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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

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PYROLYSIS OF ZINC CONTAMINATED BIOMASS FROM PHYTOREMEDIATION

ABSTRACT

The aim of this study is to stabilize of zinc (Zn) from soil to pyrolysis solid product. For this aim, phytoremediation and pyrolysis were sequentially applied. In the phytoremediation stage, contaminated soil with zinc was cleaned up via sunflower (*Helianthus annuus*), corn (*Zea mays*) and rape (*Brassica napus*). After harvesting, the plants were pyrolyzed at 500°C with the heating rate of 35 °C/min in a fixed bed stainless steel reactor. The phytoremediation results indicated that high phytoremediation efficiency (79%) were observed. Beside the main property analyses, Zn contents were determined on the pyrolysis solid and liquid products. According to pyrolysis results, Zn content of the contaminated biomass species is fixed into the ash/char fraction.

Keywords: Hazardous waste, Phytoremediation, Pyrolysis, Soil.

FİTOREMEDİASYON SONRASI ÇİNKOYLA KİRLENMİŞ BİYOKÜTLENİN PİROLİZİ

ÖZ

Bu çalışmanın amacı, çinkonun topraktan piroliz katı ürününe stabilize edilmesidir. Bu amaçla, ardışık olarak fitoremediasyon ve piroliz işlemleri uygulanmıştır. Fitoremediasyon aşamasında, çinkoyla kirlenmiş topraklar, ayçiçeği (*Helianthus annuus*), mısır (*Zea mays*) ve kanolayla (*Brassica napus*) temizlenmiştir. Hasattan sonra bitkiler, 35 °C/dk ısıtma hızıyla 500°C sıcaklıkta sabit yatak bir reaktörde piroliz edilmiştir. Fitoremediasyon sonuçlarına göre, en yüksek fitoremediasyon verimi %79 olarak belirlenmiştir. Piroliz katı ve sıvı ürünlerinin temel özelliklerinin yanısıra, Zn içerikleri de analiz edilmiştir. Piroliz sonuçlarına göre, kirlenmiş biyokütlelelerdeki Zn içeriğinin katı üründe stabilize edildiği görülmüştür.

Anahtar Kelimeler: Fitoremediasyon, Piroliz, Tehlikeli atık, Toprak

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1.INTRODUCTION

Zinc (Zn) is an important element for living organisms. The adequate levels of total Zn for plants is 10-300 ppm but it can be toxic at greater than 400 ppm (Eisler, 1993). Major sources of anthropogenic zinc in the environment include electroplaters, smelting and ore processors, domestic and industrial sewage, combustion of solid wastes etc. Zn, listed as number 75 (of 275) in the priority list of hazardous materials according to Agency for Toxic Substances and Disease Registry (ATSDR), is toxic to humans and plants in higher concentrations. Therefore, Zn-contaminated sites should be remediated with suitable remediation methods. Phytoremediation can be used as an alternative methods. In this approach, plants are used to absorb and translocate contaminants from the soil (Latiff et al., 2012). Many studies are related to phytoremediation involving different plants and a variety of contaminated soils. Remediaiton potential of four forage grasses in remediation of Cd and Zn contaminated soils was investigated by Zhang et al. (2010); Cd and Zn phytoextraction was searched by McGrath et al. (2006); effects of bacteria inoculating on phytoremediation of Zn and Cd contaminated soils were investigated by Marques et al. (2013), phytoremediation of Ni, Pb, and Zn contaminated soil with different plants was researched by Amer et al. (2013), a dose-response study was performed on contaminated water/land with zinc by Romeo et al. (2014).

Despite phytoremediation has been applied to wide range, production of contaminated plant is concerned. At that point, after phytoremediation, application of biomass utilization techniques should be applied. These techniques can be physical/biochemical/thermochemical processes. Among the thermochemical methods, pyrolysis is transforming biomass into energy and products. Stals et al. (2010 a,b), Koppolu and Clements (2003a,b) and Lievens et al. (2008 a,b) studied pyrolysis of heavy metal contaminated biomass after phytoremediation for different kinds of plants. Therefore, phytoremediation was applied to zinc contaminated soil via sunflower (*Helianthus annuus*), corn (*Zea mays*) and rape (*Brassica napus*). After harvesting, contaminated biomass was pyrolyzed.

2. MATERIAL AND METHODS

This study involves two stages. The first stage consists of model soils preparation, sowing cultivation, harvesting and plant and soil analyses. The second stage composes of pyrolysis process and analysis of solid and liquid products. The flowchart of the study is given in Figure 1.

2.1. Soil Characterization

The tested soil was collected from a depth of 20 cm below the soil surface at an agricultural area in Eskişehir/Turkey. Physical and chemical properties of the soil are given in Table 1. According to the water saturation and structural analysis results, it was found that the soil can be classified as clay loam (CL). The soil is suitable for cultivation according to the chemical analyses and especially the organic matter, lime, total salts and nutrient content.

2.2. Phytoremediation

Soils of 3,5 kg were passed through a 5 mm sieve and put into polyethylene pots with a diameter of 23.5 cm and a height of 18.5 cm. According to Annex I-A of Regulation for the use of Urban and Municipal Sewage Sludge on Soil in Turkey (03.08.2010 no: 27661) the limit value of Zn in soil is 200 mg/kg dry soil (pH > 7). Thus, in this study, the initial concentration was set at 900 mg Zn/kg (three times the limit value) as moderate contamination in all treatments. 500 ml distilled water containing $ZnSO_4.7H_2O$ was added to the sample pots to form of 900 mg Zn/kg contaminated soil models. After, the sunflower (*Helianthus annuus*), corn (*Zea mays*) and rape (*Brassica napus*) seeds were separately sown in 15 sample pots containing model soils. The soil moisture content was maintained according to the field capacity by weighing and adding deionized water every two days. Therefore, it was not obtained any leachate from the pots. All of the plants were harvested at the end of the 8th week. After harvesting, plants were dried in a laboratory at ambient temperature for 8 days.

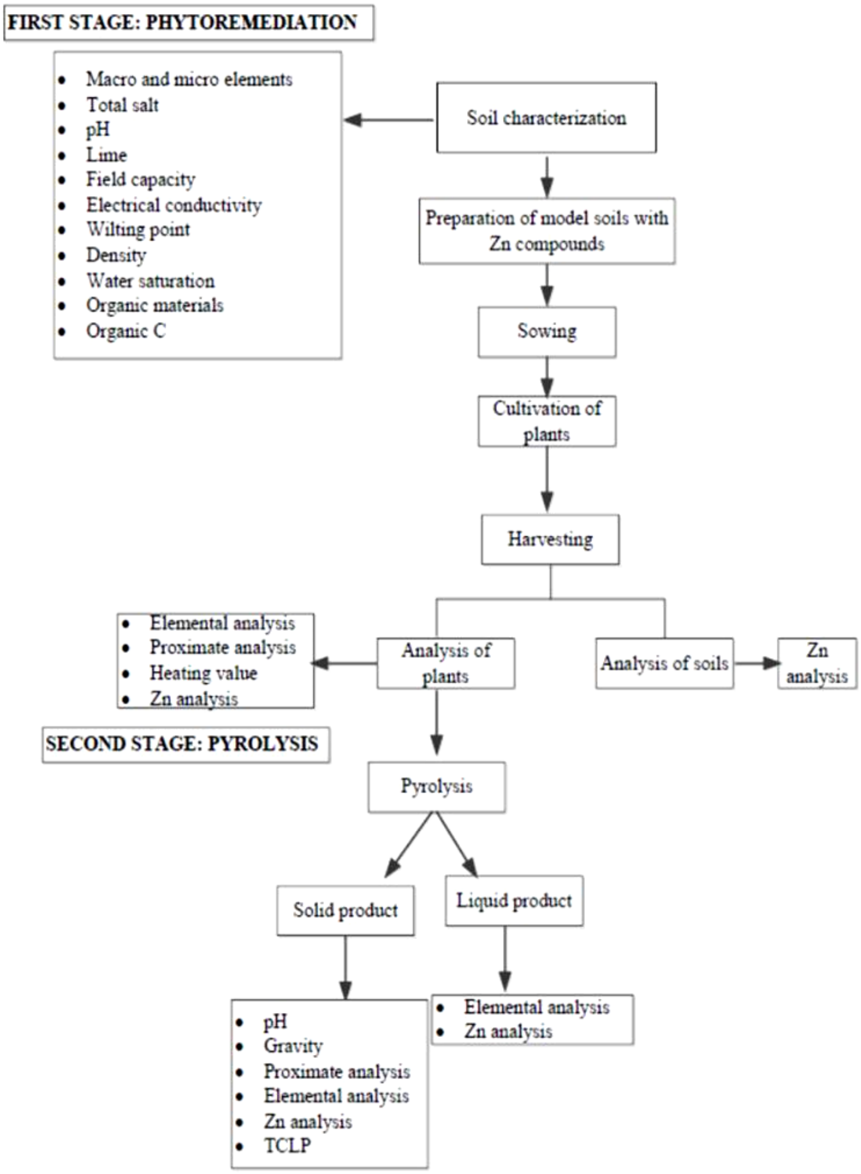

Figure 1. The Flowchart of the Study

Table 1. Properties of the soil

Micro and macro elements (mg / kg)						Other physical and chemical properties			
Al	1540	Fe	769	Ni	27	Total Salt %	0.0	Wilting point, %	21
Ca	4264	K	975	P	364	pH	8.0	Density g/cm^3	1.3
Cd	0.19	Mg	656	Pb	7.5	Lime, %	7.1	Water Saturation,	62
Cr	7.97	Mn	304	S	260	Field capacity, %	31	Organic	3
Cu	10.05	Na	181	Zn	22.3	Electrical	0.6	Organic C, %	2

2.2.1. Soil and Plant Analyses

The soil samples were digested according to EPA Method 3051 A to determine the Zn content as follows: 0.5 g of the soil was carefully weighed into PTFE vessels (CEM Mars 5). 10 ml of HNO_3 (Merck, 65%) was added to the vessels and the temperature of each sample was raised to 175 ± 5 °C over approximately 5.5 ± 0.25 min, remaining at 175 ± 5 °C for 4.5 min. The plant samples were digested by microwave according to Kaçar and Inal (2008) and Kalra (1998) as follows: 0.1 g of the plant was carefully weighed into a PTFE vessel (CEM Mars 5). 9 ml of HNO_3 (Merck, 65%) and 3 ml $HClO_4$ were added to the vessels and the temperature of each sample was raised to 200 ± 5 °C over approximately 15 min, remaining at 200 for 15 min. For method validation, certified reference materials (CRM033 for soils and NCS DC73350 for plants) were also digested. After digestion, the samples were diluted with purified (18 MΩ) water up to 100 ml. Following this, the samples were analyzed with ICP-OES (Varian 720) according to the EPA Method 200.7. As a result of the method validation, Zn recovery rates were obtained as 97% and 98% for the CRM033 (soil) and the NCS DC73350 (plant), respectively.

Elemental and proximate analyses (moisture, ash, volatile matter and fixed carbon content) were also performed for the dried plant samples. The elemental composition (C, H, N, S) of the plants was determined using Leco TruSpec CHN and S. The moisture, ash, volatile matter and fixed carbon contents of the plants were determined according to ASTM D 2016-74, ASTM D1102-84, ASTM E-897-82 and ASTM E-897-82, respectively.

2.2.2. Data Analysis

The variables were tested for the effects of plant type on Zn accumulation on soils and plants using Two-Way ANOVA's (significance level α=0.05). ANOVA is a powerful technique that explores the factors affecting the response. A statistical analysis was performed using the licensed Minitab 16 software.

2.3. Pyrolysis

The pyrolysis experiments were carried out under atmospheric pressure at a 500 ºC pyrolysis temperature with a 35 °C/min heating rate in a fixed bed stainless steel (380 S) 240 cm^3 reactor (Figure 2). The pyrolysis experiments were conducted in a well-swept fixed bed reactor with nitrogen. In a typical run, 10 g of sample was placed into the reactor and after the reactor had reached the set temperature, it was maintained there for 1 hour. As a result of the pyrolysis process, liquid, solid and gas phases were produced. The liquid phase was collected in a cold trap maintained at about 0 °C using ice. The solid and liquid product yields were determined gravimetrically for each experiment. The gas product yields were determined by the mass difference

After pyrolysis, physical and chemical analyses of solid and liquid products were carried out. The proximate (moisture, ash, volatiles and fixed carbon content) and elemental composition to identify the solid products were determined using the same procedures for plant characterization as earlier mentioned. In addition to these analyses, Zn contents of the liquid products were determined according to the Stals et al. (2010a, b) by using a microwave digestion method with HNO_3 and H_2O_2. The metal contents of the solid products were determined according to Liu et al. (2014) with HCl, HNO_3 and HF. Then, the samples were analyzed with ICP-OES (Varian 720) according to the EPA Method 200.7. Furthermore, the heavy metal stabilization capacity of the solid product was determined by TCLP tests according to EPA Method 1311. pH and gravity were determined according to ASTM D-1512 and ASTM D-1513, respectively.

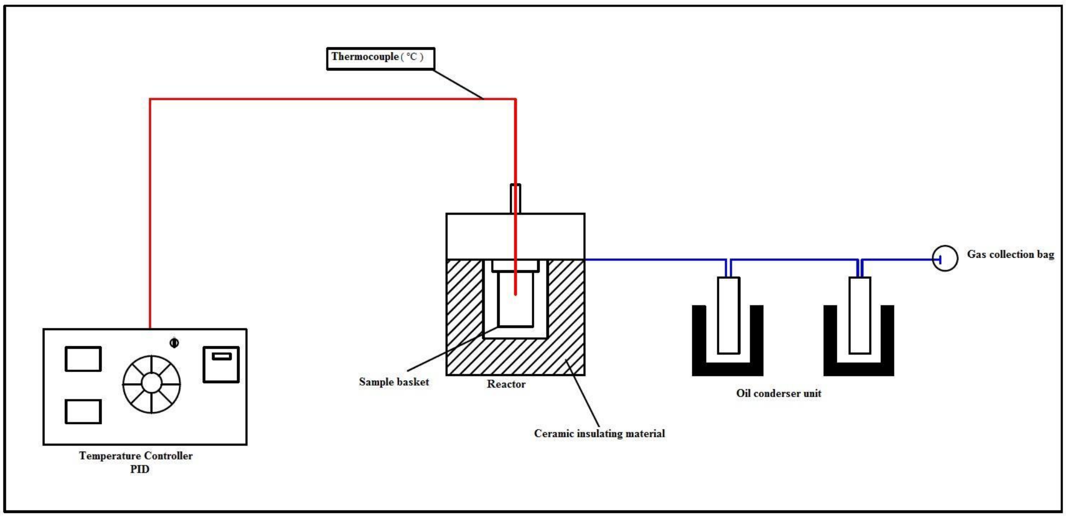

Figure 2. The Pyrolysis System

3. Results and Discussion

After phytoremediation the initial value (900 mg/kg) decreased in soils whereas it increased in plants (Table 2). Also, mass balance for Zn in soil and plant was realized for one pot (Table 2). Table 2 indicates that concentrations of Zn in the plant roots were significantly greater than that of the stems. Among the plants, the best Zn removal efficiency from soil was obtained with rape. The results seen in Table 2 were also evaluated by analysis of variance (ANOVA) to test the significance of plant effect on the Zn removal. Table 3 shows the ANOVA statistical terms for Zn concentration in soils and plants. It is clear from Table 3 that plant type is the significantly affected to the variability of the results with a 95% confidence level.

The analysis of the plants as raw material of pyrolysis are given in Table 4. The solid, liquid and gas products yields that were obtained by pyrolysis of Zn contaminated plants are presented in Figure 3. The pyrolysis solid, liquid and gas product yields were changed as 34.85-38.49, 3.24-8.75 and 52.76-61.91, respectively.

Zn content of the pyrolysis products are listed in Table 5. According to the Table 5, Zn contents of solid products are higher than that of liquid product's. The solid product obtained by the pyrolysis of rape has higher heavy metal content than that of the other solid products. For this reason, the lower metal concentration was found in gas product of rape pyrolysis.

The properties of solid and liquid products are listed in Table 6. According to the table, carbon content of the liquid products were observed higher than that of solid products. It was determined higher heating value of the liquid product as 30.5-36.2 MJ/kg according to Dulong equation. These results are similar to previous studies (Özçimen and Karaosmanoğlu (2004), Gerçel (2002) and Capunitan and Capareda (2012)). Further comparison of H/C ratios with conventional fuels (1.55-1.84) indicates that the H/C ratios (1.54-1.80) of the oils obtained in this study are similar to light and heavy petroleum products (Onay, 2007).

Heavy metal stabilization capacity of solid products obtained by pyrolysis of Zn contaminated sunflower, corn and rape was determined by leaching tests. The test results were compared with the limit value given in the Turkish Regulation of Sanitary Landfill. These results were lower than limit of quantification (LOQ) value (0.0013 mg/L) of the test method obtained from validation studies. According to the comparison, it can be said that the solid products can be safely landfilled as inert waste.

Table 2. Heavy metal contents and mass balance for one pot (mg)

mg Zn /kg	Initial	Sunflower	Corn	Rape
Soil	900	291	248	185
Plant root		82312	112458	121646
Plant stem		125	160	280
mg Zn for one pot				
Soil	2205*	713	607	453
Plant root		1440	1686	1825
Plant stem		6.25	12.8	8.4
* It was calculated with multiplying of soil weight in a pot (3.5 kg) by initial Zn concentration.				

Table 3. The Two-way ANOVA Results

Factors	DF*	Sum of squares	F factor	Significant level
For Soil Samples				
Plants	2	342225	23.15	0.000
Other/Error	90	665211		
Total	92	1143220		
For Plant Samples				
Plants	2	124608	36.52	0.000
Other/Error	18	30706		
Total	20	234104		
*degree of freedom				

Table 4. Composition of Plants

	Sunflower	Corn	Rape
Elemental analysis (wt.%)			
Carbon	27.68	37.75	27.06
Hydrogen	2.99	4.31	3.33
Nitrogen	3.90	2.49	4.44
Sulphur	0.37	0.42	0.52
H/C	1.30	1.37	1.48
Proximate analysis (wt.%)			
Moisture content	0.12	0.14	0.13
Ash	14.60	6.80	10.55
Volatile matter	80.72	82.67	81.48
Fixed carbon	4.56	10.39	7.84
HHV (MJ/kg) (daf*)	4.8	10.4	4.4
Zn content (mg/kg)	7597	10369	11313
*daf: dry ash free basis			

Table 5. Zn contents of the pyrolysis products

Pyrolysis products	Sunflower			Corn			Rape		
	(mg Zn/kg product)	(mg Zn)[a]	%	(mg Zn/kg product)	(mg Zn)[a]	%	(mg Zn/kg product)	(mg Zn)[a]	%
Solid product	19523	75.1	98.9	28652	99.8	96.3	30856	113	99.9
Liquid product	12.01	0.01	0.01	33.41	0.01	0.01	34.8	0.01	0.01
Gas product [b]		0.811	1.06		3.82	3.69		0.09	0.08

[a] calculated for one pyrolysis experiment (10 g) and calculated by pyrolysis product yields and metal content (mg/kg)
[b] calculated from initial and products value's
[c] calculated by mass difference according to initial metal content

Table 6. The main properties of pyrolysis products

	Sunflower	Corn	Rape
Solid product			
Elemental analysis (wt. %)			
C	23.36	38.92	27.58
H	0.57	0.6	0.16
N	<0.01	<0.01	<0.01
S	0.47	0.43	0.46
Proximate analysis (wt.%)			
Moisture content	0.11	0.13	0.12
Ash	54.51	38.19	48.80
Volatiles	40.05	40.11	46.48
Fixed carbon	5.33	21.57	4.60
pH	9.79	9.45	10.3
Density (g/cm^3)	0.15	0.11	0.13
Liquid product			
Elemental analysis (wt. %)			
C	67.20	69.25	64.72
H	9.80	10.38	8.32
N	5.97	6.59	6.25
S	1.35	1.46	1.52
Heating value (MJ/kg)	34.1	36.2	30.5
H/C molar ratio	1.75	1.80	1.54

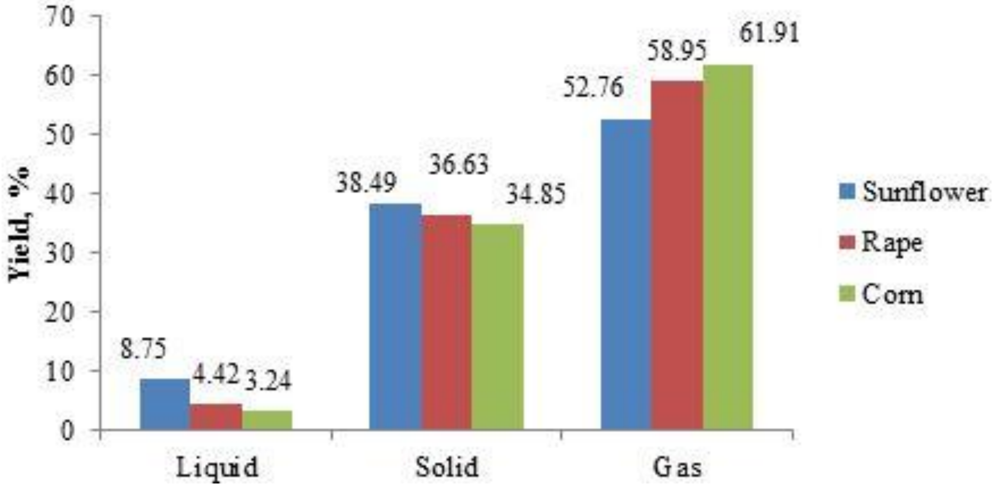

Figure 3. Pyrolysis Product Yields

4. CONCLUSION

In this study, high phytoremediation efficiencies were observed on zinc contaminated soil by using sunflower, corn and rape. Rape was the most effective plant species for the phytoremediation. In the second part of the study, as a result of rape pyrolysis, most effective plant, the highest liquid and solid product yields were found to be 4.42 % and 36.63 %, respectively. As a result of pyrolysis, the heavy metal contaminated biomass species are not only reduced in weight or volume, in addition to their heavy metals content is fixed into the ash/char fraction (interesting for recycling). Also, it was seen that the liquid products have very low levels of Zn and have high heating value that would give them a potential to utilize as a fuel if increasing the yield of liquid products for instance catalyzer.

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