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Phytoremediation of seleniferous soil leachate using the aquatic plants *Lemna minor* and *Egeria densa*

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ABSTRACT

Phytoremediation of selenium (Se)-containing Hoagland solution and seleniferous soil leachate using two aquatic plants *Lemna minor* and *Egeria densa* was evaluated. *L. minor* showed the highest Se removal efficiency (97%) in the Hoagland solution with a bioconcentration factor (BCF) of 504.35 (± 0.83). In artificial soil leachate with addition of 2 mg L^{-1} $MnSO_4$, *L. minor* and *E. densa* showed a Se removal efficiency of 77% and 60%, respectively. The addition of $K_2S_2O_8$ decreased the Se uptake by both plants by 40% and the medium pH decreased from 7 to 3, whereas the addition of SO_4^{2-} decreased the removal efficiency of both aquatic plants by 30%, in which only 3% of Se was taken up by the plants. *L. minor* was selected to remove Se from a real seleniferous soil leachate which contained 74 μg L^{-1} Se and a 76% efficiency was achieved, with a Se uptake of 29 μg g^{-1} dry weight and a BCF of 393.2 (± 13.6). This study demonstrates that aquatic plants such as *Lemna minor* and *Egeria densa* can be used to remove Se from seleniferous soil leachate and that the phytoremediation efficiency depends on the composition of the extractant used for soil washing.

1. Introduction

Selenium (Se) is an essential trace element, which plays an indispensable role in the functioning of oxidoreductase enzymes in humans and animals (Hatfield et al., 2014). In plants, Se has positive effects on growth and it gives resistance towards pathogens and herbivores (Yasin et al., 2015; Handa et al., 2015). In adult human diet, the recommended daily dose for Se is 0.04–0.4 mg per person (FAO/WHO, 2001). In order to achieve optimal Se levels in the human diet, Se is commonly added as inorganic fertilizer to crops in Se deficient regions such as Finland and Mediterranean countries (Vita et al., 2017).

Excess Se in the human diet, on the contrary, can cause Se toxicity which leads to skin diseases and gastrointestinal and neurological dysfunctions (Sunde et al., 2012). Due to high levels of Se in soils in north India, China and Australia, Se toxicity is one of the major concerns in these regions. According to Dhillon and Dhillon (2003), soils containing as low as 0.1–0.5 mg Se kg^{-1} soil are considered as seleniferous. Major sources of selenium in soil are either lithogenic (Haug et al., 2007) or anthropogenic, i.e. mining and agriculture activities (Winkel et al., 2012). When such soils are used for agricultural purposes, they may directly influence the dietary Se intake of the local population (Hira et al., 2004).

Treatment of seleniferous soils using *ex situ* techniques such as soil washing has several advantages over conventional soil bioremediation techniques such as bioamendment or phytoremediation (Wuana and Okiemen, 2011). Soil washing is a fast and cost-effective procedure that not only decreases the volume of soil that needs to be treated (Dermont et al., 2008), but also assists in recovery of Se from soil (Wadgaonkar et al., 2018). Aquatic plants are usually invasive species and produce large amounts of biomass even under low nutrient conditions (Crites et al., 2014; Wu et al., 2015). These plants are known to be tolerant to mining and industrial wastewaters and are able to remove organic and inorganic contaminants (Rezania et al., 2016). Recent studies have shown that aquatic plants are also able to take up Se from solutions either as selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) (Mechora et al., 2011). Thus, phytoremediation using aquatic plants could also be used to remove Se from seleniferous soil leachate.

In a previous study of soil washing of seleniferous soils from Punjab (India), the oxidizing agents such as potassium permanganate ($KMnO_4$) and potassium persulfate ($K_2S_2O_8$) showed the highest Se removal efficiency (around 40–50%) from these seleniferous soils (Wadgaonkar et al., submitted). After soil washing, a post treatment is usually

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required to either treat or recover chemicals and heavy metals from the soil leachate. The most common techniques applied to treat soil leachates are precipitation, coagulation and ion exchange (Reynier et al., 2015). But these techniques can be costly and may involve the use of more chemicals. This study combines soil washing procedures with phytoremediation of the soil washing leachate using aquatic plants. The aim of this research was to evaluate the efficiency of the aquatic plants *Lemna minor* and *Egeria densa* for the phytoremediation of Se from seleniferous soil leachates. Different parameters such as Se concentration, soil leachate composition and the effect of oxidizing agents on Se removal and Se uptake by plants has been evaluated.

2. Materials and methods

2.1. Soil washing

Soil was collected from the northwest region of India in the state of Punjab. The geographical co-ordinates of the sampling location are 31° 07′ 45.5″N and 76° 12′ 43.1″E. The soil was collected from a sampling depth of 0–22 cm of the agricultural region. The soil was air-dried, sieved and stored at room temperature for further analysis.

The soil washing procedure was performed according to the procedures mentioned by Wadgaonkar et al. (submitted). Briefly, 2 g soil was washed with 20 mL of 0.1% oxidizing agent. Soli washing was performed using two oxidizing agents, i.e. $KMnO_4$ or $K_2S_2O_8$ separately. The mixing was provided during soil washing at ambient temperature in a rotary shaker (Model: INNOVA 2100, New Brunswick Scientific, New Jersey, USA) at 150 rpm for 6 h. Similarly, 2*g* of soil was washed with 20 mL milliQ (MQ) water as control. After washing, the solutions were centrifuged at 4550*g* at 20 °C and the supernatant was filtered through 0.45 µm cellulose-acetate filters. The composition of the filtrate was analyzed (Table 1) and was applied for formulation of the composition of artificial soil leachate for further studies.

2.2. Collection and growth of plants

Aquatic plants, *L. minor* and *E. densa* were collected from a private aquarium and an Aquariumshop (Romberg, the Netherlands), respectively. The plants were grown in 5 L buckets with diluted Hoagland solution in a laboratory greenhouse for two weeks prior to exposure to selenium containing effluent. The temperature in the greenhouse varied between 25 and 30 °C and light was provided with a minimum light intensity of 100 µmol $m^{-2} s^{-1}$ photons. The composition of the Hoagland solution was based on Megateli et al. (2009) as follows (in mg L^{-1}): $Ca(NO_3)_2{\cdot}4H_2O$ (118), KNO_3 (5), $MgSO_4{\cdot}7H_2O$ (5), KH_2PO_4 (0.68), $FeSO_4{\cdot}7H_2O$ (0.3), K_2SO_4 (0.35), H_3BO_3 (0.3), $MnSO_4{\cdot}7H_2O$ (0.15), $ZnSO_4$ (0.022), $CuSO_4$ (0.008), $NiSO_4{\cdot}7H_2O$ (0.005), $Na\text{-}WO_4{\cdot}2H_2O$ (0.00179), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.00128), $CoCl_2{\cdot}2H_2O$ (0.004). All analytical-grade chemicals used for soil washing were purchased from Merck. The plants were then harvested to assess the effect of Se exposure under varying conditions.

Table 1
Macro and trace element composition of the soil leachates using MQ water as well as $KMnO_4$ and $K_2S_2O_8$ washing solutions.

Elements	MQ water	$KMnO_4$ soil washing	$K_2S_2O_8$ soil washing
Macro elements (mg L^{-1})			
Na	6.09 ± 0.07	6.42 ± 0.34	7.10 ± 0.62
Mg	6.64 ± 0.02	7.29 ± 0.21	18.02 ± 0.49
Al	0.69 ± 0.08	0.13 ± 0.04	0.057 ± 0.02
K	6.18 ± 1.65	88.8 ± 1.63	130.81 ± 7.04
Ca	11.76 ± 0.06	8.54 ± 0.38	33.49 ± 0.67
Fe	0.88 ± 0.22	0.22 ± 0.10	0.065 ± 0.04
Cl^-	13.11 ± 1.02	4.06 ± 0.66	28 ± 0.05
NO_3^-	1.73 ± 0.75	1.69 ± 0.68	1.1 ± 0.20
SO_4^{2-}	3.77 ± 0.28	5.58 ± 0.31	151.41 ± 8.26
PO_4^{3-}	0.45 ± 0.03	0.38 ± 0.02	0
Trace elements (µg L^{-1})			
Se	43.00 ± 1.40	130.0 ± 3.5	90.0 ± 0.8
Mn	20.55 ± 2.47	46.80 ± 19.66	39.95 ± 37.55
Cr	1.60 ± 0.14	39.60 ± 0.14	0.95 ± 0.21
Co	0.35 ± 0.07	0.35 ± 0.07	0.45 ± 0.35
Ni	2.25 ± 0.07	1.75 ± 0.21	1.55 ± 0.07
Cu	22.20 ± 0.28	28.80 ± 3.68	18.50 ± 1.98
Zn	12.00 ± 0.28	9.60 ± 3.11	16.25 ± 6.43
Cd	less than 0.10	0.13 ± 0.04	0.10 ± 0.14
Pb	0.70 ± 0.14	0.30	0.10 ± 0.14
As	13.70 ± 2.40	4.0 ± 0.3	3.5 ± 1.2

2.3. Experimental design

For the experiments in the Hoagland solution, the plants were exposed to increasing Se concentrations (50, 100 and 500 µg L^{-1} SeO_4^{2-}). For each test, 1 g (wet weight) of each plant was exposed to 100 mL solution in 135 mL transparent plastic cups. All the experiments were performed in duplicate. After one week of exposure and daily visual inspection, the plants were harvested and dried at 70 °C overnight for further analysis. The volume of the solution of each bucket was measured after the experiment to recalculate the Se final concentration.

The artificial soil leachate was prepared to mimic the composition of the solution of the soil washed with MQ water, $KMnO_4$ or $K_2S_2O_8$ (Table 2). Heavy metals were excluded from the artificial soil leachate in order to study exclusively the effect of the oxidizing agents on the selenium removal efficiency by the aquatic plants. The pH of the artificial soil leachate was maintained at 7 by the addition of carbonate as Na_2CO_3.

Before the experiments in soil washing leachate, the plants were grown in the prepared medium (without Se) and then exposed to different soil washing solutions for 7 days. These contained 100 µg Se L^{-1} of SeO_4^{2-} with varying $MnSO_4$ (0, 0.5, 1 and 2 mg L^{-1}), $K_2S_2O_8$ (0, 1, 5, 100, 500 mg L^{-1}) or SO_4^{2-} (0, 50, 100, 500 mg L^{-1}) concentrations. An experiment was done using 1 g of *L. minor* exposed to 100 mL real soil leachate of the soil washed with MQ water for 7 days.

2.4. Calculations

The Se removal efficiency (%) was calculated by the difference between the initial Se concentration and the concentration of Se remaining in solution (mg L^{-1}), according to:

$$\text{Removal efficiency} = \frac{\text{Se inital} - \text{Se day 7}}{\text{Se initial}} \times 100 \quad (1)$$

The bioconcentration factor (BCF) was calculated by measuring the Se concentration in the plants (mg kg^{-1} dry weight) divided by the initial Se concentration (mg L^{-1}), according to the following equation:

Table 2
Chemical composition of artificial soil washing leachate.

Salt	Concentration (mg L^{-1})
KNO_3	6.50
Na_2CO_3	3.00
$MgSO_4$	4.00
$MgCl_2{\cdot}6\ H_2O$	45.00
KH_2PO_4	0.40
$CaCl_2$	30.0
$FeSO_4{\cdot}7\ H_2O$	1.00
$MnSO_4{\cdot}7\ H_2O$	0.10
$NiSO_4{\cdot}7\ H_2O$	0.01
$CuSO_4{\cdot}5\ H_2O$	0.09
$ZnSO_4{\cdot}7\ H_2O$	0.06