

PATHWAYS FOR THE BIOREMEDIATION OF VANADIUM FROM THE SOIL-PLANT ECOSYSTEM

Abstract

The process of removal of toxins from the environment is termed as bioremediation. The native microorganism in the environment has a key role in lowering the concentration of toxins. The environmental condition in a particular area has a great influence on bioremediation technique. Degree of pollution, pollution type, cost, location is some factors on which bioremediation technique is based. Biological remediation technologies are also considered as environmentally friendly steps to treat polluted soils. Vanadium is an important mineral for various processes in industries, from the last few decades its mining has been increased to many folds which eventually shows its toxic effect on plants, humans and animals. This overview reflects various bioremediation Pathways for vanadium. Vanadium presents in various forms (chemical) in soil environment majorly Vanadium (V) and Vanadium (IV). Factors like soil p^H , organic matter, redox potential and microorganism affect the biogeochemical behavior of Vanadium in the soil environment. The objective of this overview is about various processes of remediation of vanadium from the soil ecosystem including microbial bioremediation. Metabolism in plants with many associated biological processes is also discussed. Lastly, advanced methods of bioremediation of vanadium are discussed which include microbial remediation.

Keywords: Vanadium, Bioremediation, Microbial Remediation.

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I. INTRODUCTION

The fifth most common element in the crust of the Earth is vanadium (V), which has been widely mined in China, South Africa, North America, and Russia [1]. The earth's crust contains vanadium in a number of valence states, with vanadium (V) being the most prevalent (e.g., -3, -2, 0, +2, +3, +4, and +5) [2]. Vanadium causes major environmental and health problems to humans, plants and animals. Major Sources of vanadium are the mining and industry. Fertilizers, pesticides, livestock manure, wastewater are the sources in the agriculture sector. Vanadium accumulated in soil shows its adverse effects. Low concentrations of vanadium are beneficial for plant growth and play biological roles in plants, such as boosting the levels of amino acids, sugars, and chlorophyll[3][4]. High (i.e. hazardous) levels of V in soils, on the other hand, harm plants by causing chlorosis and stunted growth [13]. Plants such as *Setaria viridis*, *Phaseolus vulgaris* L, and *Zea mays* L, are potential V hyper accumulators and can absorb and translocate high amount of vanadium from roots to shoots [7][8][22]. In order to lessen the toxicity of V, plants have developed efficient detoxifying processes, including precipitation in roots, adherence to cell walls, & localization in the apoplast. [13]. Therefore, there is an urgent need for a thorough understanding of the biogeochemical behavior of V and the phytotoxicity of excessive V in the soil-plant system. The goal of Bioremediation techniques is to restore polluted environments in an eco-friendly manner. There are various techniques of bioremediation modeled around the type and nature of pollutants. Native microorganisms present in polluted environments help in solving most of the bioremediation and biodegradation problems of polluting substances. Cost saving and Eco-friendly are the key features of bioremediation in contrast to various chemical and physical processes. When we consider the area related to application, bioremediation techniques are divided into two groups ex situ and in situ. There are many factors which affect the success of a bioremediation technique e.g. (oxygen, pH, nutrient concentration, temperature and abiotic factors) are the factors that are determined prior to the bioremediation process. Most of the techniques are focused on the pollution of soil and groundwater.

II. THEORY

1. Vanadium in the Soil: Vanadium was first discovered in 1801 by Spanish-Mexican mineralogist Andres Manuel del Rio being a constituent of the brown lead mineral ($Pb_5(VO_4)_3Cl$) [1]. In the natural world, vanadium can be found in bauxite, igneous rocks, sandstone, titaniferous magnetites, and uranium deposits. It is widely used in industries such as steel, battery, and pharmaceutical industries. In 1960, the world's vanadium mining production was 70,900 tons, but by 1970 it had climbed to 194,960 tons. Mineral resources for vanadium are mostly found in the USA, China, Russia, and South Africa. South Africa was the global leading generator of the mineral V before 2000. with the country's output making up around 50% of the total global production [10]. Though China has recently been the world's top producer of the mineral V, its 410,000 tons of mined V in 2014 represented 53% of the world's total V production. China has also become the largest V user in the meantime because of the rapid growth of its steel sector [1]. Nevertheless, industrial discharge and mineral mining increase the risk of V contamination in soil. Understanding the biogeochemical behavior of vanadium in the soil-plant system and the risk of V contamination in the soil environment are therefore critical. High-temperature industrial activity, like mining, burning of industrial waste,

applying fertilizer and insecticides, all contribute significantly to the deposition of V on soils. Of these activities, mining and industrial activities are the main contributors to V pollution [1]. Furthermore, the environment faces a greater threat from the disposal of solid waste that contains V [1][13]. Volcanic activity, rock weathering, and atmospheric deposition are the other natural sources of vanadium in the environment [12].

- 2. Permitted Levels of Vanadium in Soil:** Different types of soil have varying ranges of allowable Vanadium concentrations. The average value of concentration of vanadium in soil is estimated to be 108 mg/kg. 130 mg/kg is the soil V recommended value given by Canadian researchers (CCME, 2007). For circulatory plants and soil invertebrates, the standard value of soil V (130 mg/kg) also falls within the optimal soil V range. (CCME, 2007). The permissible level for V in soils is 130 mg/kg according to the Environmental Quality Specification (GB-15618-2008) in China.. Similarly, many other countries also developed a similar kind of allowable levels for vanadium in soil for e.g The Czech Republic (180 mg/kg), Slovenia (120 mg/kg), & the Netherlands (42 mg/kg) [14].

Table 1: Vanadium Level in Soil Samples from Various Nations (Mg/Kg) (Chen, Li, Et Al. 2021)

Country	Vanadium Concentration	Data Source
Japan	94 (Gleysols)	Takeda et al., 2004
China	87.36	Yang et al., 2017b
United States of America	36	Guagliardi et al., 2018
Russia	79-91	Protasova and Kopayeva1985
Finland	79	Koljonen, 1992
Italy	34	Cicchella et al., 2015
Denmark	31	Baken et al., 2012
Europe	25	Reimann et al., 2014
Poland	18.39	Dudka and Market, 1992
Portugal	32	Ferreira et al., 2001

- 3. Impact of Microorganism on Vanadium:** Soil fertility is greatly affected by the microorganism present in the soil .They help in sustaining the fertility of soil and plant growth. Additionally, microbes can influence environmental complexation, adsorption-desorption, reduction and oxidation and precipitation reactions are examples of Vanadium biogeochemical processes.. Microbes may have had an impact on the geochemical behavior of V (V) because it's been precipitated through microbial metabolism in anoxic settings and adsorbed upon suspended particles, according to [16]. Additionally, microorganisms can speed up the conversion of V (V) to V (IV), changing the geochemical behavior of V.(V). According to, microorganisms were crucial to the process of V(V) reduction in microbial fuel cells with biocathodes. Many microorganism were found that have reducing potential for e.g. Pseudomonas [17], Acidithiobacillus ferrooxidans [18], Geobacter metallireducens [19], Methanosarcina mazei , Lactococcus and Enterobacter [16], Rhodocyclus and Proteobacteria [9].
- 4. Absorption of Vanadium By Plants:** Due to increasing V-mining, industrialization activities in recent years and its harmful effect on plant and human health studies are now

focused on vanadium [13]. As a result, measuring the quantity of Vanadium absorption by flora in land-plant systems has emerged as a key issue for risk assessment and soil remediation. Multiple heavy metals, including V, can be absorbed by plant roots; however, it is unclear how Vanadium is absorbed by plant roots. Vanadium is primarily taken by plant roots from the soil through the same transporters as other crucial plant nutrients [21]. For e.g. Green beans and dog tail grass were potential Vanadium hyper-accumulators as their shoot tissues absorb a lot of V [6]. According to Studies, V treatment inhibits plant biomass and reduces P uptake in the leaf tissues of *C. lanatus*. (Thunb). It was discovered that treating *Setaria viridis* seedlings to significant amounts of V greatly reduced the accumulation of Phosphorus and Iron, implying that these elements competed for plant absorption and assimilation. Also, liquid digestate with high amounts of minerals, humic and fatty acids can considerably reduce V uptake by dog's tail grass and mitigate the deleterious effects of V poisoning on the germination of seeds and development of seedlings. Because alkaline pH promotes the mobility and possible availability of Vanadium in the soil-plant system, high pH increases V uptake by plants [23]. Furthermore, additional research has shown that increased CEC (cation exchange capacity) improves V uptake in the shoots of *Setaria viridis* when soil V concentrations are lower than allowable limits [24].

5. **The Ability of Plants to Accumulate Vanadium:** The ability of plants to accumulate metals is a crucial component of phytoremediation. Plants with higher bioaccumulation factors (toxic amount of metal in plant aerial regions / toxic metals levels within corresponding soils > 1) as well as transfer factors (toxic metal amounts in plant aerial parts / toxic metal concentrations in plant roots > 1) are better able to remove toxic metals from contaminated sites. Hyperaccumulators would ideally develop quickly and produce large amounts of biomass, particularly shoot biomass. However, the vanadium concentrations required to classify plants as vanadium the hyperaccumulators are yet to be identified. Meanwhile, there are fewer plants than for other dangerous metals like cadmium, lead, zinc, copper, or manganese that can store, translocate, along with survive high doses of V. *Setaria viridis*, a potential V hyperaccumulator, has been observed to accumulate up to 1100 mg V kg⁻¹. *Zea mays* L. and *Phaseolus vulgaris* L. were also recognised as possible Vanadium hyperaccumulators [6, 8]. Highly toxic metals are changed inside hyperaccumulator plants into less hazardous and immobile forms, which lowers toxic V stress while enhancing metal accumulation. Vanadium accumulation by plants primarily depends on three processes: 1. improved compartmentalization and bio-transformational plant tolerance to vanadium stress. 2. enhanced root exudate production, which raised the amount of bioavailable vanadium in the rhizosphere soil. 3. Enhanced xylem loading results in increased vanadium absorption and transport via root to shoot tissues.
6. **Vanadium Benefit:** Although they are not deemed necessary, beneficial elements can have a good impact on seed germination, blooming, and plant development [27]. All plants contain small levels of the metal vanadium. Vanadium is often found in plant soil. Plants with low levels of V stimulate their physiology and growth. Tomato plants' height, biomass, number of leaves, flowers, and rate of Fe metabolism were all boosted when 0.25 g L⁻¹ V was applied [28]. The shoots and roots of sweet basil (*Ocimum basilicum* L.) were given doses less than 40 mg L⁻¹ V to increase their dry mass [29]. When 0.59 mg L⁻¹ vanadium was applied to pepper plants, it led to a rise in plant height, number of

leaves, stem diameter, fresh weight of shoot and root, and mineral element uptake of potassium, magnesium, nitrogen, calcium, copper, manganese, and boron. It also led to an increase in amino acid and total sugar concentrations Garca-Jiménez et al. (2018). Furthermore, V imparts increased flexibility to the tissue, allowing for greater water volume, which is connected with cell expansion, allowing plants to develop faster.

7. **Vanadium Toxicity:** In general, low levels of Vanadium promote plant growth and development, but excessive levels of V have a negative effect by impairing critical plant processes [1]. Vanadium speciation, plant species, and V dose are the main determinants of its detrimental effects on plants. The developmental and physiological processes of plants, including seed germination, root and shoot development, photosynthesis, and nutrient absorption, may be negatively impacted by high levels of V.
8. **Effect on Seed Germination:** Seed germination is decreased as a result of V poisoning. Because germination catalysts only function optimally within a specific pH range, and pH values outside of that range prevent them from working, pH variations have a significant impact on seed germination. The germination process is impacted by soil pH changes brought on by vanadium contamination.
9. **Root Biomass:** It is not surprising that vanadium stress slows root development because vanadium preferentially aggregates in plant roots [31]. According to research on *Brassica juncea* L., *Opuntia microdasys*, and *Cicer arietinum* L., vanadium has been demonstrated to decrease root biomass. [11, 32]. Membrane lipid peroxidation, membrane integrity degradation, and suppression of mitotic cell division all result in a significant decrease in root development well as growth. Decreased root biomass under V stress indicates a considerable decrease in root volume, which finally leads to decreased cell division and suppression of shoot development [33]. Additionally, at dangerous concentrations, V transfer from a plant's root to a shoot interferes with physiological processes associated to phosphate, transpiration, and photosynthesis, which retards the growth of the plant.
10. **Photosynthesis:** For a plant to grow and flourish, photosynthesis is necessary, but it is also extremely prone to abiotic stress, especially V stress. Regarding the production of carbon dioxide, lipid peroxidation, electron transport, and photophosphorylation, water uptake, and nutritional intake, excessive levels of V may be detrimental to photosynthesis in plants [32]. The amount of chlorophyll in the leaves, including chlorophyll-a, chlorophyll-b, along with carotenoids, is reduced by excess vanadium; this stress is significantly impacted by the concentration, speciation, type of plant, and other environmental variables of V. *Ipomoea aquatica* Forsk, *Brassica juncea* var. *gracilis*, and *Cuphea viscosissima* [34] have all shown comparable drops in the amount of chlorophyll in the leaves.

III. BIOREMEDIATION TECHNIQUES

The exploitation of plants or microbes to repair environmental contamination and safeguard human health is known as bioremediation. Plants are typically employed to eliminate or stabilise hazardous materials in polluted soil, whereas microorganisms break down toxic compounds or change harmful substances into other, harmless ones [9].

- 1. Phytoremediation:** Because it is low-cost, ecologically benign, and can be spread over broad regions, phytoremediation is a potential approach for eliminating V from soils [35]. Nonetheless, phytoremediation has certain drawbacks in practice, such as a lengthy remediation cycle and invalid treatment in deeply polluted soil. Phytoextraction and phytostabilization are two of the most used phytoremediation processes. Phytoextraction is mostly used on soils with significant V contamination. Vanadium-contaminated soils can be removed from the area using phytoextraction, which involves using plants to move the metal from the soil into the tissues of above-ground plants. The ability of hyperaccumulator plants to absorb significant amounts of V from the soil and then transfer it to aboveground plant tissues makes them crucial for phytoextraction. According to Aihemaiti et al. (2017), *Setaria viridis* had a potent capacity for accumulating V from soils. The fact that the plant grows well in V-contaminated soil shows how resilient it is to V stress [7]. The possibility for *Setaria viridis* to function as a V hyperaccumulator.
- 2. Phytostabilisation:** A technique known as phytostabilization prevents excessive concentrations of metal pollution from entering the food chain, thereby reducing risks to the health of humans and the environment. In metal-contaminated soil, low-accumulators are employed to phytostabilize the soil, however they frequently have high root enrichment coefficients alongside low translation coefficients. According to Vachirapatama (2011), V has a translation coefficient of 0.101 and a root enrichment coefficient of 100.25. Tomato has the potential to be a successful vanadium phytostabilizer because it is a low-accumulator, has a significant root enrichment coefficient, & a low translation coefficient.
- 3. Microbial Remediation:** Microorganisms not only have a high tolerance for toxic metals due to their tendency to interact directly or indirectly with metals, but they also have the capacity to remove high-valence hazardous metals from soils. Microbial remediation has been seen as a potential remediation approach because to its low cost, high effectiveness, and lack of secondary pollutant creation. While environmental elements like soil temperature and pH can easily have an impact on remediation approaches, they are typically challenging and time-consuming. Bio-reduction and precipitation are two promising techniques for microbial remediation of vanadium-contaminated soil [9]. Many microorganisms have been observed to reduce V(V) to V(VI) when electron donors are present. According to Zhang et al. (2019a), soil-inoculated bioreactors using indigenous microorganisms had 98.7% V(V) bioremediation efficiency after 72 hours. The phytotoxicity of vanadium in the soil-plant system rises with its valence state. Microorganisms can effectively reduce toxicity by converting V(V) to V(VI). Vanadium (V) can be removed by microbes in two separate methods. The first is intracellular reduction, where the vanadate oxyanion is first reduced by the intracellular reducing agents of microorganisms and then further diminished. The cell's vanadyl is pushed out [37]. During this process, a little amount of vanadium may gather inside the bacterial cell. No vanadium ions enter the cell during the second procedure, which involves V(V) reduction through the vanadate reductase machinery found in the cell wall [9].

IV. DISCUSSION

Growing anthropogenic activities are contaminating soil with more vanadium, which could provide a direct or indirect risk to plants, animals, and people. This study focuses on the biogeochemical behavior of vanadium in soil-plant systems and the detrimental effects of surplus vanadium on plants in order to gain a better understanding of how to correctly and efficiently deploy bioremediation methods. Different oxidation states of vanadium exist, with V being the most prevalent.(V). In the soil-plant system, microbial activity has a significant impact on V speciation and biogeochemical behavior. The vanadium uptake mechanism may be involved in vanadium absorption by plant roots, which is the first step in its introduction into the food chain. However, potential Vanadium hyper-accumulators possess the capacity to deliver substantial amounts of V to tissues above the surface. Low levels of V are essential for the proper growth and development of plants, however high levels of V accumulation in plant tissue are poisonous and delay germination, growth, chlorophyll synthesis, nutrient uptake, and cell division. In addition, V poisoning may result in an increase in lipid peroxidation. The main factors that affect V's influence, whether positive or negative, are plant species, chemical speciation, and concentration.

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