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Enhanced phytoaccumulation dynamics of chromium and nickel from spent engine oil-contaminated soil amended with biomass-derived bulking agent

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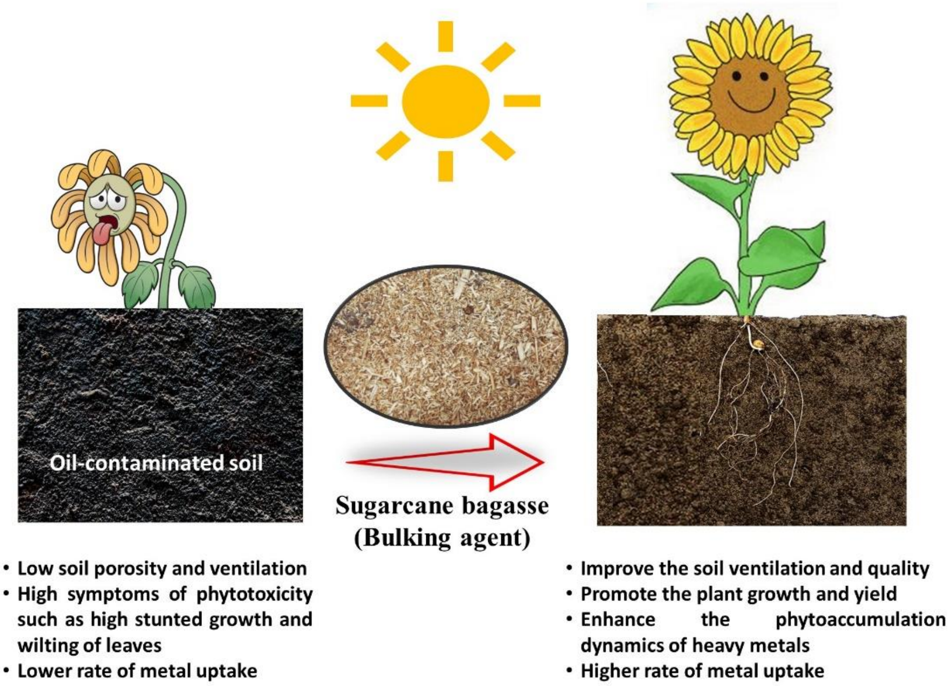

- Low soil porosity and ventilation
- High symptoms of phytotoxicity such as high stunted growth and wilting of leaves
- Lower rate of metal uptake

- Improve the soil ventilation and quality
- Promote the plant growth and yield
- Enhance the phytoaccumulation dynamics of heavy metals
- Higher rate of metal uptake

Abstract: Phytoremediation is a promising sustainable approach for the remediation of soil contaminated with inorganic and organic pollutants. In the lands affected by petroleum-derived compounds, their massive toxicity towards the plants, however, hinders the efficacy of the phytoremediation process. Hence, adopting a green approach to enhance phytoremediation is highly recommended and desirable. Here, sugarcane bagasse (SCB) was used as a bulking agent enhancing the hyperaccumulation of heavy metals chromium (Cr) and nickel (Ni) by sunflower plants from 0.5%, 2.5%, and 5%

oil-contaminated soil. Accumulation of Cr and Ni was observed higher in roots than shoots. The bioconcentration factor (BCF) of Cr and Ni was higher in soil amended with SCB than that without amended. The highest rate of Ni and Cr uptake was also noticed in all treatments amended with the bulking agent except in the case of 0.5% oil-contaminated soil without SCB. Overall, the phytoremediation of oil-contaminated soil is most effective when it is amended with SCB as a bulking agent which provides water and air well to plants, improving plant growth and then increasing phytoaccumulation of heavy metals.

Keywords: Phytoaccumulation, Chromium, Nickel, Spent engine oil, Contaminated soil, Sugarcane bagasse, Bulking agent

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Introduction

The growth of the petroleum industry in the world and the marketing of petroleum products have resulted in extensive environmental pollution by oil leakage into soil and water bodies. This pollution affects soil structure itself and thus microorganisms such as bacteria and fungi, as well as, on the roots of plants and animals [1]. The basic work of the lubricating oil is to prevent metal-to-metal contact and to transfer heat from friction away from the contact points. Spent engine oil as one of the sources of oil-contaminated soil contains several compounds such as heavy metal contaminants e.g. copper, aluminum, cadmium, chromium, iron, lead, nickel, and silicon that come from engine parts as they wear down. Additionally, it has aliphatic and aromatic hydrocarbons, polychlorinated biphenyls, chlorodibenzofurans, lubricating additives, and decomposition products [2,3].

The content of heavy metals in used engine oil is dangerous in high concentrations such as chromium, copper, and nickel causing hazardous effects on human health such as anemia, nervous system disorders, and depressed immune systems, resulting in mortality and effects on population levels [4]. Moreover, it was reported that some heavy metals are harmful and carcinogenic or toxic, affecting the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium) [5]. Chromium which is a heavy metal component of spent engine oil has been recognized as a priority pollutant and found to be toxic, carcinogenic, and teratogenic, particularly hexavalent chromium, when present at high concentrations. Hexavalent chromium has a high tendency to bind with oxygen, and unless it is rapidly reduced, it can oxidatively damage the DNA via the production of free radicals. It has been reported that hexavalent chromium causes lung cancer, chromate ulcer, perforation of the nasal septum, and kidney damage in humans, and it is also toxic to other organisms as well [6,7]. On the other hand, nickel exposure causes the formation of free radicals in various tissues in both humans and animals which become neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic, and carcinogenic agent [8].

Phytoremediation is a promising technology in which plants have the potential to accumulate, remove, stimulate microorganisms in the rhizosphere zone, and detoxify environmental contaminants. The advantages of phytoremediation compared with other approaches are: (1) it preserves the natural structure and texture of the soil; (2) energy required for the photosynthesis process of the plant is derived primarily from sunlight; (3) high levels of microbial biomass in the soil can be achieved; (4) it is low in cost; and (5) it has the potential to be rapid [9,10]. Furthermore, plants can enhance the bioremediation process by absorbing, translocating, or sequestering the heavy metals and organic contaminants from the soil rhizosphere [11]. Nevertheless, at high concentrations, the plant tolerance inclines gradually to weaken performance due to the phytotoxicity of heavy metals and total petroleum hydrocarbons (TPHs).

Bulking agents are materials, mainly biomass-based materials, with low density that enable the intensified bioremediation process via reducing the density of soil bulk, increasing the porosity, promoting oxygen diffusion, and forming water-stable aggregates [12,13]. Thence, the amendment of contaminated soil by a bulking agent not only improves the soil ventilation and quality but also enhances the plant growth and consequently the microbial activity and pollutants uptake and microbial activity.

Herein, this investigation aims to study the potential of sunflower plants for phytoaccumulation of Cr and Ni in soil contaminated with 0.5%, 2.5%, and 5% spent engine oil amended with sugarcane bagasse SCB as a bulking agent. The metal accumulation efficiency and the rate of metal uptake were deduced. Furthermore, the plant growth and biomass dry yield were also monitored.

Materials and Methods

Preparation of oil-contaminated soil

Uncontaminated soil was collected from a desert in Sohag Governate, Egypt, where some chemical and physical characteristics of the obtained soil are shown in Table 1 and the determination methods were described in detail in supporting information. Used motor oil was collected from a local car oil center; Sohag Governate. Sugarcane bagasse used as a bulking agent in the experimental runs was obtained from the Gerga sugar factory; Sohag

Governate. Characteristics of utilized sugarcane bagasse were as follows: (total nitrogen= 0.29%) (potassium= 0.15%) (phosphrous=0.06%).

Table 1. Some chemical and physical characteristics of the soil.

Parameter	Uncontaminated soil
pH	7.88
EC (dS/m)	1.17
SP	23.1
Chemical analysis	
CO_3^{2-} (mmol/L)	0.00
HCO_3^-	0.63
Cl^-	6.11
Ca^{2+}	3.01
Mg^{2+}	1.86
Na^+	4.21
K^+	0.49
Zn	0.21
P	0.03
Fe	1.50
Mn	0.35
$CaCO_3$ (%)	2.35
Organic matter (%)	0.12
Physical analysis	
Sand (%)	90.57
Silt (%)	4.03
Clay (%)	5.4
Soil texture	Sand

*pH was measured based on 1:2.5 suspension ratio of 1 g soil:2.5 mL DI water, EC: electrical conductivity, SP: Saturation percentage.

Table 2. Experimental Design for phytoremediation of oil-contaminated soil.

Sample	Oil weight, g	Final soil weight, kg	Sugarcane bagasse amendment, g	Percentage of oil in the soil, %
A	60	12	0	0.5
B	60	12	250	0.5
C	300	12	0	2.5
D	300	12	250	2.5
E	600	12	0	5
F	600	12	250	5
T	0	12	0	0

*Treatments were arranged in a completely randomized design (CRD) with 3 replications.

The soil was air-dried, sieved, washed, dried, and weighed. Each treatment was placed in plastic polyethylene pots. 60 g, 300 g, and 600 g of spent oil were thoroughly mixed with uncontaminated soil to obtain 12 kg of contaminated soil for each treatment (i.e. 0.5%, 2.5%, and 5%, respectively) and allowed to stand for one week to obtain aged and mature contaminated soil. For the contaminated soil amended with SCB, SCB was weighed and added to mature contaminated soil and mixed thoroughly and uniformly, and then distributed in the pots. Control treatment consisting of the soil without spent engine oil or sugarcane bagasse was also set up. The pots were marked A, B, C, D, E, F, T and the content of each pot is shown in Table 2.

Phytoremediation treatment

Pots received the recommended doses of N, P, and K (for each pot, 1.176 g urea, 0.6 g potassium sulfate, and 2.4 g superphosphate were applied). Five sunflower seeds were planted in each pot. All the pots were watered twice a week with a proper amount of water to reach saturation as needed. The plants were allowed to grow for 3 months. During the different stages of plant growth, soil samples were collected from the rhizosphere zone of the plant to determine Cr and Ni. The first sampling was taken at the first of the experiment and the second sampling was taken after 30 days then 60 days and finally after 90 days (the end of the experiment). Collected samples were kept for chemical analysis. After 90 days, plants were removed, cleaned, washed, dried at 60°c for 48 h and weighed.

Determination of heavy metals

Heavy metals in the soil sample (1 g) were digested by 10 mL aqua regia (3:1 hydrochloric acid to nitric acid) by heating for 2 h to 140 °C, gradually increasing the temperature to control foaming. Distilled water was added to cool the digestates and then filtered with Whatman filter paper and topped up to 100 mL with distilled water [14], and determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Spectrometry (Ultima 2 JY Plasma), K and Na were determined by flame photometer.

For the plant, an aliquot concentrated sulfuric-perchloric acid mixture (10:1) was added to accurately known weight of the dry sample (0.5 g), then digested on the hot plate for 6 h [15]. After digestion, the solution was left until a clear solution was obtained. Later, the digested solution was quantitatively transferred to a 50.0 mL volumetric flask and completed to the mark using deionized water then kept till determinations of heavy metal concentrations by ICP-OES.

Metal accumulation efficiency by sunflower

For plants, the Bioconcentration Factor (BCF) is a measure of the metal accumulation efficiency. A BCF value of greater than one is an implication of plant potential for phytoextraction. BCF was calculated using the following formula [16]:

$$BCF = \frac{C1}{C2} \qquad (1)$$

Where C1 is the average heavy metal concentration in the whole plant tissue (mg/kg), and C2 is the concentration of heavy metal in the soil (mg/kg).

Rate of metal uptake by sunflower plant

The uptake rate of Cr and Ni by sunflower plant was determined by a first-order kinetics model as expressed in the following equation [17]:

$$k = -1/t\,(ln\,M/M_o) \qquad (2)$$

where k is the first order rate constant of uptake of metal per month, t is time in a month, M is the concentration residual of metal in the soil (mg/kg) and M_o is the initial concentration of metal in the soil (mg/kg).

Results and discussion

Bioaccumulation of Cr and Ni by sunflower plant

To evaluate the bioaccumulation of Cr and Ni in contaminated soil, the sunflower plant was used as a tolerant phytoremediation strategy for extracting the heavy metals. Besides that, SCB was evaluated as a bulking agent to enhance the bioaccumulation process. As shown in Table (3), Cr and Ni concentrations of all treatments in the soil have declined. It was observed that all treatments amended with SCB in contaminated soil had a higher reduction in concentrations of Cr in the soil except in 0.5% oil-contaminated soil without SCB A treatment. The high reduction of A treatment might be relied on the low concentration of Cr which has a less toxic effect on the sunflower performance. Reduction in Cr concentrations in contaminated soil after 90 days was 89%, 85.5%, 79.2%, 87.5%, 70.4%, and 86.2% in A, B, C, D, E and F, respectively. In the case of nickel, there are no significant differences in Ni concentration reduction. After 90 days, the highest reduction was observed in 2.5% oil-contaminated soil with SCB (90.7%). The reason for the high reduction of Cr and Ni concentrations with the soil amended with SCB might be attributed to the ability of SCB as a bulking agent to increase soil bulk and porosity and promote the ventilation of the plant growth and thus boost the bioavailability of heavy metals to plant roots.

Table 3. Concentrations of Cr and Ni in the contaminated soil after 30, 60, and 90 days in all treatments.

Treatments	Initial concentration (mg/kg)		30 days (mg/kg)		60 days (mg/kg)		90 days (mg/kg)	
	Cr	Ni	Cr	Ni	Cr	Ni	Cr	Ni
A	13.80 ± 0.17	5.50 ± 0.15	7.03 ± 1.02	3.20 ± 0.40	5.00 ± 0.69	1.33 ± 0.23	1.50 ± 0.80	0.63 ± 0.25
B			10.53 ± 1.22	2.20 ± 0.35	5.60 ± 0.70	1.23 ± 0.45	2.00 ± 1.06	0.77 ± 0.06
C	20.50 ± 0.10	9.70 ± 0.24	13.80 ± 2.30	2.83 ± 0.75	7.57 ± 1.17	2.00 ± 0.26	4.20 ± 0.93	1.30 ± 0.30
D			9.10 ± 1.20	2.73 ± 0.42	5.40 ± 1.71	2.23 ± 0.38	2.53 ± 0.76	0.90 ± 0.36
E	28.17 ± 0.90	12.20 ± 0.39	17.57 ± 0.55	7.27 ± 0.80	13.23 ± 2.45	4.13 ± 0.70	8.43 ± 0.75	2.33 ± 0.12
F			21.07 ± 3.45	7.87 ± 0.81	8.10 ± 1.32	5.63 ± 0.45	3.93 ± 0.31	2.67 ± 0.23

The bioaccumulation of chromium concentrations in sunflower roots and shoots in all treatments is presented in Fig 1. The bioaccumulation of chromium by roots was recorded from 1.03 to 12.5 mg/kg. It was observed that the highest chromium concentration was in 2.5% oil-contaminated soil amended with SCB (D) (12.5 mg/kg) and the lowest concentration was in 5% oil-contaminated soil without SCB (E) (1.033 mg/kg). Cr concentrations accumulated by sunflower shoots were 2.23, 1.43, 8.52, 5.60, 5.74, and 4.03 mg/kg in A, B, C, D, E, and F, respectively. The highest accumulation of Cr in shoots was observed in 2.5% oil-contaminated soil without SCB (C). That may be ascribed to high concentrations of Cr in the contaminated soil. The values of chromium concentrations in roots are higher than the corresponding values taken up by shoots except in the case of C and E. These results go along with those indicated by Davies, et al. who observed that chromium accumulation was the greatest in sunflower roots than that in the shoots [18]. The same findings of higher accumulation of other heavy metals by sunflower roots than shoots were also reported such as cadmium, lead, copper, zinc, and iron [19-21]. The highest Cr concentration in roots that grew in oil-contaminated soil amended with SCB can be attributed to several mechanisms. Firstly, SCB as a bulking agent improves soil condition and provides an efficient amount of water and nutrients to the plant, thereby enhancing the growth of plant roots. After that, plant roots have the ability to reduce insoluble oxidized forms of metals through the release of organic acids and reductants which oxidize insoluble

Cr(III) to soluble Cr(VI) and become available in soil solution for uptaking by the plant [22]. SCB may be considered a chelating agent due to the composition of the bulking agent (lignin, cellulose, hemicellulose, nitrogen ratio, and proteins) [23]. The formation of metal-chelate complexes prevents sorption of the metals on soil thereby maintaining their availability for plant uptake. Finally, the addition of NPK fertilizers to the soil helped in the growth of plant roots, in addition, phosphate may be used to extract the anions of Cr from soil based on the competition of metal ions in soil solution for sorption sites [24].

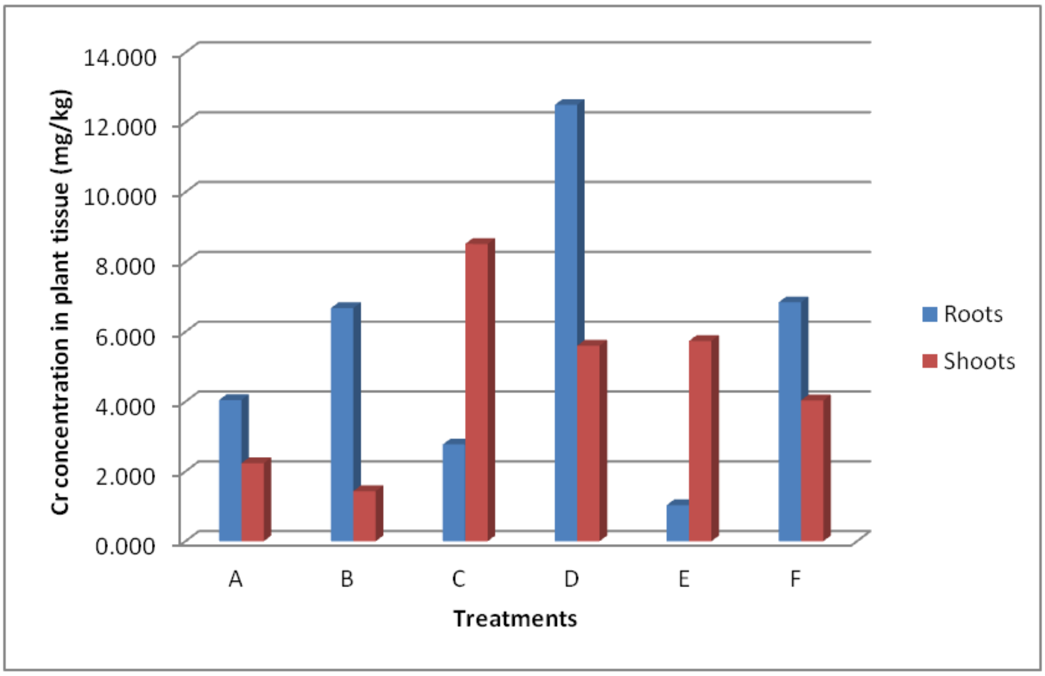

Fig 1. Concentration of Cr in sunflower roots and shoots.

On the other hand, the concentrations of nickel in sunflower roots were 2.02, 3.71, 7.70, 8.26, 0.37, and 4.57 mg/kg in A, B, C, D, E, and F, respectively, as presented in Fig 2. The highest value of Ni concentration in root was 8.26 mg/kg in D treatment due to the high value of Ni concentration in 2.5% oil-contaminated soil amended with SCB which in turn increases the bioavailability of Ni to be accumulated by roots. The concentration of Ni in E treatment was the lowest may be due to the high pollution of hydrocarbons which reduce the oxygen and water supply to the plant and hence impact the root growth. In contrast to the accumulation of Ni by roots, Ni accumulated by sunflower shoots was recorded as the highest accumulation of Ni (4.33 mg/kg) in E treatment as shown in Fig 2. That probably imputed to the tolerance and resistance of sunflower towards the toxic effects resulting from the high concentration of hydrocarbons and Ni by detoxifying the heavy metals once they enter the cells and translocation of heavy metals from root to shoot to reduce the stress of Ni toxicity on the root. That explains why Ni accumulated by shoots is higher than that by roots. Additionally, the plant tissues develop and improve heavy metals-resistant metabolism [25,26].

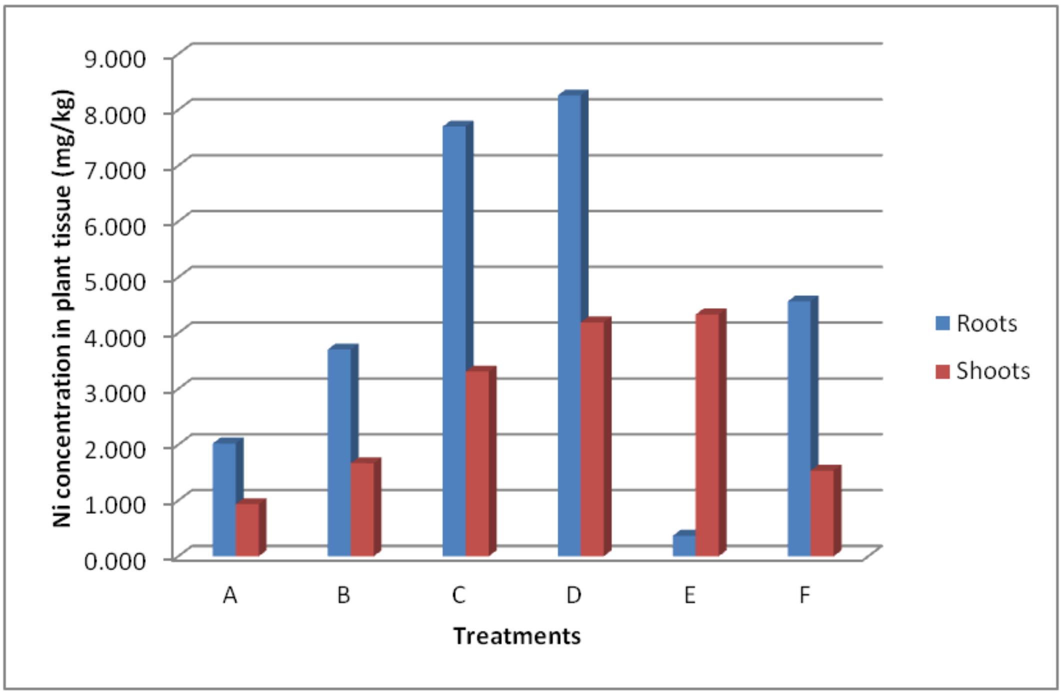

Fig 2. Concentration of Ni in sunflower roots and shoots.

Metal accumulation efficiency by sunflower plants.

Bioconcentration factor (BCF) is a useful parameter to evaluate the potential of the plants in accumulating metals and this value was calculated on a dry weight basis. As shown in Table (4), the BCF of Cr was higher in those treatments amended with SCB compared with the soil without amendment. This might be because of available nutrients for the plant growth by SCB as a bulking agent that produced high plant biomass, thereby causing bioaccumulation of the metals in the plant tissues more than those of the unamended treatments. The highest BCF was observed in 2.5% oil-contaminated soil amended with SCB D (0.896), while the lowest value was in 5% oil-contaminated soil without amended E (0.238).

The highest BCF of Ni was observed in all treatments amended with SCB except C treatment as shown in Table (4). The highest BCF was observed in 2.5% contaminated soil with SCB D which was more than one (1.283) and then in 2.5% contaminated soil without amended C (1.135) and closely with 0.5% oil-contaminated soil with SCB B which proves that sunflower plants are considered to be hyperaccumulation plants. While the lowest BCF was in 5% oil-contaminated soil without amended E (0.385).

Table 4. Bioconcentration factor of Cu and Ni with sunflower plants.

Treatment	Bioconcentration factor (BCF)	
	Cr	Ni
A	0.454	0.537
B	0.587	0.976
C	0.558	1.135
D	0.896	1.283
E	0.237	0.385
F	0.381	0.500

Rate of metal uptake by sunflower plants

The uptake rate of each metal (Cr and Ni) per month by sunflower plants was determined using a first-order kinetic model. The results in Table (5) revealed that the rate of uptake of Cr and Ni by sunflower within the period of the three-month study was higher in soil contaminated with 0.5% and 2.5% used engine oil than those in soil contaminated with 5% oil. Also, it was observed that the rate of Cr uptake is higher in all soil amended with SCB compared with soil without SCB except 0.5% oil-contaminated soil A (0.023). In the case of the uptake rate of Ni, the highest rate was recorded in D (0.024) and A (0.024) and close to B (0.022). The reason for the higher uptake rate shown by the treatments amended with SCB as a bulking agent can be attributed to the high permeability of water and air in oil-contaminated soils and then improved the rate of plant growth in those treatments which were much taller and better than plants in treatments without amended [27]. The high rate of Cr and Ni uptake in A might be due to the lower concentration of hydrocarbons and heavy metals (Cr and Ni) in the soil than in other treatments, hence the plants in A treatment can grow better and uptake the metal at a higher rate than the others treatments without amendment. Generally speaking, the utilization of bulking agents enhances the potential of the plant for efficient removal of TPH and heavy metals from oil-contaminated soil. For example, the amendment of oil-contaminated soil with sawdust as a bulking agent showed also the ability to increase the tomato growth performance owing to its capability of increasing the soil nutrient content and reducing the soil's total hydrocarbon content [28].

Table 5. Rate of Cr and Ni uptake by sunflower plants.

Treatment	Rate of uptake k (month^{-1})	
	Cr	Ni
A	0.023	0.024
B	0.021	0.022
C	0.017	0.021
D	0.023	0.024
E	0.013	0.018
F	0.023	0.016

Plant growth and biomass

After 90 days, the ability and response of plant species to grow in the oil-contaminated soil were monitored. It was observed that remarkable decrease in plant growth in contaminated soil relative to the control. No plant death was recorded in all the treatments of soil contaminated with 0.5%, 2.5%, and 5% used engine oil, however some of the plants in 0.5% and 2.5% showed signs of phytotoxicity such as yellowing of leaves and delayed sprouting compared with the control. Plants in 5% oil-contaminated soil showed high symptoms of phytotoxicity such as high stunted growth and wilting of leaves. The dry weight of the sunflower plants in each treatment was determined at the end of 90 days as shown in Fig. 3.

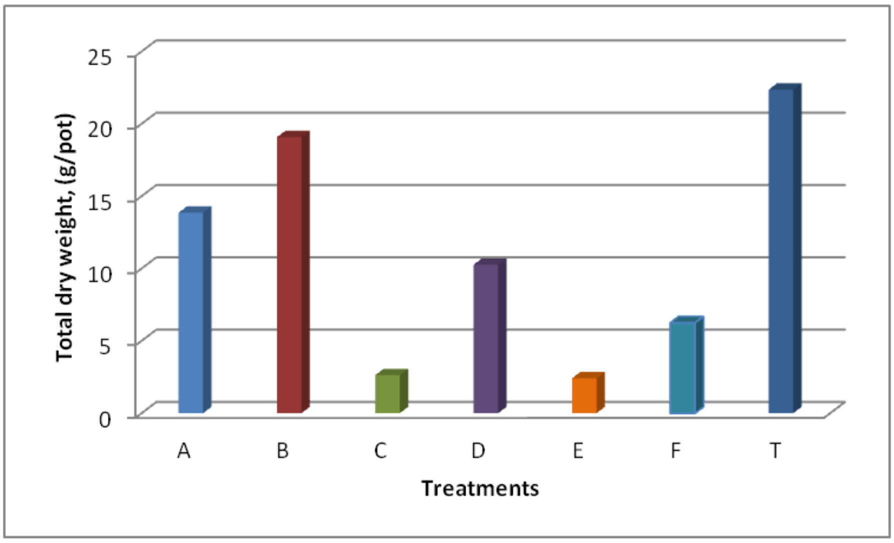

Fig. 3. Dry weight of sunflower plants used for phytoremediation.

A high reduction of plant yields was noted in E, C, F, D, A, and then B by 89.22%, 88.52%, 72%, 54%, 38%, and 14.7% respectively, compared to the control. The signs are in line with the findings of Anoliefo and Vwioko, who noted poor germination of Capsicum annum and Lycopersicon esculentum when treated with 4 and 5% of spent oil [29]. The reduction of plant growth may have been owing not only to the high toxicity of total petroleum hydrocarbons (TPH) and heavy metals such as Cr but also to the decline in biomass production in highly contaminated soil which reduces water and nutrients provided to plants. Wassem et al also observed the decline of sunflower growth and negative impacts on roots and shoots fresh and dry weight in Cr-contaminated soil due to the reduced plant photosynthetic activity [19]. It was noted that a high yield of sunflower (85.3%) was in 0.5% oil-contaminated soil amended with SCB, compared with the control, which improves water and nutrients provided to the plant.

Conclusions

In conclusion, this study investigated the potential of the sunflower plant in phytoaccumulation of Cr and Ni from oil-contaminated soil in low 0.5%, medium 2.5%, and high 5% concentrations of spent engine oil amended with SCB. The obtained results concluded that sunflower plants have hyperaccumulation properties toward Cr and Ni under the amendment of SCB. A higher reduction of Cr and Ni concentrations was observed for contaminated soil amended with SCB compared to unamended soil. Besides that, the accumulation of Cr and Ni in the root zones was higher in the amendment soil than that without amendment. The addition of SCB to the contaminated soil not improved only the water and nutrients provided to the plant but also enhanced the growth of sunflower and increased bacterial activity in the soil. In the amended soil, the sunflower's growth and dry mass were significantly enhanced with minor phytotoxicity signs compared with that in unamended soil. The enhanced sunflower biomass, thus, accelerated the rate uptake of Cr and Ni by sunflower roots and shoots and increased the efficiency of metals accumulation. This study provides an alternative green strategy for the cleanup of soils contaminated with petroleum-derived substances.

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