RESEARCH PAPER

COMBINATION OF SUPERABSORBENT POLYMER AND VETIVER GRASS AS A REMEDY FOR LEAD-POLLUTED SOIL

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ABSTRACT. Heavy metal pollution in the soil environment is a worldwide environmental problem as it has negative effects on both human health and the environment. Remediation of heavy metal-contaminated soil is essential to improve soil quality, provide land resources for agricultural production, and protect human and animal health and the ecological environment. There is the possibility of remediating these contaminated soils through the use of several heavy metal absorbing plants and Superabsorbent polymers. Superabsorbent polymers (SAPs) are 3D polymer networks having hydrophilic nature, which can swell, absorb and hold a large amount of water or aqueous solutions in their network. This study evaluates the effect of superabsorbent polymer on Pb absorption capacity of Vetiver (*Vetiveria zizanioides.L*) that was grown on contaminated soil in Trai Cau iron ore dumpsite, Dong Hy district, Thai Nguyen province. The experiment was designed with five recipes and three replicates. The contents of SAP studied were 0, 0.6, 0.8, and 1.0 g/kg of soil. Uncontaminated soil was used as the control treatment. In the supplemented recipe of SAP, Vetiver showed better Pb treatment efficiency than the recipes without adding polymers. After 120 days of planting, SAP increased the tolerance and Pb absorption of Vetiver, improving soil properties. The best Pb treatment efficiency is achieved when using SAP with content from 0.8-1.0 g/kg soil.

KEYWORDS: Superabsorbent polymers, Vetiver (Vetiveria zizanioides L.), lead, absorption, soils

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INTRODUCTION

Heavy metal pollution in the soil is a global environmental problem (Liuwei Wang et al. 2021; Sarwar et al. 2017) and has been increasing as a result of various human activities as well as the process of industrialization and urbanization (Hong-Giang Hoang et al. 2018; Rama Karna et al. 2021) etc. Among all kinds of heavy metals, lead (Pb) is considered as one of the most toxic substances and a major cause of environmental pollution (Kumar 2015). Pb has many toxic effects on human health as it disrupts many bodily functions, such as nervous, cardiovascular, hematological, and reproductive systems (Pal et al. 2015). In pregnant women, the exceeding amount of lead in the body can cause miscarriage (Amadi et al. 2017). In the case of plants, high concentrations of lead can slow down plant growth, inhibit photosynthesis, disturb water balance, blacken roots, and cause other symptoms. Lead toxicity is one of the most hazardous metal toxicities after arsenic (Bikash Debnath et al. 2019).

Soils contaminated with lead or other heavy metals mainly come from human activities such as mining (Shah V et al. 2020), metallurgy, metal production, recycling, use of chemical fertilizers, and use of leaded gasoline (Indah Lestari 2018). Many studies have shown that Pb contamination in soil occurs around non-ferrous metal mining areas (Amjad Alia et al. 2017; Nicolae Cioica et al. 2019). Soil heavy metal pollution from non-ferrous metal mining has been an important and increasing problem in Vietnam. Thai Nguyen is a mountainous province in the North of Vietnam, where there are many mineral mines with large reserves. Studies have shown that in some mining areas of Thai Nguyen province, the concentration of heavy metals such as Cd, Pb, As in the soil after mining is exceeded the allowed criteria (Bui Thi Kim Anh et al. 2011; Takashi Fujimori et al. 2016; Dang et al. 2011).

There are many methods to treat heavy metals in the soil, such as: washing the soil, fixing heavy metals by chemical methods, treating plants, etc. (Liuwei Wang et al. 2021; Nan Lu et al. 2021). The technology of plant treatment (Phytoremediation) is widely applied to treat metal pollution in industrial and mining zones (M. Lambert et al. 2021; Bouzid Nedjimi 2021). Compared with other treatment methods, plant treatment technology is more environmentally friendly. This technology has advantages such as stabilizing the surface soil structure, improving soil nutrition, and significantly reducing the content of metallic pollutants (S. Haq et al. 2020). In addition, pollution remediation and ecological restoration can be carried out in a mining area simultaneously. Plant remediation of lead pollution has been carried out early in many parts of the world, such as the United States, Germany, China, etc. *Thlaspi rotundifolium (L.), Brassica juncea (L.), Artemisia capillaris, Taraxacum mongolicum, Phragntic australis, Medicago sativa, Plantago asiatica L (Zahra Derakhshan* et al. 2018), *Phragntic australis* (Tran Thi Pha et al. 2014) Hardy 'Limelight' Hydrangea (*Hydrangea paniculata*) and the common sunflower (*Helianthus annuus*) (Forte J et al. 2017), Sunflower (*Helianthus annuus L.*), Sorghum (*Sorghum bicolor L.*) and Chinese Cabbage (*Brassica chinensis*) (Rodrick Hamvumba et al. 2014), etc. have been used to absorb Pb with promising efficacy.

Superabsorbent polymers (SAPs) with superabsorbent and water-holding capacity have been applied to improve agricultural water use efficiency, help maintain soil moisture and reduce irrigation water (Q. Guiwei et al. 2008) thanks to their large amount of hydrophilic groups and a three-dimensional network structure with cross-linking. These characteristics ensure their ability to store a large amount of water even under certain pressures (Luq man AliShah et al. 2018; Mohammad et al. 2008). They also have the ability to cross-link with metallic ions. When added to the soil, it will increase the water-holding capacity of the soil, reduce the toxicity of metals to plants, and stimulate the growth of plants (Guiwei et al. 2009; Liangyu et al. 2021).

Therefore, the combination of superabsorbent polymers and metal-tolerant plants offers a new prospect for the restoration and remediation of heavy metal-contaminated soils (Tran Quoc Toan et al. 2021). In this research, we present the results of studying the effects of superabsorbent polymers on Pb absorption capacity of Vetiver grass grown on contaminated soil at Trai Cau iron ore dumpsite, Dong Hy district, province Thai Nguyen. Vetiver grass (*Vetiveria zizanioides. L*) is an easy-to-grow plant, appearing commonly in areas after mining (Luu Thai Danh et al. 2009; Ha Xuan Son et al. 2018). Vetiver grass gives high biomass, has the ability to absorb and accumulate heavy metals, and can live in environments polluted by toxic metals. So it has been widely used in the world to stabilize vegetation, and handling heavy metals (Suelee et al. 2017; Truong, P., & Danh, L. T. 2015; Norbert Ondo Zue Abaga et al. 2021).

MATERIALS AND METHODS

Materials

- Superabsorbent polymers (Vietnam): opaque white solids with a water absorption capacity of 350 mL of water per 1 g of polymer.
- HNO_3 solution (Merk)
- $HClO_4$ solution (Merk)
- Experimental soil was taken according to TCVN 7538-2:2005 on soil quality - sampling. Soil samples were taken from the surface layer, with a depth of 0-20cm. Pb-contaminated soil samples were taken at different locations around Trai Cau iron ore mine waste dump, Dong Hy district, Thai Nguyen province. Unpolluted soil samples were taken from a garden in Dong Hy district, Thai Nguyen province. The physicochemical properties and Pb content of the studied soil samples are presented in Table 1, in which the allowed limit of Pb is 70 mg/kg dried soil was demonstrated in accordance to QCVN 03-MT:2015/BTNMT, the Vietnam national technical regulation on the allowable limits of heavy metals in the soils
- Vetiver grass (*Vetiveria zizanioides. L*) was selected as the grass in the period of strong growth (3-4 months old), cut the stem 25 cm long and the root 5 cm long. Grasses are rooted in moist sand for two weeks before planting. Each pot planted three cloves of grass, daily watering for moisturizing to create conditions for the plants to grow well.

Experiments

- Vetiver grasses were grown in Polyethylene (PE) nursery posts with a height of 20cm, a top diameter of 26cm, and a bottom diameter of 22 cm. The experiments were arranged in a completely randomized block design with five treatments, and each of them was replicated three times. The experimental formulas are as follows:

+ Treatment 1 (CT1- Control): Grass was grown on unpolluted soil.

+ Treatment 2 (CT2): Grass was grown on contaminated soil without SAP

+ Treatment 3 (CT3): Grass was grown on contaminated soil with 0.6 g SAP/kg soil

+ Treatment 4 (CT4): Grass was grown on contaminated soil with 0.8 g SAP/kg soil

+ Treatment 5 (CT5): Grass was grown on contaminated soil with 1.0 g SAP/kg soil

- In the treatment using SAP, we mix the soil with a determined amount of SAP.
- Experiment time: from August 15, 2021 to December 15, 2021.

Sample processing method

- Vetiver grass: the grasses after being harvested will be washed, then rinsed with distilled water, separated the leaves and roots, dried at 80oC until completely dry, crushed, and stored in a clean plastic bag with a tight seal for metal analysis.
- Soil sample: After being collected, it is necessary to remove the roots and impurities in the soil, dry it in the air at room temperature, then grind it into small pieces and sieve it through a 1mm sieve. The soil samples were stored in clean plastic bags with a tight seal to determine the chemical composition of the soil.

Analytical methods

a. *Determination of heavy metals in soil and grass samples:* Soil and Vetiver grass samples after being crushed were automatically digested in the Velp DKL. Pb metal contents were analyzed by atomic absorption spectroscopy (AAS) on an Analytik Jena novAA 400P instrument.

Table 1. Some physicochemical properties of the soil samples studied

Soil samples	pH_{KCl}	CEC	OM	Pb concentration	Pb according to QCVN 03-MT:2015/BTNMT
		(meq/100g)	*(%)*	*mg/kg*	*mg/kg*
Unpolluted soil	5.12	11.84	3.12	16.13	
Polluted soil	6.12	7.3	2.03	441.75	70

b. *Determination of Vetiver grass biomass:* After being harvested, the grass was washed, dried, and weighed on a Mettler Toledo analytical balance to determine the weight of leaves and roots of a cluster in grams.

c. *Data processing:* The biomass indicators and analysis results of heavy metal content in soil samples and Vetiver grass were processed using SAS 9.1 software and Excel 2016.

RESULTS AND DISCUSSION

Effect of SAP on Vetiver grass biomass formation

Even though Vetiver grass has the ability to absorb heavy metals not as high as some super-accumulators of heavy metals, Vetiver grass is one of the species that is widely used to treat heavy metal pollution present in the world due to its high biomass and strong regenerative capacity. In this study, the effect of SAP on biomass (weight of stems, leaves, roots) of Vetiver grass grown on lead-contaminated soil is presented in Table 2 - 3. The results showed that after 30 days of planting, the biomass of Vetiver grass was not high because it began to adapt to the new soil environment. Over time, the biomass of grass increased sharply because lead has a positive effect on the growth and development of the grass, helping the number of branches/ clusters, leaf height, length, and biomass higher than the non-polluted soil treatment (CT1). The treatment using SAP for biomass (mass of leaves and roots) was higher than that of CT2 without SAP, in which CT3 gave the highest biomass at 95% statistical significance. SAP has increased the water-holding capacity of the soil, and optimized the metabolism of nutrients in the soil (including heavy metal ions) to help plants grow and develop well with high biomass. In the treatments using SAP with a high content (CT4, CT5), the biomass of grass increased sharply, in which CT5 gave the highest biomass parameters (weight of leaves: 56.14 g/clump, the weight of roots: 23.66 g/clump) compared with formula CT1, CT2 at 95% statistical significance after 120 days of planting.

Effect of SAP on the ability to accumulate Pb in leaves and roots of Vetiver

The ability to accumulate heavy metals in the parts of the Vetiver (stems and roots) is the main route of metal removal from the soil (Ha Xuan Son et al. 2018). The results of determining the ability to accumulate Pb in the leaves and roots of Vetiver over time are presented in Table 4-5.

Table 2. Effect of SAP on Vetiver leaf weight

Treatment	Time			
	30 days	60 days	90 days	120 days
	Leaf weight (g/cluster)	Leaf weight (g/cluster)	Leaf weight (g/cluster)	Leaf weight (g/cluster)
CT1	$10.96^{bc} \pm 1.07$	$17.63^{c} \pm 1.18$	$23.87^{c} \pm 1.69$	$39.52^{c} \pm 1.34$
CT2	$10.42^{c} \pm 1.19$	$19.27b^{c} \pm 1.43$	$28.66^{b} \pm 1.87$	$40.82^{c} \pm 2.09$
CT3	$13.16^{a} \pm 1.11$	$21.15^{b} \pm 1.40$	$33.10^{a} \pm 2.12$	$49.36^{b} \pm 1.27$
CT4	$13.64^{a} \pm 1.26$	$24.70^{a} \pm 1.49$	$34.27^{a} \pm 1.76$	$55.47^{a} \pm 1.50$
CT5	$12.91^{ab} \pm 1.14$	$26.32^{a} \pm 2.18$	$32.45^{a} \pm 1.77$	$56.14^{a} \pm 2.74$
$LSD_{0,05}$	2.09	2.86	3.36	3.02
CV%	9.42	7.20	6.05	3.44

Note: $LSD_{0,05}$ is the smallest statistically significant difference. CV% is the coefficient of variation. The letters a, b, and c are significant differences at the 95% level.

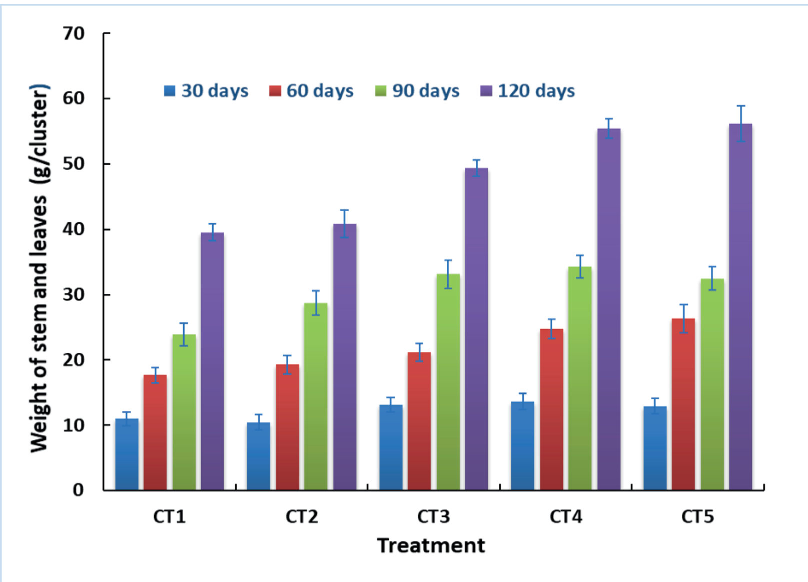

Fig. 1. Effect of SAP on Vetiver leaf weight

Table 3. Effect of SAP on Vetiver root weight

Treatment	Time			
	30 days	60 days	90 days	120 days
	Root weight (g/cluster)	Root weight (g/cluster)	Root weight (g/cluster)	Root weight (g/cluster)
CT1	3.13^{c}± 0.35	6.65^{b}±0.85	13.66^{b}± 1.60	20.26^{c}± 1.36
CT2	3.64^{bc}± 0.56	7.41^{b}± 1.12	14.37^{ab}± 1.17	22.52^{b}± 2.42
CT3	5.12^{a}± 0.55	9.56^{a}± 1.10	17.21^{a}± 1.46	25.65^{a}± 1.96
CT4	4.66^{ab}± 0.81	8.33^{ab}± 1.14	16.65^{a}± 1.53	23.73^{a}± 1.85
CT5	4.27^{abc}± 0.76	8.25^{ab}± 0.86	15.87^{ab}± 2.04	23.66^{a}± 1.28
$LSD_{0,05}$	1.36	1.86	2.88	3.25
CV%	17.89	12.67	10.18	7.72

Note: $LSD_{0.05}$ is the smallest statistically significant difference. CV% is the coefficient of variation. The letters a, b, and c are significant differences at the 95% level.

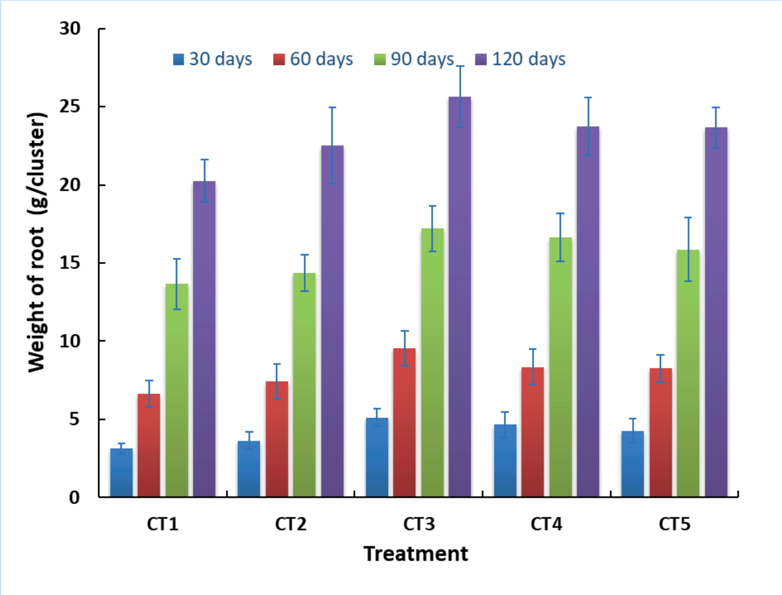

Fig. 2. Effect of SAP on Vetiver root weight

Table 4. Effect of SAP on Pb content in Vetiver leaves (n = 3, mean± SD)

Treatment	Pb content before treatment (mg/kg)	Pb content in leaves after treatment (mg/kg)			
		30 days	60 days	90 days	120 days
CT1	1.03	1.15^{d}± 0.03	1.48^{d}± 0.04	1.86^{d}± 0.28	2.94^{d}± 0.11
CT2		4.94^{c}± 0.24	5.82^{c}± 0.32	8.91^{c}± 0.71	14.35^{c}± 1.05
CT3		6.32^{b}± 0.25	9.83^{b}± 0.35	15.82^{b}± 1.02	21.12^{b}± 1.36
CT4		8.56^{a}± 0.48	14.45^{a}± 0.55	20.35^{a}± 1.25	26.45^{a}± 1.25
CT5		9.13^{a}± 1.02	15.63^{a}± 0.93	21.55^{a}± 1.12	27.57^{a}± 1.44
$LSD_{0.05}$		1.16	1.41	1.53	1.71
CV%		10.55	8.20	6.16	5.07

Note: $LSD_{0.05}$ is the smallest statistically significant difference. CV% is the coefficient of variation. The letters a, b, c, and d are significant differences at the 95% level.

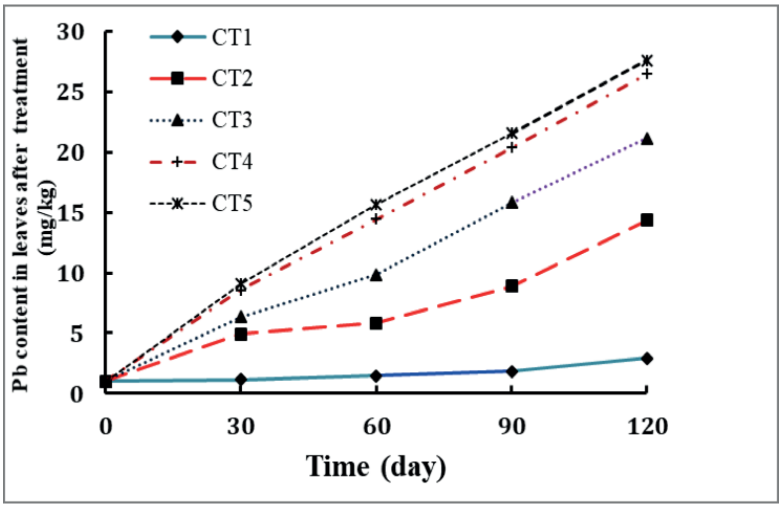

Fig. 3. Effect of SAP on Pb content in Vetiver leaves

Table 5. Effect of SAP on Pb content in Vetiver roots (n = 3, mean± sd)

Treatment	Pb content before treatment (mg/kg)	Pb content in roots after treatment (mg/kg)			
		30 days	60 days	90 days	120 days
CT1	1.98	$2.88^{e}\pm 0.11$	$4.59^{e}\pm 0.25$	$6.62^{e}\pm 0.22$	$7.05^{e}\pm 0.31$
CT2		$18.78^{d}\pm 1.24$	$34.12^{d}\pm 2.35$	$53.93^{d}\pm 2.15$	$76.64^{d}\pm 2.85$
CT3		$39.68^{c}\pm 1.45$	$82.17^{c}\pm 2.67$	$122.63^{c}\pm 4.65$	$134.12^{c}\pm 5.12$
CT4		$56.39^{b}\pm 3.15$	$113.45^{b}\pm 5.52$	$149.62^{b}\pm 5.52$	$210.57^{b}\pm 6.32$
CT5		$71.25^{a}\pm 3.18$	$144.72^{a}\pm 5.54$	$186.55^{a}\pm 6.82$	$236.44^{a}\pm 8.25$
$LSD_{0.05}$		1.82	2.23	2.55	2.91
CV%		2.65	1.61	1.35	1.20

Note: $LSD_{0.05}$ is the smallest statistically significant difference. CV% is the coefficient of variation. The letters a, b, c, and d are significant differences at the 95% level.

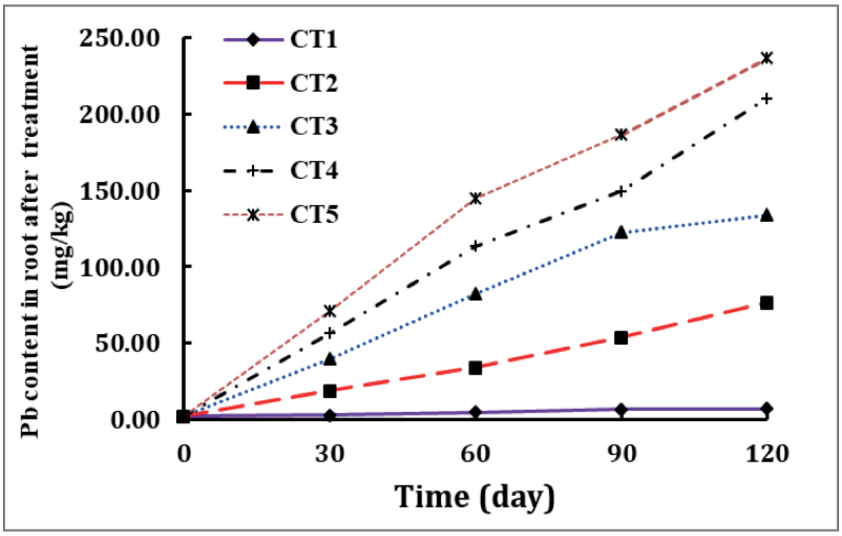

Fig. 4. Effect of SAP on Pb content in Vetiver roots

Research showed that the accumulated Pb content in leaves and roots is proportional to SAP content and experimental time. In the first 30 days, the ability to accumulate Pb of Vetiver grass increased slowly. They increased faster after 90 days of planting, then gradually slowed down in the next 30 days. In the treatments involving using SAP (CT3, CT4, CT5), the ability to accumulate Pb in leaves and roots was much higher than that of CT1 and CT2, in which CT5 gave the highest Pb accumulation value at a statistically significant level. Pb accumulation in grassroots is also proportional to Pb content in soil and experimental time. However, Pb accumulation in roots is much higher than in leaf stems. In CT1 and CT5, after 120 days of planting grass, the accumulated lead content in leaf stems increased by 2.85 times and 26.77 times, respectively, while these numbers in roots subsequently were 3.56 times and 119.41 times.

Table 6. Results of analysis of Pb content in the soil before and after the experiment

Treatment	Pb content before treatment (mg/kg)	Pb content after treatment (mg/kg)			
		30 days	60 days	90 days	120 days
CT2	441.75	387.34[a]± 2.42	298.65[a]± 3.25	225.29[a]± 4.15	132.13[a]± 2.16
CT3		345.23[b]± 6.25	236.71[b]± 5.52	175.10[b]± 3.62	119.65[b]± 2.31
CT4		305.67[c]± 4.55	216.54[c]± 4.72	152.83[c]± 3.85	100.42[c]± 3.15
CT5		286.80[d]± 5.10	193.25[d]± 5.15	141.64[d]± 2.84	97.34[c]± 2.10
$LSD_{0,05}$		7.74	7.05	6.52	5.80
CV%		1.24	1.58	1.99	2.74

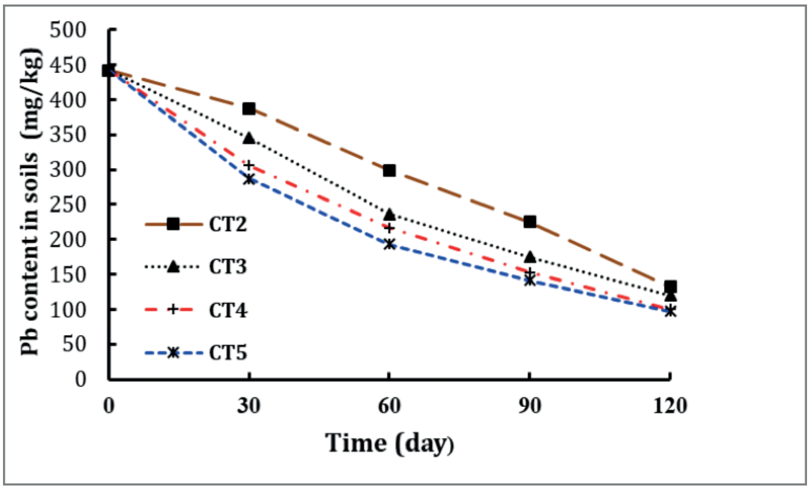

Fig. 5. Pb content in the soil before and after the experiments

Research results demonstrate that Pb first accumulated in the roots and then transported to the leaves. The higher the Pb content in the soil, the more Pb was accumulated in the plant parts. Vetiver grass not only can grow and develop well in soil contaminated with Pb, but also has the ability to absorb and accumulate Pb in its biomass. The results of this study are consistent with those of other authors (Luu Thai Danh et al. 2009; Ha Xuan Son et al. 2018).

Effect of SAP on the change of Pb content in the soil before and after the experiment

The results in Table 6 show that the Pb content in contaminated soil (CT2-CT5) tended to decrease sharply after 120 days of growing Vetiver grass in all experimental treatments, in which the formulas used SAP showed a faster decrease in Pb content compared to CT2. When combining Vetiver with SAP, the efficiency of Pb removal in contaminated soil is higher than when using Vetiver alone. After 120 days of planting Vetiver grass, the ability to treat Pb in the soil reached its highest in CT4 and CT5. However, there is no statistical difference between CT4 and CT5 at the 95% confidence level. This can be explained because SAP has increased the water-holding capacity of the soil, reduced the toxicity of metals to plants, and stimulated the growth and development of plants, thus increasing the tolerance and Pb uptake.

CONCLUSION

Vetiver grass can tolerate and grow on lead-contaminated soils due to mining activities. Vetiver grass demonstrates the ability to uptake and accumulate Pb in its leaves and roots. The amount of uptake and accumulated Pb in the biomass of Vetiver grass is directly proportional to SAP content and Pb content in the soil as well as experimental time.

Better Pb treatment efficiency was observed in the treatment with the SAP supplement than in the one without it. The presented data have also proved that SAP increased the tolerance and Pb absorption capacity of Vetiver grass after 120 days of planting. The highest Pb treatment efficiency and fastest Pb removal from contaminated soil were obtained when adding SAP with the content from 0.8-1.0 g/kg soil.

The results of this study show the high feasibility of removing Pb in contaminated soil with a combination of plants and superabsorbent polymers. It is a promising and "green" solution that can be applied not only for Pb but also for other heavy metals in polluted soil.

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