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Palladium Phytoremediation and Phytomining Potential of Vetiver Grass (*Chrysopogon Zizanioides*)

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Levels of palladium in the environment are on the rise due to anthropogenic activities. There is a need to remediate contaminated environments, while also recovering the precious metal (Pd(II)) in a cost-effective and environmentally friendly manner. The leading contributor of Pd and other catalytic metal pollution in the environment is the automotive industry where platinum group metals (PGMs) are used in catalytic converters. Recently, there is renewed interest in platinum and other PGMs due to their use in the cathode of fuel cells for hydrogen generation. In this study, the phytomining and phytoremediation potential of vetiver grass (*Chrysopogon zizanioides*) was investigated by assessing its removal and accumulation of Pd, and its tolerance towards elevated Pd concentrations. Vetiver grass was grown in Pd solutions with concentrations ranging from 10 – 120 ppm. The grass was harvested after a period of 20 d and separated into roots and shoots. The removal efficiency of Pd ranged from 80 % at 10 ppm initial concentration to 20 % at 120 ppm. The removal of Pd from the solution and accumulation in the plant was influenced by the initial Pd concentration. The highest accumulation achieved was 0.4 mg g^{-1} dry weight (DW) in the roots at 120 ppm. Low translocation factors < 1 suggested that Pd was mainly kept in the roots of vetiver grass. The toxicity of Pd to vetiver grass was observed at concentrations >20 ppm as demonstrated by the reduced growth and drying up of the aerial biomass of the grass. The results revealed that vetiver grass may have potential in the phytoremediation and recovery of palladium for reuse by burning and reprocessing of ash.

1. Introduction

Palladium falls under the six chemical elements collectively referred to as platinum-group elements (PGE) or platinum group metals (PGM). Platinum and palladium are the most commercially important because of their extensive use in catalytic converters in the automotive industry to combat toxic emissions from vehicles (Gunn, 2014). They are extremely rare on the earth's crust with the concentration of palladium and platinum both around 5 ppb (Lorand et al., 2008). Despite their short supply, there has been an increase in PGM pollution directly and indirectly through several anthropogenic activities. The largest anthropogenic contribution of palladium to the environment is from catalytic converters in vehicles. PGMs (platinum, palladium, and rhodium) are used as the catalytic active component (Zimmermann et al., 2005). These precious metals are constantly being released into the environment during the operations of automobiles (Ravindra et al., 2004).

Some PGM-chlorinated salts are highly toxic, allergic, and there have been reports of damaged DNA due to exposure to PGMs (Gagnon et al., 2006). Some researchers have suggested that palladium is the most toxic of the PGMs (Havelkova et al., 2014). The high risk posed by palladium is accounted to its rapid mobility and high bioavailability, which is comparable to that of zinc (Ek et al., 2004). The continuous increase of PGMs in the environment poses a great public health and biosphere threat as the toxicological and ecotoxicological danger of these metals is not yet known (Botre et al., 2007).

Conventional recovery methods such as pyrometallurgical and hydrometallurgical processes have been applied. While these methods are economically viable for remediating sources with high PGM concentrations, their downside is that they are not economical at low PGM concentrations, and they produce large quantities of

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secondary wastes (Das, 2010). In the search for cost-effective and environmentally friendly techniques, phytoremediation is an attractive option. Phytoremediation is the use of plants and associated microorganisms to remediate the environment (Golubev, 2011). Vetiver grass has received great attention in this field because of its tolerance towards high levels of heavy metals and harsh environments. It also has characteristics that make it a good fit for phytoremediation, such as deep and dense roots system and high biomass (Oshunsanya and Aliku, 2017). It has been successfully used in the remediation of heavy metals such as Cr(VI) (Masinire et al., 2020).

The current study aims to investigate the potential of vetiver grass in the decontamination and recovery of Pd(II).

2. Experimental

2.1 Material and methods

Vetiver grass used during this study was obtained from Hydromulch (Pyt) Ltd (Johannesburg, South Africa). 1000 ppm Pd in 0.5 N nitric acid from Labcon was used to prepare 10, 20, 40, 80 and 120 ppm of Pd(II) is water in 2 L pots.

2.2 Experimental methods

Upon collection, the grass was cut short for ease of transportation. The grass which was originally planted in soil pots was transferred to a water medium. Care was taken when detaching the roots from the soil to avoid damages to the roots and the shoots. The grass was placed in water for two weeks to acclimatize. To facilitate the growth of roots and shoots macronutrients were added. After acclimatization, vetiver grass was washed with running tap water and rinsed with deionized water, the shoot length was adjusted to 45 cm and two vetiver slips were transferred to 2 L pots for the commencement of the study.

The reduction in water levels in the pots was accounted to uptake by the plants and evaporation. It was assumed that the water vapor did not carry any Pd(II) to ensure that pot concentrations were not affected by evaporation, water was topped to the 2 L mark and mixed well before sampling. Solution samples were taken at an interval of 2 d. 1 mL solution was taken from each pot using syringe filters, followed by dilutions using deionized water making sure the concentration stayed within the detection limit.

The grass was harvested at the end of the study. Vetiver grass was washed with running tap water, rinsed with deionized water, and it was separated into roots and shoots, the root crowns were discarded because of the assumption that they do not accumulate any metals (Ladislas et al., 2013). The harvested grass was oven-dried at 70 °C until it was completely moisture-free. The dry grass was ground using a mortar and pestle. Trace palladium metals were extracted from the plant samples using acid leaching, 0.1 g of each sample was digested using nitric acid and hydrogen peroxide over a period of 48 h (Masinire et al., 2021). The digestate was filtered using 0.45 μm syringe filters, to recover the leachate. The filtrate was mixed with 10 mL deionized water before the analysis for palladium.

2.3 Analytical method

Palladium concentration in the pots was determined using Atomic Absorption Spectrometry, AAnalyst 400 spectrometer fitted with S/N 201S8070301 Autosampler Model 510. It used an air-acetylene flame, PerkinElmer Lumina Pd hollow cathode lamp at a wavelength of 244.79 nm, with corresponding energy of 79. Plant samples were analysed for total Pd using SPECTRO Analytical Instruments Genesis (ICP-OES) Spectrometer (Perkin-Elmer, Johannesburg).

2.4 Bioaccumulation factor (BAF) and Translocation factor (TF)

BAF is the quotient of Pd concentration in the roots (mg g $^{-1}$) and initial pot concentration (ppm), TF is the quotient of Pd content in the leaves and Pd content in the roots (mg g $^{-1}$). BAF is calculated on a dry weight basis using Equation 1 (Yoon et al., 2006) and TF is calculated using Equation 2 (Ali et al., 2013).

$$BAF = \frac{C_{root}}{C_{solution}} \tag{1}$$

$$TF = \frac{C_{shoot}}{C_{root}} \tag{2}$$

where C_{root} is the concentration of Pd in the roots, $C_{solution}$ is the initial pot concentration, and C_{shoot} is the concentration of the metal in the leaves.

3. Results and discussion

3.1 Pd(II) removal from solution

The removal efficiency of Pd(II) at different initial concentrations is shown in Figure 1. Vetiver grass exposed to 10 ppm Pd(II) achieved the highest removal efficiency of 80 % after 20 d and the lowest removal efficiency of 20 % was recorded at the initial concentration of 120 ppm The removal efficiency decreased as the initial concentration increased, however, the amount of palladium removed from the pot increased with the increased in initial concentration (Table 1). Similar findings were reported by Lesniewska et al. (2004), where the uptake of PGMs (Pd, Pt, and Rh) increased with the increase in initial concentration. They recorded a Pd(II) concentration reduction of 1.38 ppm from 4.41 ppm, and a reduction of 6.5 ppm from 21.6 ppm initial concentration. However, they reported that these changes were not only attributed to the uptake by the plants but also due to the precipitation or adsorption of the studied metals to the walls of the pots (Lesniewska et al., 2004). At higher initial concentration there is more plant-metal contact which results in higher metal uptake.

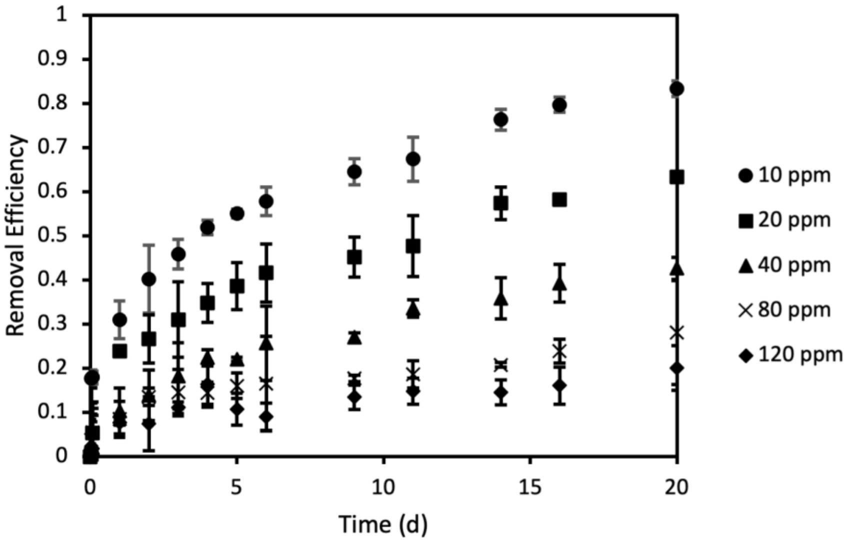

Figure 1: Palladium removal efficiency at different initial concentrations.

Table 1: Results obtained from solution samples at day 20.

Target Initial concentration (ppm)	Recorded initial concentration (ppm)	Final concentration (ppm)	Removal efficiency (%)	Removed Pd (ppm)
10	9.78	1.63	83.3	8.33
20	19.2	7.02	63.4	12.2
40	37.5	22.3	42.7	16.0
80	79.4	57.1	28.1	22.3
120	119.5	95.9	20	24.0

3.2 Pd(II) accumulation in vetiver grass

The solubility of palladium is naturally low, its concentration in plants worldwide is estimated to be less than 10 ng g^{-1} (Aquan, 2015). In this study, the concentration of palladium in the roots and leaves of vetiver grass increased with an increase in initial pot concentration. Much more Pd was accumulated in the roots compared to the amount of Pd in the leaves (Figure 2a). The amount of Pd accumulated in the roots significantly increased with initial concentration, at 120 ppm the roots accumulated 0.4 mg g^{-1} which is almost twice the amount of Pd accumulated in the roots at 80 ppm (0.21 mg g^{-1}).

A small portion of the accumulated Pd was translocated to the leaves, the roots immobilized larger amounts of Pd restricting their movement to the aerial parts, this was consistent with what was reported by other researchers regarding other PGMs like Pt (Farago and Parsons, 1986). The concentration of Pd in the shoots was low compared to the concentration in the roots, this may have been as a result of the binding of Pd to pectin and the protein fraction of the root cell walls leading to minimum translocation to the aerial parts (Verkleij et al., 1991). Similar findings were reported by Lesniewska et al. (2004), where the leaves of *Lolium mutiflorum* only accumulated about 0.05% of the Pd accumulated in the roots, which they suggested that the majority of the Pd was only adsorbed on the surface of the roots and only a little amount was available for translocation to the aerial parts of the plant. Figure 2b shows the bioaccumulation factor (BAF) and translocation factor (TF) of palladium in vetiver grass at different initial Pd(II) concentrations.

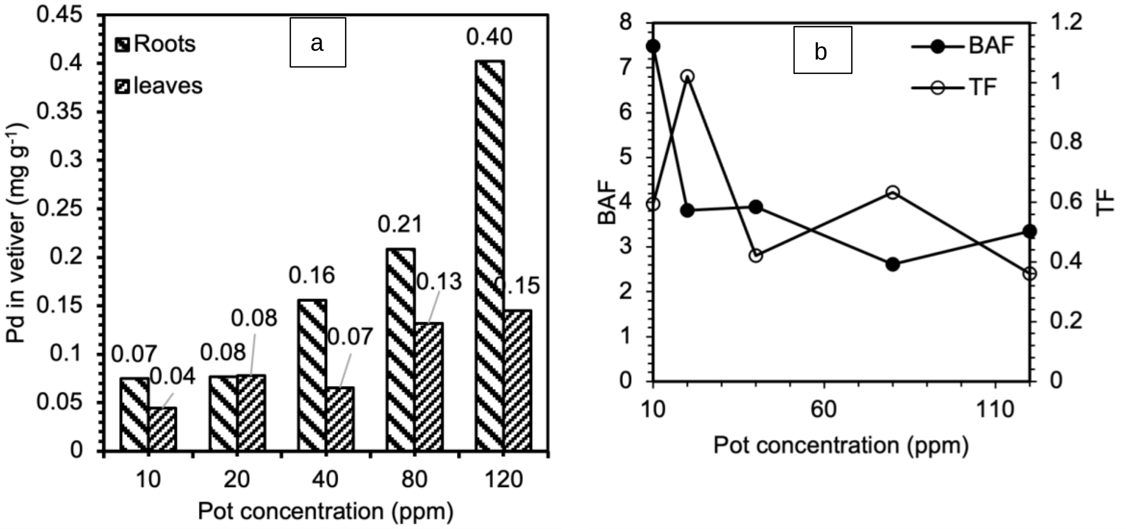

Figure 2: Distribution of palladium (Pd) in the roots and shoots of vetiver grass at different initial concentrations (a). Bioaccumulation (BAF) and Translocation factor (TF) of palladium at different initial concentrations (b).

Both the TF and BAF are important parameters in determining the phytoremediation/phytoextraction potential of a plant, their values decreased as the initial concentration increased (Figure 2b). For phytoremediation, a plant should have BAF greater or equal to one, and for phytoextraction/phytomining both BAF and TF must be greater than one (Yoon et al., 2006). The bioaccumulation factor (BAF) was above 1 at different initial concentrations indicating that vetiver grass is able to accumulate Pd to levels above the solution concentration. However, lower TF values indicate that the larger part of the accumulated Pd was retained in the roots of vetiver grass. Plant roots have been known to counteract Pd exposure stress through mechanisms including restricting Pd uptake by the synthesis and deposition of callose (Egorova et al., 2019). It has been reported that a longer exposure time results in more Pd being translocated to the aerial parts of the plants (Kińska et al., 2018). According to Aquan (2015), the threshold level of Pd hyperaccumulation in plants is expected to be 1000 ng g^{-1}, compared to 10 ng g^{-1} in normal plants, since Pd is poorly soluble in soil, and it is not naturally available to plant. Vetiver grass had Pd concentrations above 1000 ng g^{-1} in both roots and shoots showing that vetiver grass can hyperaccumulate palladium.

3.3 Plant reaction to palladium

The different concentrations of Pd affected the growth of vetiver grass (Figure 3). Although adverse toxic effects of Pd(II) were experienced by the grass at concentrations above 40 ppm, vetiver grass showed the ability to tolerate Pd in its aerial parts. After 20 d the aerial parts of vetiver grass planted in 40, 80, and 120 ppm had dried out completely. Pd affected the growth of vetiver grass at all the different initial concentrations. At the end of the experiment, the grass exposed to 80 and 120 ppm Pd(II) had a final length of 45 cm, indicating that the was no growth at these high Pd(II) concentrations. At 20 and 40 ppm initial concentration the grass grew by 3 cm to a final length of 48 cm. At 10 ppm the grass had a final length of 52 cm. The control grass which was planted in a pot with 0 ppm initial concentration had a length of 78 cm, showing that the growth of vetiver grass was inhibited at all the different concentration levels.

The content of chlorophyll is a representation of a plant’s photosynthetic capacity (Zhao et al., 2020). Metal stress can directly affect the chlorophyll content, affecting the photosynthetic activity, and subsequently the growth of the plant (Maksymiec et al., 2007). After a period of one week, the leaves at 120 and 80 ppm started to wilt, showing signs of chlorosis, and eventually dried up by the end of the second week. However, the roots remained active up to the end of the experiment as indicated by the continuous reduction of Pd concentration in the pots and much higher accumulation in the roots. The same effects were observed in plants exposed to different concentrations of heavy metals (Kińska et al., 2018, Masinire et al., 2020).

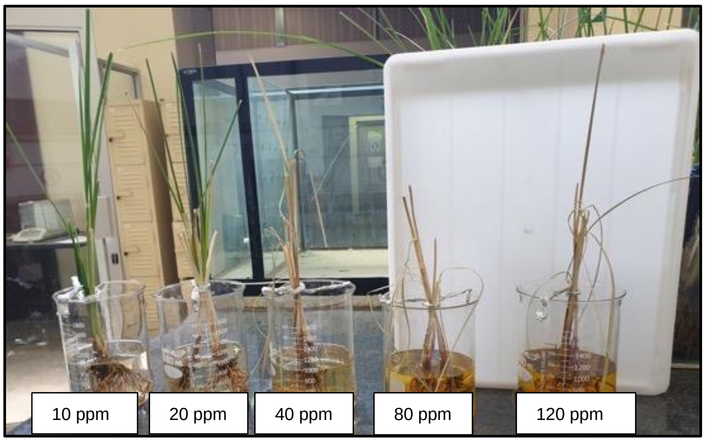

Figure 3: Reaction of vetiver grass to different initial concentrations after 20 d.

4. Conclusion

The results obtained confirm the Pd hyperaccumulation capacity of vetiver grass *(Chrysopogon zizanioides)*, because the accumulated Pd in both the roots and leaves was significantly higher than 1000 ng g^{-1}. It has shown to be a good candidate for phytoremediation of Pd(II) as the BAF values were above one for all the concentrations. However, from the current study vetiver grass isn't well suitable for the phytomining/ phytoextraction of Pd because most of the accumulated palladium is retained in the roots. For phytoextraction, the plant must accumulate higher amounts of the Pd to aerial parts that can be harvested easily for the recovery of Pd. Vetiver grass is tolerant to Pd contamination, however, at concentrations above 40 ppm the adverse effects of metal Pd poisoning results in the drying up of the grass.

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