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RESEARCH NOTE

Pyrolysis of Hyperaccumulator Plants Used for the Phytoremediation of Lead Contaminated Soil

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Abstract
This study focuses on the phytoremediation of lead (Pb) contaminated soil by hyperaccumulator plants. In this study, pyrolysis was utilized for the stabilization of Pb into a solid product. In the first stage of the study, three types of phytoremediation plants were used, rape (Brassica napus), sunflower (Helianthus annuus), and corn (Zea mays). Their seeds were sown in simulated soils prepared with the addition of Pb compounds in a laboratory. The effect of chelate on the remediation capacity of the plants was investigated by the addition of EDTA in different concentrations. In this way, the transportation of Pb from the contaminated soils to the plants was examined. In the second stage, the initial plant compositions were determined by elemental analysis (C, H, N, and S), as well as a moisture, ash, volatile matter, and fixed carbon analysis. The contaminated hyperaccumulator plants were pyrolyzed at 500°C, with a heating rate of 35° C/min, in a fixed bed stainless steel (380 S) 240 cm^3 reactor. After pyrolysis, the Pb contents of the solid and liquid products were determined. A Toxicity Characteristics Leaching Procedure (TCLP) analysis was also utilized for the solid product. In this study, high phytoremediation efficiencies were observed for the phytoremediation of Pb contaminated soil using sunflower, corn, and rape, especially in the case of the chelate addition. Of the three plants, the best Pb removal efficiency (92%) from the soil was obtained with the rape. According to the pyrolysis results, the highest yields of liquid and solid products were obtained from the sunflower with gas products being obtained from the corn pyrolysis.
Keywords: Contaminated Soil, Hyperaccumulator Plants, Lead, Phytoremediation, Pyrolysis.

Kurşunla Kontamine Olmuş Toprakların Fitoremediasyonunda Kullanılan Hiperakümülatör Bitkilerin Pirolizi

Özet
Bu çalışmada, kurşunla kirlenmiş toprakların hiperakümülatör bitkilerle arıtımı ve bu bitkilerin piroliziyle, piroliz sonrası elde edilen katı üründe kurşunun stabilizasyonu hedeflenmiştir. Çalışmanın ilk aşamasında, laboratuvarda kurşun ilavesiyle oluşturulmuş model toprağa kanola (Brassica napus), ayçiçeği (Helianthus annuus) ve mısır (Zea mays) tohumları ekilmiştir. Farklı derişimlerde EDTA ilavesiyle, bitkilerin arıtım kapasitesine şelatın etkisi araştırılmış ve böylece kurşunun, kirlenmiş topraklardan bitkilere taşınım mekanizması incelenmiştir. İkinci aşamada, bitki bileşimleri, elementel analiz (C, H, N, S), nem, kül, uçucu madde ve sabit karbon analizleri yapılmıştır. Kirlenmiş hiperakümülatör bitkiler, 240 cm^3'lük paslanmaz çelik (380 S) sabit yatak bir reaktörde 500°C sıcaklık ve 35°C/dk ısıtma hızında piroliz edilmiştir. Pirolizden sonra, katı ve sıvı ürünlerin kurşun içeriği belirlenmiş ve ayrıca katı üründe TCLP analizleri yapılmıştır. Çalışmada, özellikle şelat ilavesiyle ayçiçeği, mısır ve kanola ile kurşunla kirlenmiş toprakların fitoremediasyonunda yüksek verimler elde edilmiştir. Topraktan en iyi Pb giderimi (%92) kanolayla sağlanmıştır. En yüksek sıvı ve katı ürün verimi ayçiçeğinin, gaz ürün verimi ise mısırın pirolizinden elde edilmiştir.
Anahtar Kelimeler: Fitoremediasyon, hiperakümülatör bitkiler, Kirlenmiş Toprak, Kurşun, Piroliz.

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INTRODUCTION

The heavy metal Lead (Pb) can be toxic to both plants and animals even at very low concentrations. Human activities, such as mining, smelting, the burning of fossil fuels, dumping of municipal sewage sludge, and the manufacture of pesticides and fertilizers are the primary causes of lead contamination. Due to its potential hazard and widespread contamination, there is a high level of interest in methods aimed at cleaning up Pb at minimal cost with the least environmental side effects (Rascioa and Izzo 2011, Brennan and Shelley 1999). Traditional methods for the remediation of Pb contaminated sites include a variety of physical,

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thermal, and chemical treatments. Using conventional methods of remediation, the estimated costs of cleaning up sites in the US that are contaminated only with heavy metals has been estimated at $7.1 billion dollars, and $35.4 billion per site contaminated with both heavy metals and organic pollutants. An emerging technology that shows promise for remediating these sites at significantly reduced cost with minimal adverse side effects is called phytoremediation (Brennan and Shelley, 1999). Phytoremediation, the use of plant species to clean up soil and water, has gained importance in recent times since it is a cost effective, promising and environmentally friendly technology. The benefits of phytoremediation have been demonstrated at many sites, leading to the utilization of this technology by many environmental companies (Eapen and D'Souza, 2005). In addition, many studies are related to phytoremediation involving different plants and a variety of contaminated soils (Blaylock et al. 1997, Chen et al. 2004, McGrath et al. 2006, Tandy et al. 2006, Wua et al. 2010, Rascioa and Izzo 2011, Amer et al. 2013, Xie et al. 2013, Yaman 2014). Widespread phytoremediation application is inhibited due to the long remediation period required to clean soil successfully and the production of large amounts of metal contaminated biomass, for which no suitable treatment process has yet been found (Stals 2010). There are generally three conversion technologies that can be used for utilizing biomass; physical processes, thermochemical processes, and biochemical processes. Physical processes involve grinding, drying, filtration, extraction and briquetting. Thermochemical conversion processes include direct combustion, gasification, pyrolysis, thermal depolymerization, and plasma. When gasification and pyrolysis are applied, liquid products (pyrolytic oil), gas products (pyrolytic gas), and solid products (char) are produced. Biochemical conversion processes include anaerobic digestion and anaerobic fermentation. The major products of biochemical conversion processes are biogas, hydrogen, and ethanol. Among the thermochemical methods transforming biomass into energy and products, pyrolysis is a good option (Bay 2006, Şimşek 2006). In this study, phytoremediation was first applied to lead contaminated soil and then the biomass was pyrolyzed to stabilize the utilized plants for disposal purposes.

Experimental Methodology

This study involves two stages. The first stage consists of model soils preparation, sowing, chelate addition, and plant and soil analyses. The second stage is composed of the pyrolysis process and analysis of the solid and liquid products (Figure 1). The soil was taken from a depth of 20 cm below the soil surface from an agricultural area in Eskişehir/Turkey. The soil, 3500 g, was then passed through a 5 mm sieve and placed in polyethylene pots with a diameter of 23.5 cm and a height of 18.5 cm. Next, 500 ml of distilled water containing 5 g of $Pb(NO_3)_2$ was added to the sample pots to produce the contaminated soil samples. At the same time, 500 ml of distilled water containing 1.2 g of ammonium nitrate (33%) was added to the blank pots to provide the same amount of nitrogen as the sample pots.

After allowing for the stabilization of the soils for five days at room temperature, the rape (*Brassica napus*), sunflower (*Helianthus annuus*), and corn (*Zea mays*) seeds were sown separately in 15 sample pots containing the model soils. Additionally, each plant type was sown in 15 blank pots containing Pb free soils. The pots were watered with approximately 500 ml distilled water each week. After 7 weeks, an EDTA chelating agent (5 mmol and 10 mmol EDTA solutions) was added to 10 of the pots of each plant according to the field capacity value. All of the plants were harvested at the end of the eighth week. They were then dried in a laboratory at ambient temperature for 8 days.

After drying, the soil samples were digested according to EPA Method 3051 A as follows: 0.5 g of soil was carefully weighed in a PTFE vessel (CEM Mars 5). Then, 10 mL of HNO_3 (Merck, 65%) was added to the vessels and the temperature of each sample was raised to 175 ± 5° C in approximately 5.5 ± 0.25 min, and remained at 175 ± 5°C for 4.5 min. The plant samples were digested by microwave according to Kaçar and İnal, 2008 and Kalra, 1998 as follows: 0.1 g of plant was carefully weighed in a PTFE vessel (CEM Mars 5) and then 9 ml of HNO_3 (Merck, 65%) and 3 mL of $HClO_4$ were added to the vessels and the temperature of each sample was raised to 200 ± 5°C in approximately 15 min, and remained 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 to 100 ml. Following this, the samples were analyzed with an ICP-OES (Varian 720) according to the EPA 200.7 method. As a result of the method validation, the Pb recovery rates obtained were 98% and 101% for the CRM033 (soil) and the NCS DC73350 (plant), respectively.

Before the second stage, the plants were dried and homogenized for pyrolysis experiments and then the elemental composition (C, H, N, and S) of the plants was determined using Leco TruSpec CHN and S elemental equipment. The oxygen content of the plants was found by difference. The moisture, ash, volatile matter, and fixed carbon content of the plants were determined according to ASTM D 2016-74, ASTM D1102-84, ASTM E-897-82, and ASTM E-897-82, respectively.

In the second stage, each of the dried plant samples was individually mixed regardless of the chelate application to provide an adequate amount of sample for pyrolysis. The pyrolysis experiments were carried out under atmospheric pressure at a 500°C pyrolysis temperature with a 35°C/min heating rate in a fixed bed stainless steel (380 S) 240 cm^3 reactor (Figure 2). The reactor was encased in a resistant oven (4000 Watt). All of the experiments were conducted in a typical run, where a 3-5 g sample was placed into the reactor and, after the reactor had reached the set temperature, it remained there for 1 hour. As a result of the pyrolysis process, liquid, solid, and gas phases were produced. The liquid phase, produced as a result of the pyrolysis, was collected in a cold trap maintained at about 0°C using ice. The aqueous and oil fractions of the liquid phase were separated and weighed. The solid and liquid products yields were determined gravimetrically for each experiment. The gas yields were determined by the mass difference.

After pyrolysis, to identify the physical structure of the solid products, the moisture, ash, volatile matters, fixed carbon content, and elemental composition were determined using the same procedures for plant characterization as mentioned earlier. In addition to these analyses, the Pb content of the solid and liquid products was determined according to Stals, 2010 for the pre-operation and EPA 200.7 for the analysis. Furthermore, the heavy metal stabilization capacity of the solid product was determined by TCLP testing.

RESULTS AND DISCUSSION

The physical and chemical properties of the untreated 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 purposes according to the chemical analysis and especially the organic matter, lime, total salts, and nutrient content.

After the harvesting of the plants, the length of the stems and roots of the plants, as well as their moisture content, was determined (Table 2). It can be seen that the rape growth was lower than that of the other plants.

The initial Pb content of the model soils was

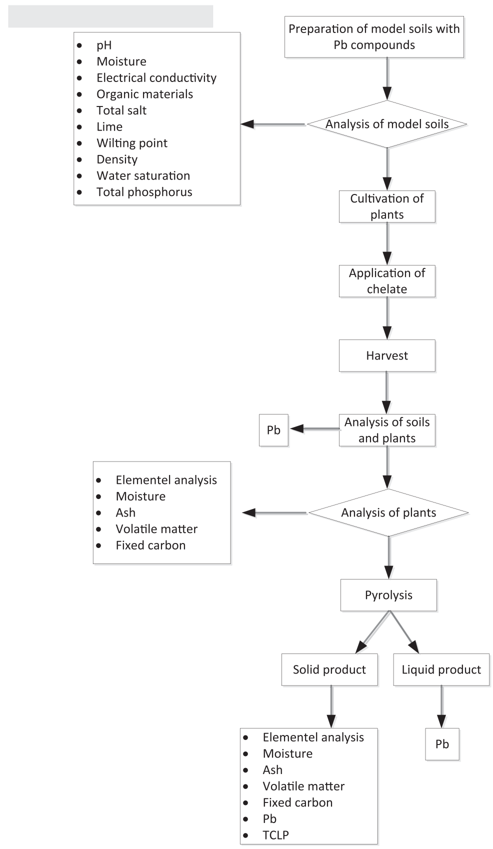

Fig. 1. Flowchart of the study.

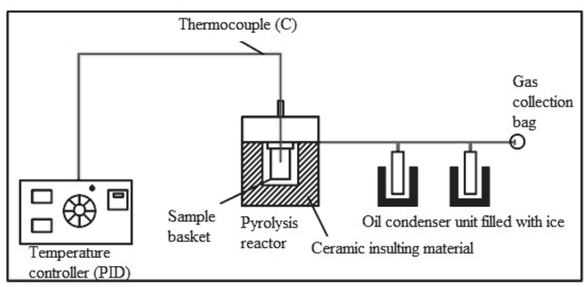

Fig. 2. The pyrolysis system.

Table 1. Properties of the soil.

Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
1539	4264	0.19	7.97	10.05	769.2	975.5	6568	304.6	181.9	27	363.6	7.5	259.9	22.3
Total Salt %	0.04	Lime, %	7.1	Field capacity, %	31	Wilting point, %	21	Water Saturation, %	62	Organic C, %	2			
pH	8.09	Structure Analysis	CL	Electrical Conductivity	0.63	Density g/cm^3	1.38	Organic Materials, %	3					

found to be 1184 mg/kg. The Pb content of the soils and plants after the phytoremediation is given in Table 3. Of the plants, the best Pb removal efficiency (92%) from soil was obtained with rape. In addition to this, the Pb uptake by plants increased as the chelate concentration was increased. In addition, the mass balance for the Pb in the soil and plant matter was realized for one pot (Table 4). According to this table, since the Pb was transported to plants' roots and stems, these plant parts should be harvested together.

The results of the dried and homogenized plant analyses before the pyrolysis process are listed in Table 5.

The yields that were obtained by the pyrolysis experiments, carried out at 500° C at a heating rate of 35° C/min, are presented in Figure 3. Of the plants, the highest yields of liquid (20.2 %) and solid (36.5 %) products were obtained from sunflower, while the highest yield of gas product (51.1%) was obtained from the corn pyrolysis. The Pb analyses results for the solid and liquid products, the mass balances for the pyrolysis products, and the main properties of the solid product are listed in Tables 6 and 7, respectively. Furthermore, the heavy metal stabilization capacity of the solid product, determined by Toxicity Characteristics Leaching Procedure (TCLP) tests, were compared with the limit values given in Annex 11-A of the Turkish Regulation of Hazardous Waste Control relating to municipal solid wastes. The TCLP results of the sunflower, corn, and rape were found to have very low values of 0.001 mg Pb/L, 0.008 mg Pb/L, and 0.005 mg Pb/L, respectively. According to the results, and when compared with the limit value (0.05 mg Pb/L), the solid product is acceptable as inert waste.

CONCLUSION

Plant-based remediation techniques are increasingly being applied for use in soils contaminated with heavy metals. Lead is a common and serious heavy metal because of its toxicity. Its solubility in soil and availability for plant uptake is limited. In the first part of the study, the phytoremediation capacities of hyperaccumulator plants, sunflower, corn, and rape, were investigated with and without the addition of EDTA (chelating agent). The phytoremediation experiments show that, of the plants, rape was the most effective plant species for the phytoremediation of Pb with a removal efficiency of 92%. Furthermore, it was observed that the addition of EDTA was shown to significantly increase the accumulation of Pb in

Table 2. The length and moisture contents of the plants.

	Length (cm)		Moisture content, %	
	Stem	Root	Stem	Root
Sunflower	35.25	5.84	95.62	87.09
Corn	30.37	11.18	88.25	61.37
Rape	7.15	3.12	85.27	78.65

Table 3. Lead content of the soils and plants.

		Sunflower	Corn	Rape
		mg Pb /kg plant		
Plants	EDTA 0	48.17	67.63	58.15
	EDTA5	168.42	116.68	185.21
	EDTA10	353.18	354.58	492.48
		mg Pb /kg soil		
Soils	EDTA 0	574.30	601.54	762.81
	EDTA 5	413.76	300.67	267.35
	EDTA10	299.83	232.63	95.97

EDTA 0: without EDTA; EDTA 5: with 5mmol EDTA;
EDTA 10: with 10mmol EDTA

Table 4. Mass banace for one pot (mg).

		Sunflower	Corn	Rape
Initial Pb content of soil: 4144				
Soil after harvesting	EDTA 0	2010	2105	2670
	EDTA5	1448	1052	936
	EDTA10	1049	814	336
Plant's bodies	EDTA 0	12	27	9
	EDTA5	42	47	28
	EDTA10	88	142	74
Plant's roots*	EDTA 0	2310	2215	1582
		2122	2012	1465
	EDTA5	2815	3108	3195
		2654	3045	3180
	EDTA10	3096	3285	3905
		3006	3188	3734
* The first values were determined by analysis, the second values were determined by mass difference using of soil and plant bodies results.				

Table 5. Composition of the plants.

	Sunflower	Corn	Rape
Elemental analysis (wt.%)			
Carbon	27.2	36.8	27.06
Hydrogen	4.27	5.2	3.45
Nitrogen	4.64	2.57	4.25
Sulfur	0.77	0.77	0.57
Proximate analysis (wt.%)			
Moisture	0.12	0.11	0.13
Ash	25.49	4.65	19.48
Volatiles	73.33	91.00	78.42
Fixed carbon	1.06	4.24	1.97
Lead (mg/kg)	190	180	250

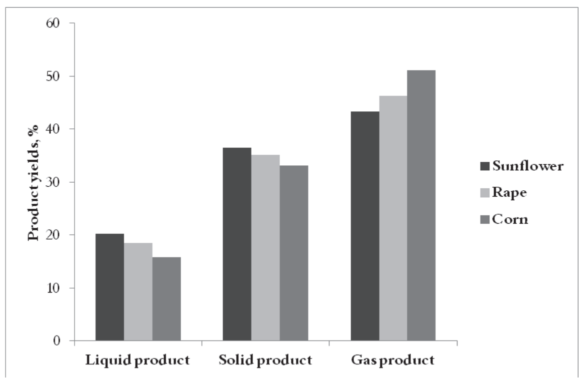

Fig. 3. Pyrolysis products yields.

Table 6. Lead content of the pyrolysis products.

Pyrolysis products	Pb contents					
	Sunflower		Corn		Rape	
	(mg Pb /kg product)	(mg Pb)*	(mg Pb /kg product)	(mg Pb)*	(mg Pb /kg product)	(mg Pb)*
Initial value before pyrolysis (mg Pb /kg plant)	190	1.9	180	1.8	250	2.5
Solid product	285	1.04	305	1.01	512	1.8
Liquid product	8.1	0.016	7.6	0.012	11.8	0.02
Gas product (by mass difference)		0.84		0.78		0.68
*It was calculated for one pyrolysis experiment.						

Table 7. The composition of the solid product of pyrolysis.

	Sunflower	Corn	Rape
Elemental analysis (wt.%)			
Carbon	23.93	44.54	27.85
Hydrogen	2.40	1.03	0.56
Nitrogen	<0.01	<0.01	<0.01
Sulphur	0.46	0.31	0.58
Proximate analysis (wt.%)			
Moisture	0.12	0.11	0.11
Ash	54.3	27.24	45.60
Volatiles	43.5	64	48.80
Fixed carbon	2.08	8.65	5.49

plants by increasing the solubility of the Pb in the soil. Optimum results were obtained using 10 mmol EDTA. These observations are supported by literature studies (Raskin et al., 1997; Pulford and Watson, 2003; Lim et al., 2004; Lai and Chen, 2004; Huang et al. 1997). In the second part of the study, the Pb contaminated plants were pyrolyzed to stabilize the Pb in the pyrolysis products. As far as we know, this is the first time Pb contaminated corn, sunflower, and rape have been utilized for pyrolysis.

As a result of the pyrolysis, the highest liquid and solid product yields were found to be 20.2 % and 36.5 %, respectively. These yields show that Pb contaminated biomass species are reduced in weight or volume. A Pb analysis on the solid products indicated that the Pb content of the contaminated biomass species is fixed in the ash/char fraction (interesting for recycling). On the other hand, it was seen that the liquid products had significantly low levels of Pb, giving them the potential to be used as fuel. We believe this is the first time Pb contaminated corn, sunflower, and rape have been utilized through fixing them in pyrolysis products, in particular the solid product.

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