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Recovery of heavy metals from canola (*Brassica napus*) and soybean (*Glycine max*) biomasses using electrochemical process

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ABSTRACT

Phytoextraction is defined as a process during which the heavy metals, causing soil contamination, are conveyed to the green parts of the plant through roots and are accumulated there. However, the main problem after phytoextraction is that because of accumulation of metal ions by plants are defined as secondary contaminants and classified as hazardous wastes since they include an excessive amount of metal. Hence, how to use plant waste after phytoextraction is still a challenge that remains to be solved. In this study, canola (*Brassica napus*) and soybean (*Glycine max*) were used for remediation of soils contaminated with heavy metals (Cd, Pb and Zn). Two different extraction methods were used to dissolve heavy metals in waste biomass. The extraction method, in which the highest efficiency was obtained, was used an electrochemical method in order to remove/recover toxic metals from the biomass of canola (*B. napus*) and soybean (*G. max*) plants, harvested after phytoextraction process. Firstly, the heavy metal ions were transferred into the solution from biomass. Then these toxic metal ions were precipitated electrochemically within 2 h. Thus, the toxic ions, causing contamination, were transformed directly into metallic form by reducing the concentration (metal recovery). It was obtained electrochemical removal efficiencies of 80% for Cd, 94% for Pb and 68% for Zn in the solution of soybean biomass while they were 97% for Cd, 99% for Pb and 46% for Zn in the solution of canola biomass.

1. Introduction

Among of the major problems which today's world encounters, environmental pollution increases year by year and damages earth irrecoverably. Environmental pollution comes into existence as soil, air, water pollution and affects the whole ecosystem which human being also included (Zhang et al., 2015). Pollution occurs mostly in anthropogenic ways as a result of exceeding the assimilative capacity of the receiving environment. Soil ecosystem, which is one of the natural and non-renewable resources, is contaminated with organic and inorganic pollutants (especially heavy metals). Heavy metals exist within the soils naturally; however, their concentration in soil has increased due to anthropogenic activities such as the excessive and unconscious use of pesticides and fertilizers, mining, wastewater discharges and sludge.

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Remediation of contaminated soils is one of the most challenging subjects of environmental engineering, and heavy metals posing serious risks to living organisms are among the most hazardous soil pollutants because of their toxic effects, non-degradability and persistence (Balkhair and Ashraf, 2016; Lu et al., 2017).

Phytoremediation technologies have been recently become attractive method since they have provided applicable, cost-efficient and an in-situ treatment for the removal of heavy metals from soil. (Ali et al., 2013; Chami et al., 2015; Gramss et al., 2011).

Phytoremediation method aims to cultivate heavy metal tolerant plants which the ability to absorb the heavy metal into plant tissue in their metabolic processes (Cuypers et al., 2013). Phytoremediation is a technique which uses plants to cleanup organic and inorganic pollutants from the contaminated soil. Using hyperaccumulator plants during this method enables to provide more productive results. The reason of using those plants is that they are able to accumulate 50 to 500 times more metal in their root and tissues (Clemens, 2006).

Phytoremediation processes take different kind of names depending on the pollutants type, levels of pollution and plant species (Padmavathiamma and Li, 2007). The names of the methods differ according to pollutant type and metabolic process of the plant, such as; rhizofiltration, phytodegradation, phytoextraction, phytovolatilization, phytostabilization and rhizodegradation.

Phytoextraction is a method used to remove metal pollutants that cause pollution in the soil by using plant roots. A plant used for phytoextraction is required to accumulate a high amount of metal, grow rapidly, be deep-rooted, easily harvested and to have a high biomass (Gałuszka et al., 2015). The success of the phytoextraction method depends on the biomass production and the ability to uptake high amounts of metals in plant shoots (USEPA, 1995a). It has been estimated that each hectare of harvested canola can produce 3–7 tons of dry biomass (Dhiman et al., 2016). In this study, canola (*Brassica napus*) and soybean (*Glycine max*) plants were preferred regarding those properties.

However, the most important disadvantage of phytoextraction is that the hyperaccumulator plants are identified as secondary pollutants because of containing an excessive amount of heavy metals in their tissues and they have been classified as hazardous waste.

Large amount of contaminated waste enters to the environment after phytoextraction and creates further pollution problems (Mohanty, 2016). That is why, phytoremediation technologies are usually not considered as final removal methods. After phytoextraction, an additional treatment such as composting, compaction, incineration, pyrolysis and direct disposal of contaminated plant biomass is required. Composting and compaction processes are defined as pre-treatment processes causing biomass to be still classified as hazardous waste (Sas-Nowosielska et al., 2004). Pyrolysis is an expensive method that limited of application area for large amounts of waste biomass that occurs after phytoextraction.

Because of these deficiencies, a new assessment method is needed for biomass in the hazardous waste class containing toxic metal. It is also a more acceptable and more economical option to recover metal from waste biomass rather than direct disposal.

In this study, recovery of the heavy metals in the waste biomass through electrochemical method is investigated as an alternative to other methods. Electrochemical treatment, which is one of the promising methods in recent years, has attractive features such as metal recovery, low cost, simple operation, slight amount of chemical usage and combination with other treatment processes (Ait Ahmed et al., 2016; Boechat et al., 2016; Chen, 2004)).

Some researchers have combined electrochemical method with phytoremediation to remove contamination and provided to have cleaner soil in the field. Jiang et al. (2015) have pursued a radical approach to solve the problem of eliminating the plant biomass by thermo-chemically converting renewable energy, and they have designed a metal recovery process from waste biomass.

Chirakkara et al. (2015) have examined on combining an electrochemical method with phytoremediation for a soil co-contaminated with heavy metals and polyaromatic hydrocarbons (PAHs). They had grown oat plant and sunflower in the electrochemical cell for 30 days. The results showed that the heavy metals and organic pollutants in the soil were significantly reduced. Biomass production of the plants increased with the application of electric current, but there was no significant improvement in heavy metal or PAH degradation in the plant biomass.

Mao et al. (2016) have coupled the electro-kinetic remediation and phytoremediation methods to remove Pb, As and Cs from contaminated soils. They showed that the solubility and bioavailability of Pb, As and Cs in the plants were significantly enhanced under the electro-kinetic field (EKF). The bioaccumulation of Pb, As and Cs were all increased upon EKF process, indicating the EKF treatment might have been a good alternative for increasing phytoextraction efficiency of Pb, As and Cs.

However, this study is completely different from the studies mentioned above, in which electrochemical method and phytoremediation have been combined consecutively. The aim of this study, after phytoextraction, is to recover heavy metals from biomass wastes electrochemically. In this study, electrolysis reactions were at the forefront for metal recovery/removal and toxic metals in the biomass were recovered by the electrodepositiom process. Electrodeposition brought originality to the study as it enabled the recovery of metals with high economic value. It has been also provided a treatment of the waste biomass, containing toxic metals by the "zero waste" principle.

For this purpose, firstly, canola (*B. napus*) and soybean (*G. max*) plants were cultivated in heavy metals (Cd, Pb and Zn) contaminated soil for phytoextraction. Afterwards, the accumulated heavy metals in biomass were turned into ionic form through microwave extraction and then converted into metallic form through electrodeposition. This integrated study has shown that biomass within the scope of hazardous waste can be included in the non-hazardous waste class after phytoextraction.

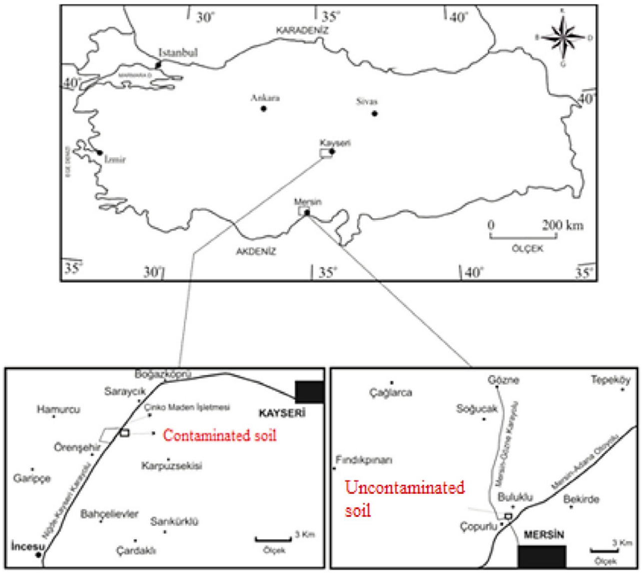

Fig. 2.1. Soil sampling areas.

2. Material and method

2.1. Soil sampling and plant cultivation

In the study, the coordinates of the places where heavy metal contaminated and uncontaminated soil samples were determined with Global Positioning System (GPS). The contaminated and the one uncontaminated soils were collected from 0–30 cm depth in Kayseri-Incesu (38° 42′ 43″ N and 35° 15′ 55″ E) and Copurlu Village, located on the Mersin-Gözne (36° 87′ 32″ N and 34° 56″ 50″ N), respectively. The study areas were shown in Fig. 2.1.

Canola and soybean plants were grown under controlled environment conditions (50%–60% humidity, 16 h of light and 8 h of dark photoperiod, 25 ± 2 °C temperature and 1500 Lux light intensity) in the climate chamber for 3 months. Ten canola and 10 soybean seeds were planted in pots during the experiment. All of the plants were irrigated regularly and the field capacity of the soil was stabilized at approximately 70% (under field conditions).

The soil contaminated with high metal concentrations was mixed with the one uncontaminated as 0% (controlled clean soil), 25%, 50%, 75% and 100% proportions. Canola and soybean plants were grown in the obtained five soil mixtures. The experimental plan was designed with randomized block method in three replicates.

2.2. Soil and biomass analyses

The soil samples were air dried at the room temperature and then sieved from 4 mm sieve for pot experiments. For some physical and chemical analyzes, soil samples were used which passed through a 2 mm.

Soil samples were analyzed for pH in a 1:1 (m:v) ratio of soil to solution, the soil texture was determined according to the hydrometer method, the organic matter by modified Walkley–Black titrations and lime by the calcimeter method. Total metal analysis of the soil was conducted in compliance with the EPA 3051A method and concentrations of the metals were detected with the Agillent brand 7500ce model ICP-MS (Inductively Coupled Plasma Mass Spectrometer) (USEPA, 1995b). The accuracy of the method was tested with a standard soil certified (CRM 7003).

Canola and soybean were used in the pot experiment as biomass materials. After harvesting green parts of the highest phytoextraction capacity canola and soybean, the moisture contents were calculated according to Eq. (1) after being kept in a drying oven at 70 °C for 72 h (Kaçar, 1984). All the data obtained from the plant material during the research were described as oven dry plant biomass at 70 °C .

$$Moisture\,Content = \frac{100 - dry\,plant\,mass}{Fresh\,plant\,mass} \times 100 \tag{1}$$

Harvested canola and soybeans were grinded and solubilized in the microwave oven for 45 min with 0.2 g, of which is 2 mL deionized water, 2 mL with 35% H_2O_2 and 4 mL with 65% HNO_3. The heavy metal concentration (Cd, Pb, Zn) of waste plant samples were determined by ICP-MS after phytoextraction. The accuracy of the analysis was controlled with a standard certificate plant (CRM 1573A-tomato leaf) sample. Cadmium, Pb and Zn concentrations on CRM 1573A-tomato leaf were 0.978, 1.846 and 85.000 mg kg^{-1}, respectively. The concentrations of Cd, Pb and Zn were determined as 0.980, 1.840 and 84.860 mg kg^{-1}, respectively in the standard certified plant sample. Cadmium, Pb and Zn concentrations on CRM 1573A-tomato leaf were 0.978, 1.846 and 85.000 mg kg^{-1}, respectively. As can be seen in the results, both values were close to each other. Thus, the experimental method and analysis were verified.

2.3. Electrochemical experimental setup

Batch electrochemical tests were carried out in an electrochemical glass cell, which was divided into two with a permeable filter. For the electrodeposition process, platinum anode (electrode surface 2 cm^2) and Pb cathode (electrode surface 2 cm^2) were used. A direct current (DC) power supply was used in order to provide the constant current during electrodeposition. The voltage was held stable for each run with a retention time for 2 h.

2.4. Determination of the effect of incineration temperature on biomass

In order to reduce the amount of biomass considered to be waste after phytoextraction, the dry incineration method comes to the forefront. For this purpose, 1 g of the ground biomass samples were weighed and put into porcelain crucibles. In order to determine the effect of the incineration temperature on dry mass loss and metal solubility, plants were incinerated in the ash furnace for 8 h at 105 °C, 205 °C, 305 °C, 405 °C and 505 °C, respectively. In the initial step of the electrochemical tests, the biomass samples were burned at 505 °C in the ash furnace because the maximum metal solubility was achieved at this temperature.

2.5. Determination of the effect of extraction methods on metals solubility

Two different methods were used to extract the metal accumulated in the waste biomass. The chemical extraction method was compared with the microwave method in terms of extracting Cd, Pb and Zn concentrations. In order to transfer the Cd, Pb and Zn accumulated by canola and soybean into the solution, a chemical extraction was performed with 0.2 M HCl solution. 1 g of the plant sample, which was incinerated at 505 °C, the optimum temperature, was dissolved in a hot plate with 100 mL of 0.2 M HCl for 2 h.

For the other extraction method, 1 g of the plant sample was digested in 5 mL of deionized water, 5 mL of 35% H_2O_2 and 10 mL of 65% HNO_3 for 45 min in microwave at 150 °C and pressure of 200 psi. After cooling, the solutions were completed up to 100 mL final volume with distilled water and passed through a 0.45 μm filter. Then, the total heavy metal concentrations were determined by ICP-MS.

2.6. Electrochemical reduction experiments

A standard solution containing 25 mg/L Cd, Pb and Zn ions dissolved in 0.2 M HCl was prepared and the optimum reduction potentials of the metals were investigated with working electrode in cyclic voltammetry. After the optimization processes, during which the reduction potential was identified, electrochemical removal efficiencies of Cd, Pb and Zn were determined in extracted solution from canola and soybean waste biomasses through the microwave method. The electrodeposition process in the solutions was conducted at −0.6 V electrode potential.

Electrodeposition processes in microwave extracting solutions were realized during 2 h by taking 0.5 mL solution from the electrochemical cell at regular times (0, 15, 30, 45, 60, 90 and 120 min) at constant voltage. The electrochemical removal efficiency (ERE) of Cd, Pb and Zn in the cell were calculated in Eq. (2), where Co is the initial metal ion concentration (mg L^{-1}) in solution and Ce is equilibrium metal ion concentration in treated solution at any time (mg L^{-1}).

$$ERE\ (\%) = \frac{Co - Ce}{Co} \times 100 \tag{2}$$

2.7. Statistical analysis

The interaction between temperature (T), dry mass (DM) and solubility of metal ions was performed for canola and soybean using the statistical package Statistical Product and Service Solutions (SPSS) 17.0 for Window. The methods included one-way analysis of variance (ANOVA) and linear regression analysis. Duncan's multiple range test was used to determine the statistical significance ($p < 0.05$).

Table 3.1
Some physical and chemical properties and standard deviations of the uncontaminated and contaminated soil samples (n = 3) (Çiftçi, 2016).

Soil properties	Uncontaminated soil	Contaminated soil	References
Sand (0.02–2 mm) (%)	20.5 ± 1.1	84.6 ± 2.3	Bouyoucos (1951)
Silt (0,002–0,02 mm) (%)	27.0 ± 0.9	8.4 ± 0.5	
Clay (<0.002 mm) (%)	52.5 ± 1.0	7.0 ± 0.6	
Texture class	C (Clay)	LS (Loamy sand)	
pH (in 1:1 saturated soil)	8.23	8.04	Soil Survey Staff (1951)
Lime ($CaCO_3$) (%)	28.34	7.26	
Organic matter (%)	3.04	5.27	
Soil Moisture (%)	5.50 ± 0.54	4.69 ± 0.24	
Water saturation (%)	60 ± 1.30	28 ± 0,90	
Total N (%)	2.24 ± 0.01	2.10 ± 0.01	Kaçar (1995)
Available P (mg P_2O_5 kg^{-1})	1.98 ± 0.23	11.34 ± 0.25	Olsen and Sommers (1982)
Available K (mg K_2O kg^{-1})	63.4 ± 3.10	19.55 ± 0.15	Richards (1954)
EPA 3051A-Total Cd (mg/kg)	1.92 ± 0.10	483 ± 32.9	USEPA (1995b)
EPA 3051A-Total Zn (mg/kg)	92.4 ± 3.35	13412 ± 0.1	
EPA 3051A-Total Pb (mg/kg)	19.1 ± 0.01	25755 ± 0.54	
DTPA extractable Cd (mg/kg)	0.05 ± 0.02	26.8 ± 0.16	Lindsay and Norvell (1978)
DTPA extractable Pb (mg/kg)	1.03 ± 0.21	31.1 ± 1.72	
DTPA extractable Zn (mg/kg)	0.75 ± 0.33	128 ± 11.6	

Table 3.2
Initial total multi-metal concentration within the shoot of soybean and canola, normal and critical concentration range and hyperaccumulation threshold value of the plant (Kabata-Pendias and Mukherjee, 2007; Baker and Brooks, 1989).

Element	Concentration of sample mg kg^{-1} DM*		Normal concentration range, mg kg^{-1} DM*	Critical concentration range, mg kg^{-1} DM*	Hyperaccumulation threshold value mg kg^{-1} DM*
	Soybean	Canola			
Cd	238 ± 1.89	1134 ± 12.3	0.10–2.40	5–30	100
Pb	554 ± 8.16	3682 ± 14.12	0.2–20.00	30–300	1000
Zn	2380 ± 12.62	6169 ± 15.83	1–400	100–400	10000

*DM: Dry Mass.

3. Results and discussion

3.1. Properties of the soils

Some physical and chemical properties of both the uncontaminated and contaminated soil, and initial metal contents were determined. Initial values of the physical and chemical parameters of the soils used in this study are given Table 3.1.

As seen in Table 3.1, pH of the soil was moderate alkaline at 8.0. The texture classification of the soil was sandy loam. Lime amount was moderate (7.26) while the amount of organic matter was high (5.27). Whereas the total amount of nitrogen (N) was considerably higher, available amounts of phosphor (P) (11.34) and potassium (19.55) were also high. According to Kabata Pendias, the critical values for Cd, Pb and Zn were between 3–8, 100–400 and 70–100, respectively (Kabata-Pendias and Mukherjee, 2007).

According to EPA Method 3051A (USEPA, 1995b), in contaminated soil, total concentrations of Cd, Pb and Zn were determined as 483.70 25755.60 and 13412.20 mg kg^{-1}, respectively. No such study has been found in the literature on soil sample with such high concentrations of heavy metals. On the other hand, the concentrations of Cd, Pb and Zn were determined as 1.92, 92.41 and 19.09 mg kg^{-1}, respectively in uncontaminated soil.

3.2. Total metal concentrations of biomasses

In this study, a soil sample with higher metal concentration was mixed with the uncontaminated soil samples as 0% (controlled clean soil), 25%, 50%, 75% and 100%. The overall picture of canola and soybean grown in the obtained soil mixtures before harvest are shown in Fig. 3.1a–b. The green parts of the canola and soybean grown in contaminated soil (100%) were used as waste biomass and the used biomasses were shown with arrow marks.

Total Cd, Pb and Zn concentrations of harvested canola and soybean were compared with the normal and critical concentrations of Cd, Pb and Zn in plants according to Kabata-Pendias (Table 3.2). It was observed that both plants accumulate metal ions in green parts (shoots). As can also be seen in Table 3.2, Cd, Pb and Zn concentrations, especially in the shoots of the canola were considerably higher than those of the normal concentration, threshold value and critical concentration value.

Evaluated in terms of total Cd, Pb, Zn concentrations, canola accumulated 5 times more Cd, 7 times more Pb and 3 times more Zn than that of soybeans. On the other hand, when evaluating total Cd, Pb and Zn concentrations in terms of

a) Canola (*Brassica napus*)

b) Soybean (*Glycine max*)

Fig. 3.1. Overall picture of the pre-harvest (a) canola (*B. napus*) and (b) soybean (*G. max*) biomasses in the obtained soil mixtures (Left to right 0% (controlled and clean soil), 25%, and 50%, 75% and 100% polluted).

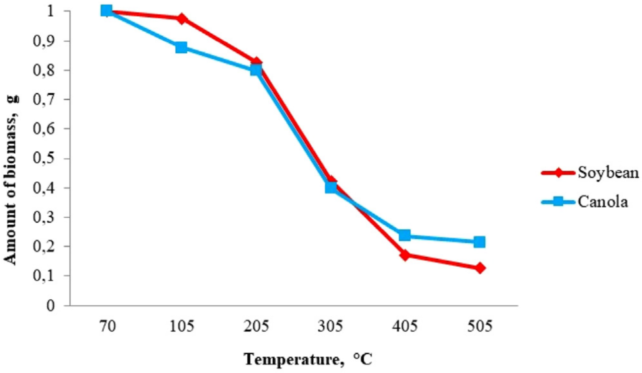

Fig. 3.2. Effect of incineration temperature on amount of biomasses of canola and soybean (mean ± SD, n = 3)

hyperaccumulation threshold limit, it was seen that the soybean plant accumulated 2.4 times more Cd and the canola plant accumulated 11 times more Cd and 3.6 times more Pb. In the literature, canola biomass has been already documented to be a good phytoaccumulator and phytoextractor (Croes et al., 2015). The results obtained in this study were in parallel with the literature.

Hyperaccumulator plants are described as the type of plants, which can include more than 100 mg kg^{-1} Cd, 1000 mg kg^{-1} Pb and 10.000 mg kg^{-1} Zn (Baker and Brooks, 1989). According to this definition and the results of this study, canola is hyperaccumulator in terms of accumulated Cd (1134 mg kg^{-1}) and Pb (3682 mg kg^{-1}) concentration while soybean is defined hyperaccumulator in terms of Cd (238 mg kg^{-1}).

3.3. *Effect of incineration temperature on amount of biomass*

In the evaluation of wastes of plant, pretreatment at high temperatures leads to mass decrease, which is important for the elimination of waste after phytoextraction.

To determine the effect of incineration temperature on dry mass, biomasses of soybean and canola incinerated for 8 h in ash furnace at 105 °C, 205 °C, 305 °C, 405 °C and 505 °C, respectively. The absolute moisture content (105°C) was determined as 2.4% and 12.34% of soybean and canola, respectively. The significant difference is about the tolerance shown towards increased Cd, Pb and Zn concentrations of the canola and soybean within the soil, which was shown in Fig. 3.1. While soybean showed necrosis in accordance with the increasing dosage, canola continued to grow showing tolerance to metals. One of the reasons for this situation is the fact that canola holds more moisture content. Fig. 3.2 shows the effect of the incineration temperature on the amount of dry biomass.

The overall accepted temperature for incineration of plant materials are 450 °C. Because evaporation losses at these temperatures are low in general and it is sufficient for the complete oxidation of the organic substance. It has been reported by Hoenig (1995) that temperatures as high as 520 °C do not cause losses of volatile elements such as Cd, Pb or

Table 3.3
Total metal concentration of extracted canola and soybean biomass, both through ash furnace and microwave methods (mg kg^{-1}).

Plant	Application	Cd (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Canola	Ash Furnace	186 ± 0.10	38 ± 0.03	483 ± 0.45
	Microwave	1134 ± 10.69	3682 ± 13.37	6169 ± 25.21
Soybean	Ash Furnace	31 ± 0.34	76 ± 0.48	261 ± 0.41
	Microwave	238 ± 0.58	554 ± 1.32	2380 ± 19.50

Zn, if the programmed temperature curve is sufficiently low in the ash furnace (Hoenig, 1995). Therefore, the maximum temperature of the study was chosen as 505 °C in this study.

As it was shown in Fig. 3.2, the amount of biomass of both plants decreased significantly with increasing temperature. According to linear regression between the dry biomass of canola and the T, it seen that there is a very strong positive correlation between two parameters ($r = 0.96$) and this relationship is found to be a high significance as statistically ($0.001< p<0.01$). According to linear regression between the dry biomass of soybean and the T, there is a very strong positive correlation between two parameters ($r = 0.97$) and this relationship is found to be a significance as statistically ($0.001<p<0.05$). When the theoretical calculation is made taking into account that decrease, the amount of biomass of canola will decrease to 214.8 kg and the soybean to 127.9 kg when 1 ton of biomass waste is incinerated at 505 °C.

This means that canola, which is accumulating more metal, is more effective compared to soybean in terms of phytomining. Since the decrease of the masses of the plants which are considered as waste after phytoextraction is important, the application of pre-treatment methods such as incineration is in the forefront. The incineration method also reduces of biomass the cost of treatment and the transportation to the landfill. However, a substantial amount of contaminants can still be in the ash after the incineration process. Sas-Nowosielska et al. (2004) found that a significant amount of contaminants is still be present in the biomass after incineration. In this study, recovery of the metals from the residual ashes was achieved after incineration and microwave extracting.

3.4. The effect of extraction methods on metal solubility in biomass waste

In the evaluation of the products after phytoextraction, the applied extraction process for transferring Cd, Pb and Zn from plants to the solution is very significant. In order to extract toxic metals from biomass after phytoextraction, acid extraction (dissolution) is applied mostly behind the incineration methods (Zarcinas et al., 1987). During metal extractions from organic matter like biomass; hydrofluoric acid (HF), hydrochloric acid (HCI), nitric acid (HNO_3), perchloric acid ($HCIO_4$) and sulphuric acid (H_2SO_4) are used individually or in mixtures (Idera et al., 2014).

Before electrodeposition process, it is one of the most important conditions that the toxic metals in the biomass were passed to the solution in high percentages. In order to determine the concentration of metal ions transferred to the solution, biomasses were incinerated by keeping in the ash furnace for 8 h at 105 °C, 205 °C, 305 °C, 405 °C and 505 °C, respectively, and then extracted with 0.2 M HCI. Total metal concentrations in canola and soybean after the acid extraction process were shown in Fig. 3.3a–b.

According to linear regression analysis between the solubility of Cd, Pb and Zn in the canola biomass and the T, there is a very strong correlation between the two parameters ($r = 0.92$, 0.87 and 0.93) and this relationship is found to be borderline significance as statistically ($0.05<p<0.01$) for all the three elements.

According to linear regression between the solubility of Cd in the soybean biomass and the T, there is a very strong positive correlation between two parameters ($r = 0.96$) and this relationship is found to be a significance as statistically ($0.001 < p < 0.05$). In the statistical analysis to figure out the relationship between Pb and T, it seen that there is a very strong positive correlation between two parameters ($r = 0.99$) and this relationship was found to be a very high as statistically ($p<0.001$). However, in the statistical analysis for Zn, it seen that there is a weak correlation between the two parameters ($r = 0.73$) and this relationship is found to be insignificant as statistically ($p > 0.1$).

The Cd, Pb and Zn concentrations of samples incinerated in the ash furnace at 505 °C and then extracted with 0.2 M HCI was compared with the performed microwave method results in same samples. Total metal concentration of the extracted from waste of biomass through two different methods were shown in Table 3.3.

When the table was examined, it can be seen that the solubilized metal amount with ash furnace was less than that of the microwave method. After ash furnace method, the percentages of extracted Cd, Pb and Zn from canola and soybean were found as 16%, 1% and 8% and 13%, 14% and 11%, respectively. The percentage of extraction obtained from the soybean was relatively higher than the canola because the initial metal concentrations in the soybean biomass are lower than that of canola. Effectiveness of chemical reagent during metal extraction changes depending on initial metal concentration, pollutant types, extraction type and experimental conditions (Hoenig, 1995).

Yıldırım (2016) stated in her study, which was conducted for the evaluation of metals in safflower and castor oil plants, that Cd, Pb and Zn concentration extracted with 1.0 M H_2SO_4 was higher than that of with 0.5 M H_2SO_4. However, the researcher indicated that Cd, Pb and Zn concentration transmitted into solution after extraction was unable to reach the total metal concentration extracted through the microwave method (Yıldırım, 2016).

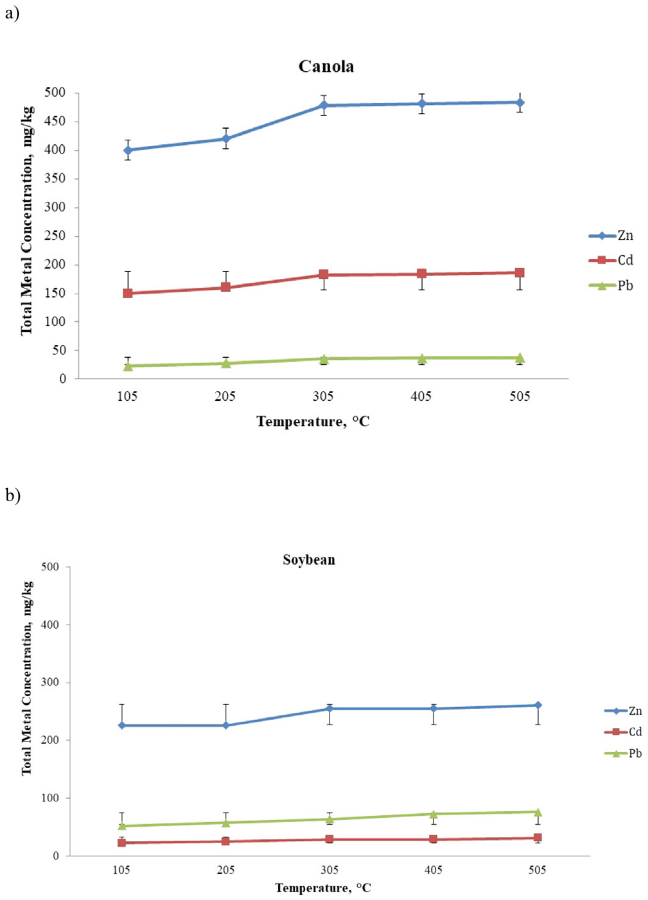

Fig. 3.3. Effect of temperature and acid extraction on total metal concentration ; (a) extracted from canola and (b) extracted from soybean (mean ± SD, n = 3).

Hetland et al. (2001) utilized chelating agents (EDTA and N-(2-acetamido) iminodiacetic acid) for the purpose of recovery of the Pb from harvested biomass after phytoremediation. Researchers were able to extract 98.5% of Pb with EDTA at pH 4.5 after two series of washing. They reduced the Pb concentration from 2000 mg kg^{-1} to 30 mg kg^{-1} after liquid extraction from residual biomass. Thus, the plant biomass, initially defined as hazardous waste, was not hazardous waste after the extraction (Hetland et al., 2001).

In this study, metal concentrations of the biomasses digested in the microwave were also found higher than that of those conducted with ash furnace. Thus, the biomass solution extracted with the microwave method was used in the electrodeposition tests.

3.5. *Electrochemical recovery of metal ions transferred to the solution from biomass*

The harvested canola and soybean biomasses were grinded and then digested by the microwave method and thus solution was prepared for the electrodeposition then the initial metal concentrations (Ce) of the solution were determined. Electrodeposition tests were performed in a 150 mL of the solution at −0.6 V electrode potential depending on time. Initial metal concentrations (Ce) in the solution obtained from biomass of canola and soybean by the microwave method for Cd, Pb and Zn were determined as 1134, 3682 and 6169 mg L^{-1} and 238, 554 and 2380 mg L^{-1}, respectively.

The change of metal ions concentrations with electrochemical removal tests were shown in Fig. 3.4a–b. As it is shown in Figure; Cd, Pb and Zn concentrations reduced homogeneously in the whole solution.

Electrochemical removal efficiencies determined in accordance with the initial metal concentration for biomass solutions of canola and soybean were shown in Fig. 3.5a–b. In the first 30 min; Cd, Pb and Zn were removed by about 91%, 97% and 41%, respectively, in the electrochemical cell from the solution of canola biomass. At the end of 2 h, the electrochemical removal efficiencies were calculated 97% for Cd, 99% for Pb and 46% for Zn (Fig. 3.5a).

The removal efficiency in the electrochemical cell with regard to the initial metal concentration in solution of soybean biomass was shown in Fig. 3.5b. At the end of 2 h, the electrochemical removal efficiencies from the solution of soybean biomass for Cd, Pb and Zn were found 80%, 94% and 68%, respectively.

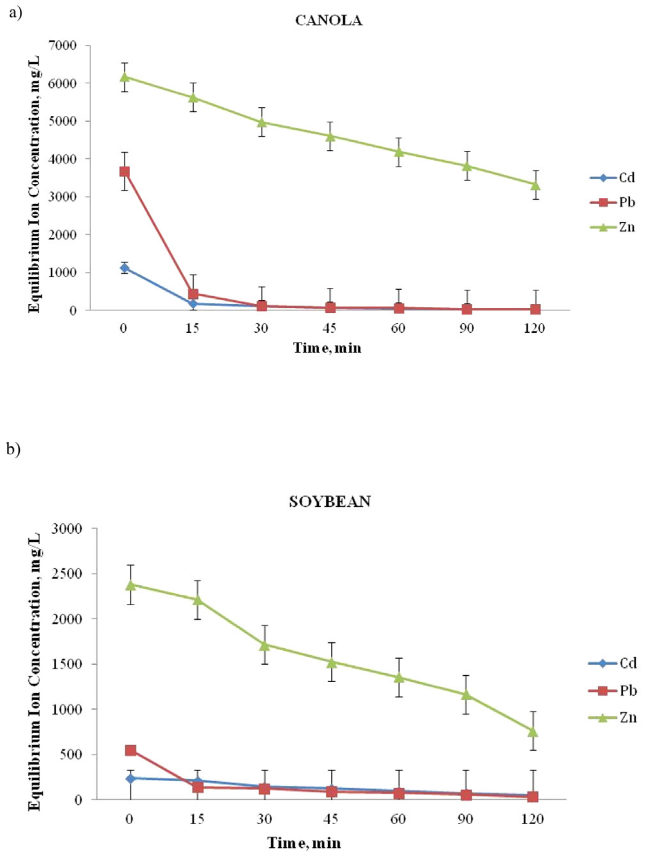

Fig. 3.4. Time-dependent change of metal ions concentration at −0,6 V electrode potential in the extracted solution from biomass of plants; (a) electrochemical removal of metal ions from of canola biomass solution (b) electrochemical removal of metal ions from of soybean biomass solution.

The yield of electrochemical metal removal in soybean biomass, which has less metal accumulation compared to canola, was found to be high. It was concluded that after conducting the extraction step with high efficiency, the recovery of metals was also higher by electrochemical method.

The findings were compatible with the results of the study by Yıldırım (2016) and Eke (2010), conducted for the utilization of safflower (*Carthamus tinctorius*), castor oil (*Ricinus communis*) and nickel hyperaccumulator *Thlaspi elegans* Boiss plant after phytoextraction.

After the electrochemical process, the reduced metal ions from the extraction solution of the canola biomass were separated from the surface of the Pb electrode by scraping. The scraped metal was considered as the recovered quantity and approximately 0.0048 g of solid reduced material was obtained after electrodeposition. The reduced material is not in hazardous since it is in metallic form. The material obtained was dissolved in concentrated HF and HCl in a ratio of 1: 3 to determine whether it contained Cd, Pb and Zn in ICP-MS. Since the electrodeposition process takes place on the Pb electrode (cathode), Pb concentration was neglected in the solution, but Cd and Zn concentration was determined in the treated biomass solution.

The transformation of Cd, Pb and Zn ions into electrochemically reduced metallic form after phytoextraction, is very important from an environmental point of view. These metals are classified as precious metals and quite overpriced (Cd-3750 \$ ton^{-1}, Pb-817 \$ ton^{-1} and Zn-1007 \$ ton^{-1}). In other words, it will be possible to contribute to the economy of the country with the electro recovery process (Robinson et al., 1997). According to Jiang et al. (2015) recycling of metals is critical to the sustainability of industrial development, as natural reserves are depleting. The recovery of the elements may be lower than the cost of disposal of potentially toxic biomass in large quantities (Jiang et al., 2015).

4. Conclusions

In this study, a considerable amount of metal removal was provided through electrodeposition from extracted solutions obtained from canola and soybean biomass. The contamination of soil with more than one metal has reduced the

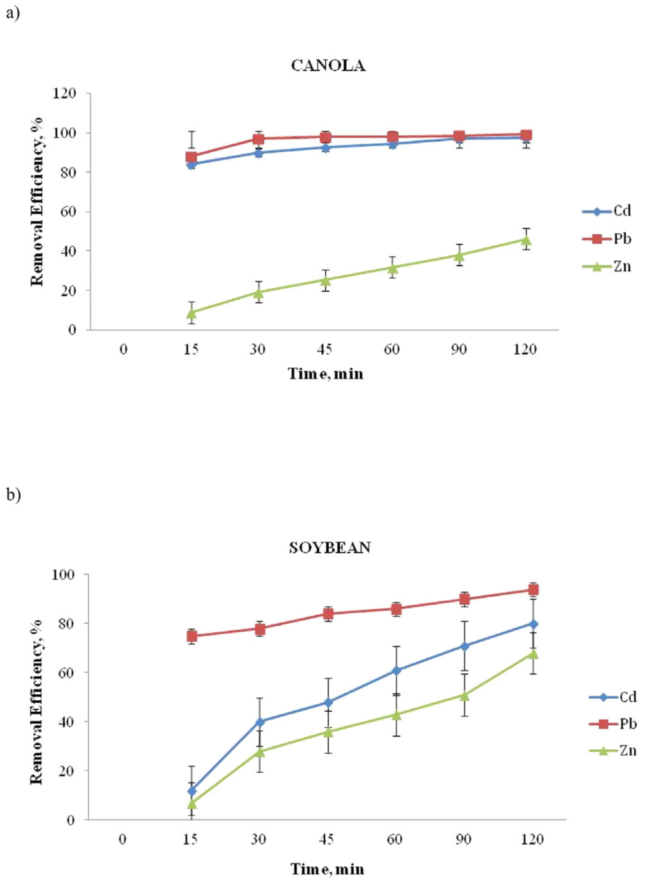

Fig. 3.5. Time-dependent change of the removal efficiencies of Cd, Pb and Zn at −0.6 V electrode potential in the extracted solution from plants; (a) biomass of canola (b) biomass of soybean.

phytoextraction yield. Since the phytoextraction efficiency of soybean plant was lower than canola, it was determined that this plant was not a suitable plant for phytoextraction.

This study revealed that extracting toxic metals from the biomass of plants with a decent extraction/solvent/acid with maximum efficiency is the most important step in metal recovery. The extraction process conducted by the microwave method was found to be more effective than ash furnace method with 0.2 M HCl. The extraction process is very important for the second step (electro-recovery) and more studies about extraction methods are required to be conducted to increase the recovery efficiency. The implementations of microwave method and following usage of the electrodeposition has been provide toxic metal ion removal and metal recovery. The electrodeposition process tested in this study can be defined as a significant method for the removal of metals toxic effect and recover valuable metals.

The recommended combined method is an alternative advanced technique that can be used instead of composting and compaction, combustion and gasification in the assessment of contaminated plants.

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