Pathways for the bioremediation of vanadium from the soil-plant ecosystem.

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##  ABSTRACT

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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 pH, 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

## 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, +, 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.

## THEORY

A. **Vanadium in the soil**

A Spanish-Mexican mineralogist named Andres Manuel del Rio made the initial discovery of vanadium in 1801 as a component of the brown lead mineral (Pb 5(VO4)3Cl) [1]. Vanadium can be found in the environment as titaniferous magnetites, igneous rocks, sandstone, uranium deposits, and bauxite. 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 V in the soil-plant system and the risk of V contamination in the soil environment are therefore critical. Anthropogenic activities such as mining, burning of industrial wastes, applying fertilizer and pesticides, and high-temperature industrial activities 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].

B. **Allowable 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. Netherlands (42 mg/kg), Slovenia (120 mg/kg), and Czech Republic (180 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 Amrica | 36 | Guagliardi et al., 2018  |
| Russia | 79-91 | Protasova and Kopayeva. 1985 |
| 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 |

C. **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].

D. **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].

E. **The ability of plants to accumulate V**

The key element in phytoremediation is plants' capacity to accumulate metals. The ability to remove toxic metals from contaminated sites is improved by plants having elevated bioaccumulation aspects (toxic metal concentrations in plant aerial parts / toxic metal levels in corresponding soils > 1) as well as translocation factors (toxic metal amounts in plant aerial parts / toxic metal concentrations in plant roots > 1). In a perfect world, hyperaccumulators would have a short development period and high biomass output, especially in the case of shoot biomass.The concentration levels of vanadium in plant tissue needed to categorize plants as vanadium hyperaccumulators have not yet been found, though. 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. A putative V hyperaccumulator named Setaria viridis has been found to accumulate more than 1100 mg V kg1 in shoot tissues. Phaseolus vulgaris L. [6] and Zea mays L. [8] were also identified as potential Vanadium hyperaccumulators. Inside hyperaccumulator plants, highly toxic metals are transformed into less toxic and immobile forms, reducing toxic V stress while boosting metal accumulation. Plant’s ability to accumulate vanadium is essentially reliant on three procedures: 3. increased plant resistance to vanadium stress by bio-transformation and compartmentalization. 1. increased bioavailable Vanadium level in the rhizosphere soil via root exudate production. 2. Increased absorption and translocation of vanadium through root to shoot tissues through enhanced xylem loading. 3.

F. **Vanadium benefit**

Although they are not deemed necessary, beneficial elements can have a good impact on seed germination, blooming, and plant development [27]. Vanadium is a metal element present in low amounts in all plants. Vanadium is typically present in the soil of plants. Low amounts of V in plants promote physiology and growth. Applying 0.25 g L-1 V increased plant height, biomass, number of leaves, number of flowers, and accelerated Fe metabolism in tomato plants, according to [28]. (Solanum lycopernici). 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]. The application of 0.59 mg L-1 vanadium increased plant height, stem diameter, number of leaves, fresh weight of shoot and root, and promoted mineral element uptake of nitrogen, potassium, calcium, copper, manganese, and boron, and increased amino acid and total sugar concentrations in pepper plants 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.

G. **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.

H. **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.

I. **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.

J**. Photosynthesis**

For a plant to grow and flourish, photosynthesis is necessary, but it is also extremely prone to abiotic stress, especially V stress. In terms of enzyme activity, lipid peroxidation, electron transport, photophosphorylation, carbon dioxide generation, 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 V; 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 similar decreases in leaf chlorophyll content.

 **Ⅳ . Bioremediation techniques**

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

A. **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 .

B. **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. Low-accumulators are used for phytostabilization in metal-contaminated soil, however they often have high root enrichment coefficients and low translation coefficients. Vachirapatama (2011) states that V has a root enrichment coefficient of 100.25 and a translation coefficient of 0.101. Because tomato is a low-accumulator and has a high root enrichment coefficient and a low translation coefficient, it has the potential to be an effective vanadium phytostabilizer.

C.  **Microbial Remediation**

Due to their potential to interact directly or indirectly with metals, microorganisms not just have a high tolerance for toxic metals but also the ability to eliminate high-valence hazardous metals from soils. Due to its low cost, high effectiveness, and lack of secondary pollutant generation, microbial remediation has been viewed as a promising remediation strategy. While environmental elements like soil temperature and pH can easily have an impact on remediation approaches, they are typically challenging and time-consuming. Two potential methods for microbial remediation of vanadium-contaminated soil are bio-reduction and precipitation [9]. Numerous microorganisms have been seen to lower V(V) to V(VI) in the presence of electron donors. Zhang et al. (2019a) found that after 72 hours, soil-inoculated bioreactors using local microorganisms achieved V(V) bioremediation efficiencies of 98.7%. As the valence state of vanadium in the soil-plant system increases, so does its phytotoxicity. V(V) to V(VI) conversion is an efficient way for microorganisms to lessen toxicity. Microbes can eliminate vanadium (V) in two different ways. 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 membrane [9].

 Ⅴ **. 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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