

Soil Toxicity Around the Textile Industry in Bantul using Spinach Seeds (*Amaranthus gangeticus*) and Bean Sprouts (*Phaseolus aureus*)

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ABSTRACT. The toxicity test of zinc metal in soil samples around the textile industry in Bantul on the growth of spinach (*Amaranthus gangeticus*) and bean sprouts (*Phaseolus aureus*) has been investigated in relation with the environmental assesment for the impact of industrial activities. This research was conducted to study physicochemical properties, adsorption-desorption, and zinc metal toxicity in the soil around the textile industry on the growth of spinach and bean sprouts. The study of physicochemical properties were water content, pH, electrical conductivity, ash content, total organic carbon, cation exchange capacity, metal content, and characterization using FTIR (Fourier transform infrared) spectrophotometry. Various zinc concentrations were studied for the adsorption capacity, whereas citric acid concentrations were used for the desorption. Atomic absorption spectrophotometry (AAS) was applied to measure metal concentrations for all samples. A toxicity tests were conducted on the growth of spinach and bean sprouts. The maximum zinc concentration was measured in point I, at 532.03 mg kg⁻¹. Adsorption of zinc followed the Langmuir and Freundlich isotherms, and desorption process occurred at optimum concentration 0.7 mol L⁻¹ citric acid and a pH of 3. In the zinc metal toxicity test, large concentration of zinc metal revealed inhibition effect on spinach and bean sprouts growth.

Keywords: Adsorption, desorption, toxicity test, zinc.

INTRODUCTION

Indonesia is a country in the Southeast Asia region that is moving to become a developpecountry. The industrial and manufacturing sectors are growing rapidly in line with the increasing investment in the development of Indonesia. Industrial activity is essential for economic growth and urban development (Li et al., 2013). However, industrial activities not only provide benefits for economic, but also cause many environmental problems. The large number of pollutants produced from industrial activities can cause potential health risks and negatively impact the environment (Xing et al., 2019).

Water pollution in the Special Region of Yogyakarta, especially in Yogyakarta City and Bantul Regency, is mainly caused by textile waste, such as in the batik-making industry (Erwindo, 2019). The waste comes from various stages of the textile materials production steps, such as the spinning of cellulosic materials (cellulose and cotton), starching and sizing, removing the original color (bleaching), releasing (waxing), and dyeing (Muthu, 2014). The dyes wasted in the soil and waters contain heavy metals such as As, Cd, Cr, Hg, Pb, Sb, and Co. Several essential metals needed for plant metabolism as activators or regulators of enzymes, such as Fe, Cu, Mn, Zn, and Ni are also present in textile waste (Hassan et al., 2013).

Soil can be an object of research in detecting residual substances from the textile industry in the form of heavy metals, organic compounds, or inorganic compounds (Suherman et al., 2013). One alternative solution to reduce the impact of heavy metal pollution in the soil is by using low molecular weight organic acids (LMWOA). LMWOA includes oxalic, succinic, tartaric, formic, malic, acetic, butyric, lactate, fumaric, maleic, and citric acids (Xiao & Wu, 2014). In this study, soil sampling was carried out around the textile industry, then analyzed the physico-chemical properties of the soil sample and heavy metal content to determine the adsorption and desorption processes of zinc metal in the soil. This research will also study the toxicity of zinc metal in the soil on the growth of spinach (*Amaranthus gangeticus*) and bean sprouts (*Phaseolus aureus*) for the environmental evaluation regarding the industrial activities effect on the agricultural field.

EXPERIMENTAL SECTION

Materials

The materials used are KCl and CaCl₂.2H₂O powder for pH determination; while BaCl₂.2H₂O and MgSO₄.7H₂O powder for cation exchange capacity analyses. In addition, citric acid powder, Zn solution 1000 mg/L, HF 40% solution, HNO₃ 65% solution,

HCl 37% solution, base solution, distilled water and Whatman 42 filter paper were used during the experiments.

Instrumentations

The instruments used were magnetic stirrer, porcelain dish, analytical balance (Mettler Toledo AB54-S), shaker (Marius Instrumenten), oven (Kirin), muffle furnace (Fisher model 184), centrifuge (Universal Centrifuge Z 446). pH meter (Hanna H198103), magnetic stirrer plate (Thermolyne Cimarec 1), conductivity meter (OHAUS ST 10C-B), Atomic Absorption Spectrophotometer (AAS, Perkin Elmer 3110), and Fourier Transform Infrared Spectroscopy (FTIR, IPRPrestige-21 Shimadzu).

Determination of Physico-chemical Properties of Soil Samples

All the soil samples parameter were evaluated according the standard method which were adopted in previous report (Suherman et al., 2013 and Suherman et al., 2019). The water content of the soil samples was determined using the International Organization for Standardization (ISO) 11465; and pH level of soil samples were analyzed by using the ISO 10390 method. For the electrical conductivity is determined according to DIN CEN/TS 15937, while ash content of the soil samples were determined by DIN CEN/TS 14775. Total organic carbon was measured by using the *American Standard Testing and Material (ASTM) D2974* method. While cation exchange capacity (CEC) method is based on DIN ISO 11260.

Determination of Metal Content

Metal content is determined based on the British Standards European Norm (BS EN) 13656 method (Anonymous, 2002). A total of 1 g of soil sample was extracted with 4 mL of 40% HF solution and shaken for 24 h. The mixture was added with 12 mL of aquaregia and shaken again for 24 h. The filtrate was separated, and the metal content was measured using AAS. Data collection was repeated three times to calculate the standard deviation.

Study of Adsorption of Concentration Variations

A total of 15 mL of Zn solution with concentrations of 5, 10, 25, 50, and 75 mg/L were applied to a 1 g soil sample. The mixture was mixed for 24 h before being centrifuged for 15 min at 5000 rpm. The AAS instrument measured the remaining Zn concentration in the filtrate. The data collection process was repeated three times to compute the standard deviation.

Study of Desorption of Concentration Variations

A total of 15 mL of citric acid solution with concentrations ranging from 0.1, 0.3, 0.5, 0.7, and 0.9 mol L⁻¹ was added to a 1 g soil sample. After shaking for 24 h, the mixture was centrifuged at 5000 rpm for 15 min. The filtrate was collected, and the remaining Zn content was determined using an AAS

instrument. The data collection process was repeated three times to compute the standard deviation.

Determination of Optimum pH

Soil samples with a mass of 1 g were added with as much as 15 mL of aquadest. The pH variations used were 3; 4; 5; 6; 7 and 8 by using the HNO₃ and NaOH solution. The mixture was shaken for 24 h then the filtrate was separated. The concentration of Zn metal in the filtrate was analyzed using the AAS instrument. Data were collected three times to calculate the standard deviation.

Toxicity Test of Zn

At the desorption step, the soil eluate was filtered with metal concentrations of Zn 0.14; 0.32; 2.08; 4.70; 4.80; 4.85 mg L⁻¹ and aquadest as a control. In aquadest, a Zn standard solution bearing the same concentration of Zn metal as the desorbed soil eluate was created. Pipette 5 mL of each solution onto Whatman 42 filter paper. On moist filter paper, a total of 25 spinach and bean sprout seeds were put at a proportional distance from one another. The petri dish was then sealed and cultured for three days at room temperature in the dark for germination. Afterwards, the root and hypocotyl lengths of the seeds were measured, and the inhibition was computed for each solution concentration.

RESULTS AND DISCUSSION

The soil sample for this investigation was taken in the vicinity of a textile factory in Panggungharjo Village, Bantul Yogyakarta. The topsoil layer was sampled after cleaning it from gravel, grass and other debris. A topsoil is a form of soil that is naturally rich in nutrients. It is found in the top layer of soil, approximately 5-30 cm below the earth's surface. The sampling technique utilized in this investigation is random sampling. Measuring the soil's physicochemical qualities entails determining its water content, pH, electrical conductivity, ash content, total organic carbon, cation exchange capacity, and heavy metal concentrations.

The moisture content is more significant when dried at 105 °C than when dried at ambient temperature. It is because drying at 105 °C is excellent for H₂O evaporation, as it passes through the H₂O boiling point of 100 °C. The water content data just comparable with the data from previous result (Suherman et al., 2019) which was around 40% in the tannery industry area. As shown in **Table 1**, the pH value obtained with the H₂O extractor was more significant than that obtained with the KCl and CaCl₂. According to Gavriloaiei (2012), when soil is treated with H₂O extract, most protons remain linked to the soil, and when salt solutions such as KCl and CaCl₂ are added, the cations in the salt exchange with protons in the soil, resulting in a pH more significant than that of KCl and CaCl₂.

Table 1. Physicochemical parameters of soil samples around textile industry

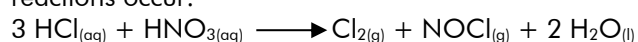
Parameter	Sampling Point I	Sampling Point II	Sampling Point III
Water content (%)			
Temp. 105°C	35.12 ± 1.51	34.70 ± 1.40	32.40 ± 0.52
Room temp.	14.60 ± 1.25	16.63 ± 1.22	13.14 ± 1.45
pH			
H ₂ O	6.2 ± 0.20	7.7 ± 0,10	7.4 ± 0.05
KCl	5.5 ± 0.00	7.0 ± 0.10	6.6 ± 0.15
CaCl ₂	5.3 ± 0.15	6.6 ± 0,15	6.6 ± 0.00
Electrical conductivity (μS cm ⁻¹)	380.70 ± 3.05	212.0 ± 1.00	134.0 ± 1,15
Ash content (%)	93.38 ± 0.68	92.54 ± 1.57	90.32 ± 0.57
Total organic carbon(mg g ⁻¹)	86.43 ± 1.29	83.15 ± 1.79	28.27 ± 1.64
Cation exchange capacity (cmol kg ⁻¹)	37.54 ± 0.57	34.27 ± 0.00	34.21 ± 0.10
Concentration of Zn (mg kg ⁻¹)	532.03 ± 16.79	329.96 ± 5.30	261.51 ± 2.17

Electrical conductivity is measured at sampling points I, II, and III resulted the highest number in point I. Electrical conductivity refers to the number of mineral salts ionizing in the soil, allowing the soil to conduct electricity via ions dissolved in groundwater. Highest number of soil electrical conductivity related with the highest metal ions existences in soil comparing the others as found in sample I where the zinc concentration was the highest (**Table 1**).

The ash level of the three samples drastically reduced from highest to lowest, namely sample I, sample II, and sample III. Ash content refers to the amount of inorganic material that cannot be burned during the ashing process and hence remains as ash. Carbon's affinity for water increases the water retention capacity as the TOC percentage grows. The TOC content of the sample is directly proportional to the ability of the soil structure for retaining the metal ions. As can be seen in Table 1, soil sample I with the highest TOC content also containing highest metal concentration. Organic functional groups in the soil structure such as carbonil and carboxyl groups, hydroxyl groups and other organic functional groups

are believed to have major roles in metal bonding to the soil structures.

Cation exchange capacity (CEC) is the parameter related to the soil capacity to receive and exchange cations or return them to the soil solution. The CEC is the number of cations the soil can bind, which is linearly related to the amount of negative charge in the soil. The metal content is determined using the wet digestion method, which combines the sample with a mixture of oxidizing and non-oxidizing mineral acids (Adamczyk-Szabela et al., 2017). The following reactions occur:



$\text{Cl}_{2(\text{g})}$ and $\text{NOCl}_{(\text{g})}$ will convert the metals present in the soil sample into a stable metal-chloride complex so that it can be analyzed using the AAS instrumentation.

Based on **Table 2**, Zn concentrations increase over the threshold (above 300 mg/kg) at points I and II, where the point I is directly behind the factory, resulting in a high metal content value exceeding the threshold. As a result, points I and II established that Zn metal pollution existed in the soil around textile industry.

Table 2. The concentration of metals in soil samples.

Sample	Concentration (mg kg ⁻¹)		
	Zn	Co	Cr
Point I	532.03	10.15	8.24
Point II	329.96	85.53	8.68
Point III	161.51	76.93	9.48

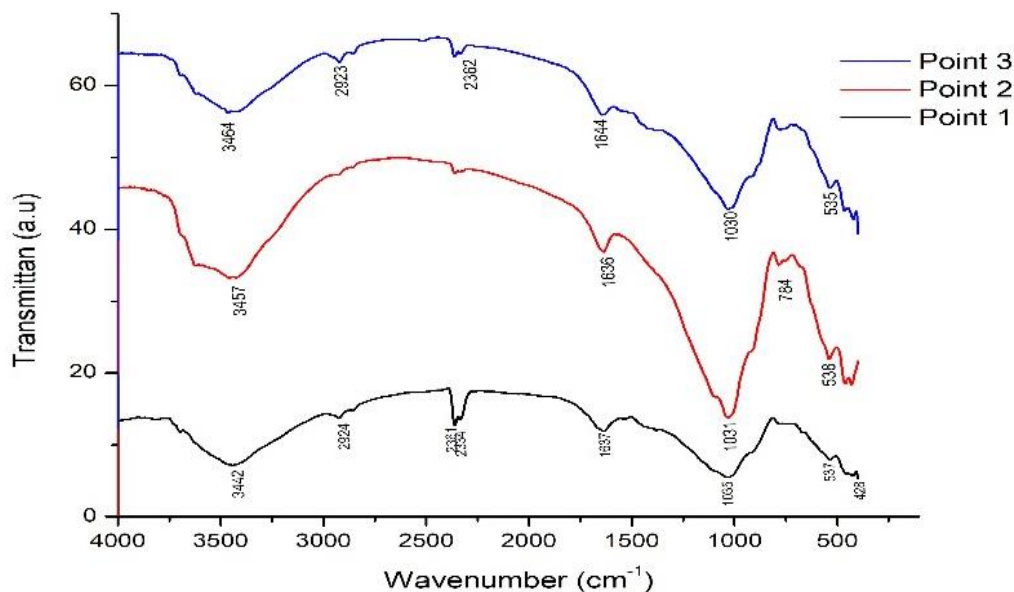


Figure 1. FTIR spektra of soil samples.

The objective of FTIR analysis is to determine the functional groups existed in a soil samples. This technique is based on the fact that infrared light is absorbed by molecular bonds, resulting in stretching or bending vibrations. As shown in **Figure 1**, the absorption for OH is represented by the wavenumbers 3442, 3457, and 3464 cm^{-1} at points I, II, and III. The area between 1637, 1636, and 1644 cm^{-1} have a wavenumber corresponding to the absorption region of the silanols –OH group. While, the absorption area for Si-O and Si-O-Si stretching vibrations is represented by the wavenumbers 1035, 1031, and 1030 cm^{-1} , respectively. The presence of metal and oxygen bonding, specifically Zn-O, is shown by the wave numbers of 537, 538, and 535 cm^{-1} . In conclusion, the existence of functional organic groups

in **Figure 1** correspond to the soil ability to adsorp the metals including Zn.

Zinc Metal Adsorption and Desorption

Figure 2 illustrated the results of Zn adsorption at various solution concentrations (mg/L), demonstrating that the higher concentration of Zn metal ions, the greater the mass of Zn metal ions adsorbed by the soil sample. By varying the concentration of Zn metal ions in soil samples, the Langmuir and Freundlich equations can be used to determine the equilibrium between the soil sample and the Zn standard solution and the interaction between the Zn standard solution and the soil sample. The isotherm model calculation results are provided in **Table 3**. From the data, it seem that soil sample I and II fitted to Freundlich isotherm, while soil sample III to Langmuir isotherm model.

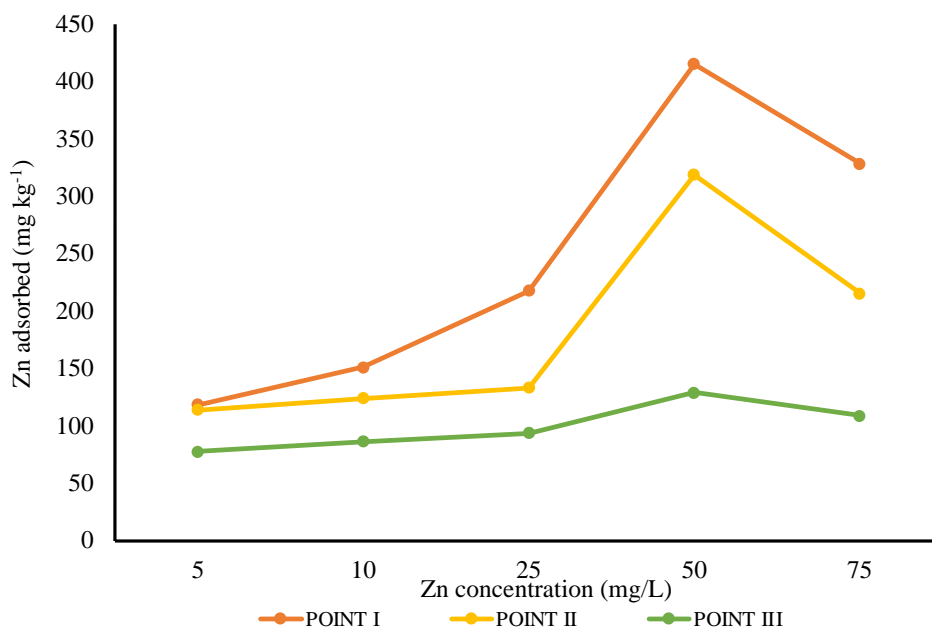
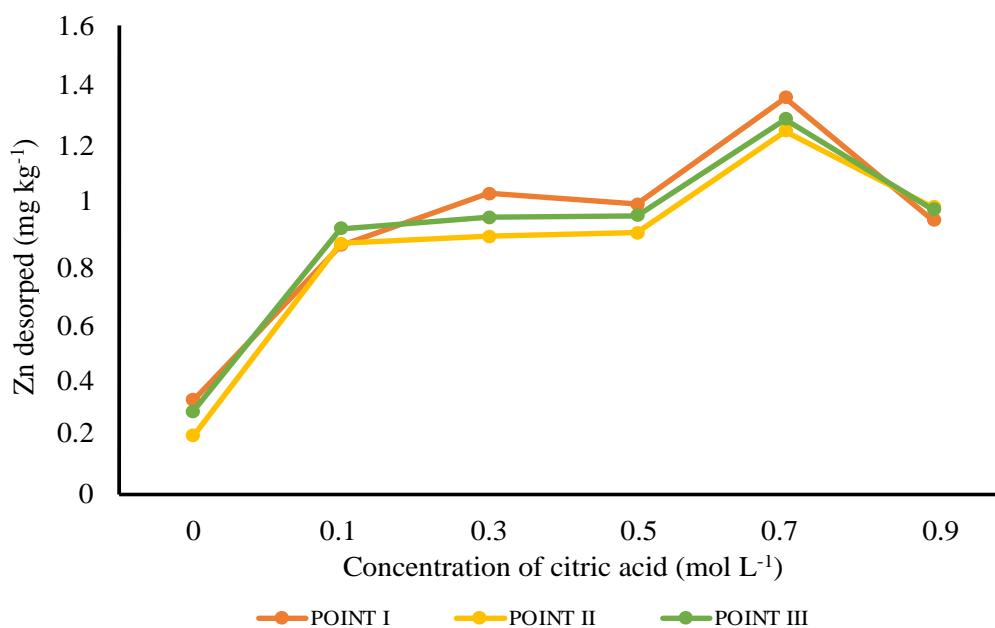


Figure 2. Determination of soil adsorption capacity.

Table 3. Parameter of isotherm for Zn metal adsorption on soil samples.

Parameter	Sampling Point I	Sampling Point II	Sampling Point III
Isotherm Langmuir			
R^2	0.5325	0.6676	0.9679
q_{\max} (mmol kg ⁻¹)	16.994	8.997	2.066
K_L (L mol ⁻¹)	2524.61	4681.64	53.191
E (kJ mol ⁻¹)	19.53	21.07	9.90
Isotherm Freundlich			
R^2	0.9594	0.9174	0.8793
n	1.350	1.666	5.252
K_f	16.01	16.39	18.71

**Figure 3.** Zn desorption from the soil samples by using citric acid.

The desorption capability of Zn metal from soil samples was determined using citric acid at varying doses (concentrations). As illustrated in **Figure 3**, with the higher acid concentration, the greater amount of Zn was desorbed. The increased concentration of the citric acid solution increases the number of citric acid molecules in the solution, increasing the amount of Zn metal interacting with citric acid. Citric acid has the functional groups (carbonil, carboxyl, and hydroxyl groups) in their structure that capable to interact with metal ions. **Figure 4** demonstrates that more zinc metal will be desorbed at a low pH because zinc metal is in the form of cations in acidic circumstances and hence easily leached. Increased soil pH decreases the positive charge in the soil, reducing Zn metal uptake and increasing metal cation hydrolysis.

For evaluation the toxicity of the soil sample, the length of root and hypocotyl in eluate and Zn standard solution were compared to the seeds germination in water as a control for the inhibition percentage values. According to **Figure 5**, spinach (*A. gangeticus*) seeds cultivated in 0.32 mg L⁻¹ Zn eluate solution and 0.14 mg L⁻¹ Zn standard solution had the lowest root and hypocotyl growth values.

According to the results of the toxicity test on bean sprouts (*P. aureus*) which can be seen in **Figure 6**, the eluate solution showed low values at concentrations of 0.14 and 0.32 mg L⁻¹, while the standard Zn solution had low values at high concentrations of 4.8 and 4.85 mg L⁻¹. It is possible because there is no organic matter available in the standard solution of Zn, so the toxicity is higher than the desorbed eluate solution. Based on the toxicity test on bean sprouts (*P. aureus*), it can be concluded that the toxic effect of Zn metal at high concentrations inhibited the root and hypocotyl growth.

The toxicity test indicated that dissolved organic matter in the soil might help mitigate the toxicity of Zn at low concentrations. Organic materials dissolved in the desorbed eluate and Zn standard solution complexed root and hypocotyl development in spinach (*A. gangeticus*) and bean sprouts (*P. aureus*); thus, could immobilized metal ions. In comparison with the previous results evaluating the chromium toxicity test (Suherman et al., 2019), the toxicity of zinc from the eluate solution appeared to be higher than the metal standard solution.

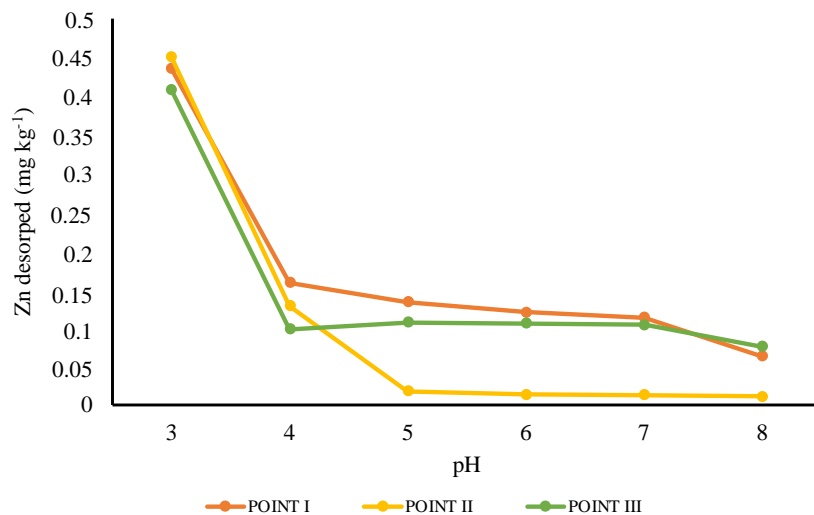


Figure 4. Determination of optimum pH toward Zn desorption.

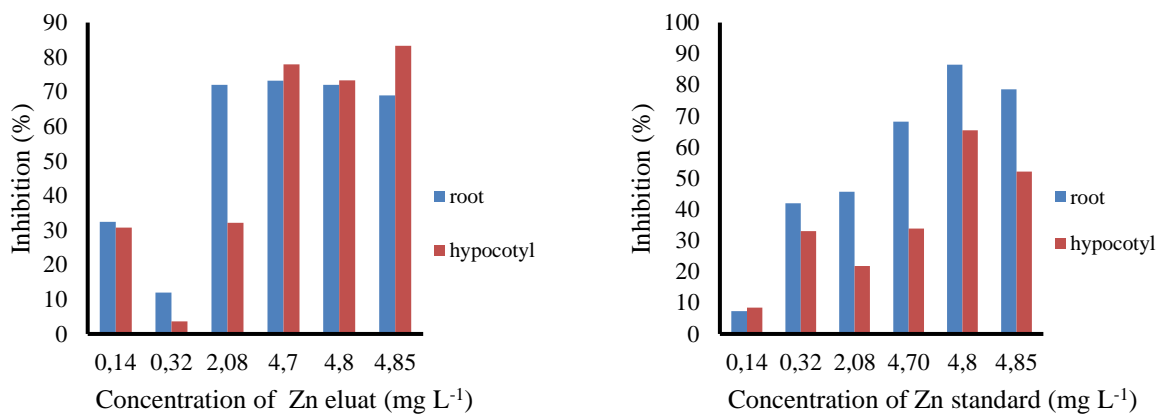


Figure 5. Percentage of inhibition of spinach roots and hypocotyls with Zn eluate and Zn standard solution.

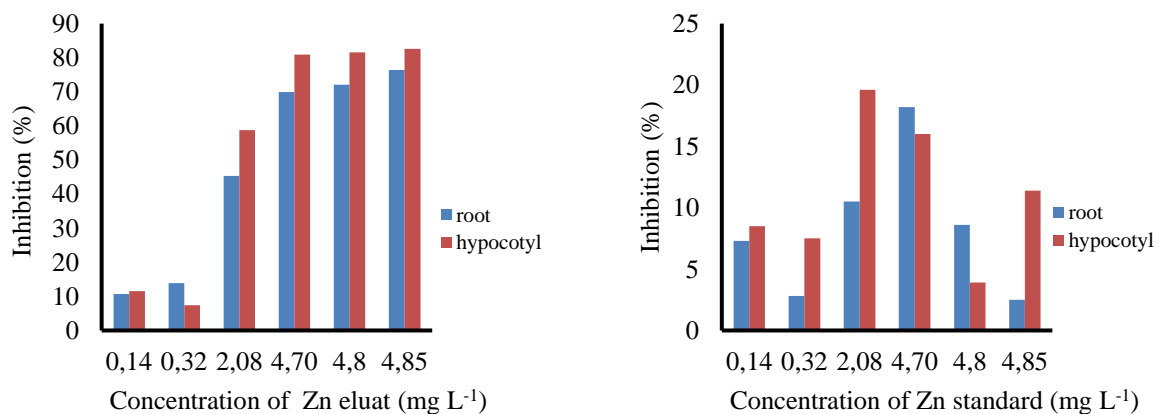


Figure 6. Percentage of inhibition of bean sprout roots and hypocotyls with Zn eluate and Zn standard solution.

CONCLUSIONS

The soil physicochemical properties affect the zinc metal cation (Zn) binding in the soil. The soil's adsorption capacity is determined by its organic matter content and follows the Langmuir isotherm model. The desorption of zinc metal (Zn) was accomplished by varying the amounts of citric acid and pH. Zinc toxicity test by using desorbed soil eluate and standard solution

revealed that low concentrations of zinc did not hinder the growth of spinach (*A. gangeticus*) or bean sprouts (*P. aureus*), but high amounts decreased seed growth.

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