32	0.15
	A	0.64	0.68	0.68	0.69	0.65
Fe	B	2.22	2.37	2.09	1.39	0.81
	(B-A)	1.58	1.69	1.41	0.70	0.16
	A	0.43	0.44	0.52	0.42	0.42
Zn	B	1.53	2.05	1.89	0.90	0.67
	(B-A)	1.10	1.61	1.37	0.48	0.25
	A	0.41	0.48	0.46	0.46	0.45
Cu	B	1.31	1.48	0.66	0.46	0.45
	(B-A)	0.90	1.00	0.20	0.00	0.00
	A	0.50	0.42	0.45	0.45	0.44
Mn	B	0.95	1.02	0.95	0.55	0.44
	(B-A)	0.45	0.60	0.50	0.10	0.00
	A	0.15	0.14	0.15	0.14	0.15
Ni	B	0.40	0.50	0.50	0.29	0.15
	(B-A)	0.25	0.36	0.35	0.15	0.00
	A	0.10	0.12	0.10	0.11	0.12
Co	B	0.30	0.36	0.29	0.11	0.12
	(B-A)	0.20	0.24	0.19	0.00	0.00
Total Metal Ions		6.27	7.20	5.00	1.75	0.56
Average Depth (cm):		2.50	7.50	15.00	25.00	35.00

*, **, *** : Average amounts of metal ions from soil colums (1, 2 and 3), soil + slag colums (4, 5 and 6) and EFP slag (Difference between B and A), respectively.

The relationship between the varying amount of heavy metal ions in the EFP slag with deionized water applied and dispersion of metal ions depending upon depth of soil was obtained from Table II and III. In order to observe these bilateral relationships, Linear, logarithmic, exponential and power methematical models were used. For chosing the most agreeable regression equation, correlation coefficients have been considered. The equations, correlation coefficients (r) and regression curves of the associations are presented in Figure 5 and 6.

In order for heavy metal ion concentrations to go down to minimum level in the leachate, the needed amount of applied water and the depth of soil so as to prevent metal ions were calculated as 145, 000 cm^3 (this amount is equal to 21 years rain water for Elazığ-Region. Calculation : 145, 000 cm^3 water in a pipe with 154 cm^2 cross section area145, 000 / 154 = 941 cm water depth. Mean annual precipitation in Elazığ-Region: 44.5 cm, 941/44.5 = 21 years.), and 90 cm from statistical models depending upon mean annual precipitation in Elazığ-Region (445 mm), respectively.

According to this experimental study and statistical models the heavy metal ions leached from EFP slag (with a 10 cm depth) into the water will not pass a 90 cm thick soil layer. This indicates that EFP slag can be applied at a rate of 2.5 kg/154 cm^2 or 1,623. tones/ha/29 years to the Elazığ-Region. However, according to the literature and guidelines of EPA this amount is harmful for plants and surface water. For that reason, it is necessary that the slag sample should keep far away from surface water and should be applied to the field lower than at a rate of 1,623 tones/ha/21 years.

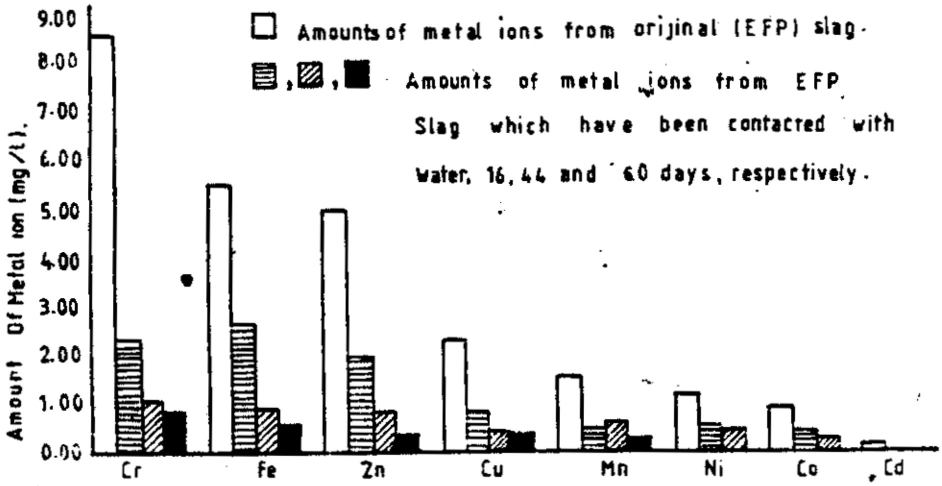


Figure 3. The Change Of Heavy Metal Potential Of EFP Slag.

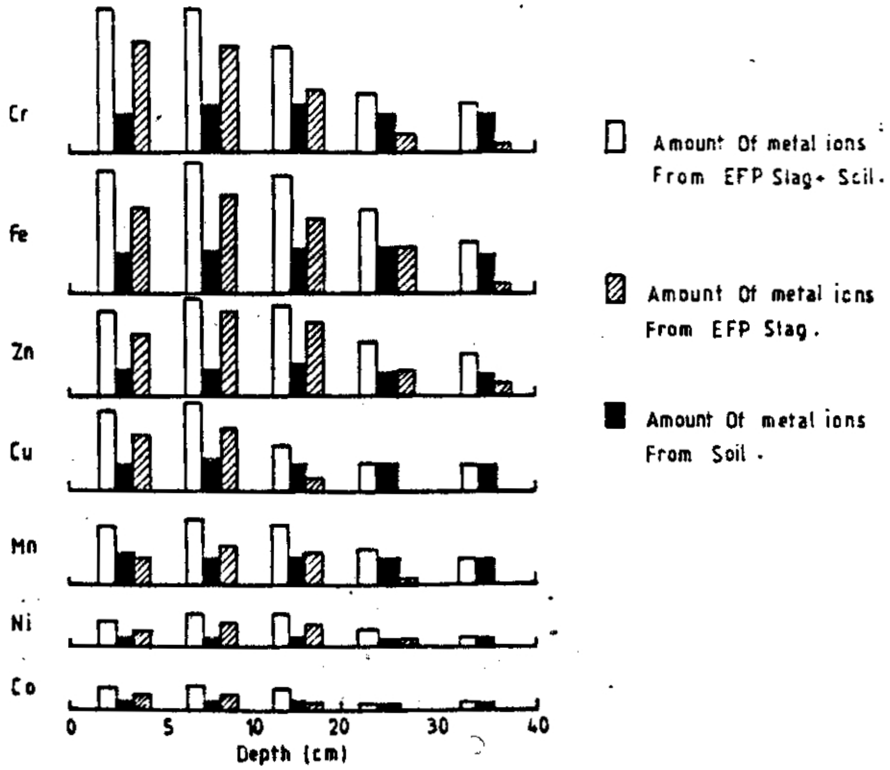


Figure 4. Dispersion Of Heavy Metal Ions Inside Of Soil.

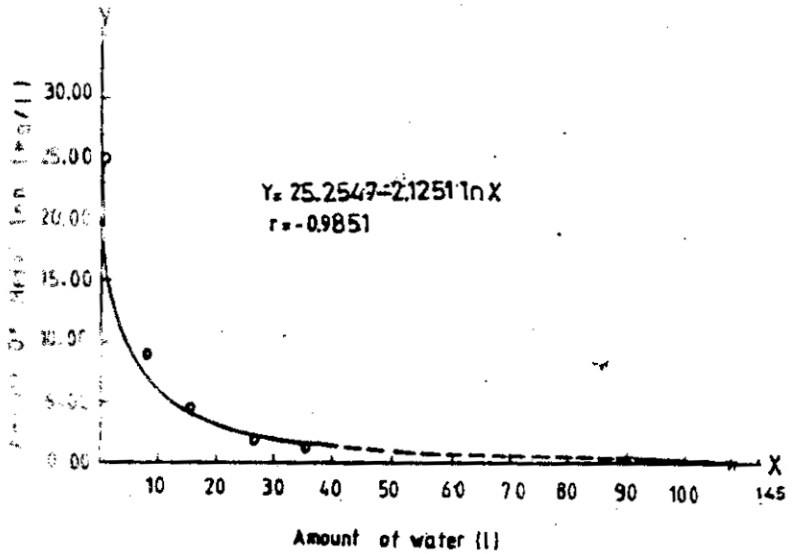
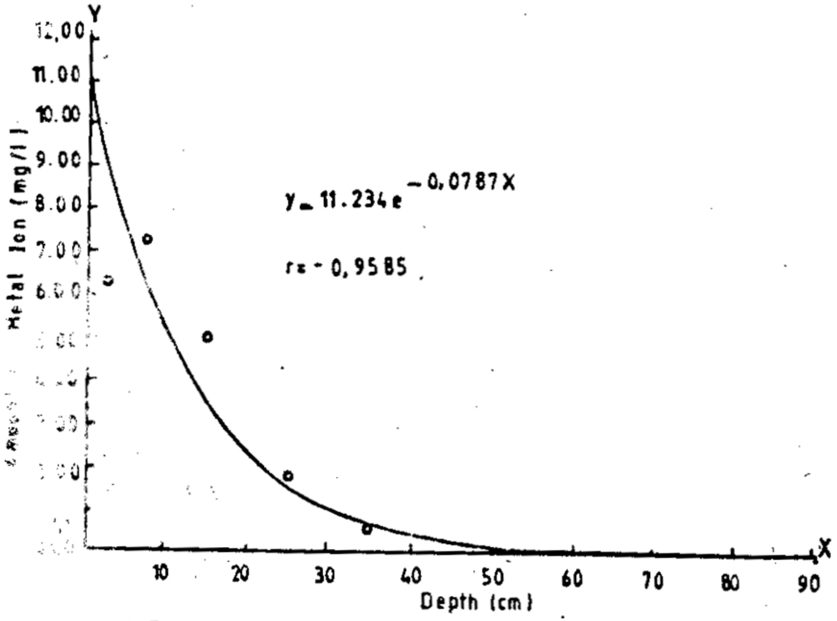


Figure 5 ..The Change Of Heavy Metal Potantial Of EFP Slag Depending Upon Applied Water.



6. The Dispersion Of Heavy Metal Ions Inside Of Soil Depending Upon Its Thickness.

4. CONCLUSIONS

The EFP slag has a significant heavy metal potential to pollute surface water and soil.

The amount of heavy metal ions originated from EFP slag, decreased with applied water and time, and can reach almost zero under rain water about 21 years.

The soil from Elazığ-Region can remove heavy metal ions from wastewaters in a significant propotion. The amount of heavy metal ions in soil decreased as the depth of soil increased.

EFP slag (with a 10 cm thicknees) can be applied to Elazığ-Region with a thickness of soil layer of at least 90 cm without any problems for groundwater, but it is recommended that this slag should keep far away from surface waters and covered up with clayey soil or this slag have to be purified before given environment.

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