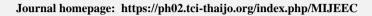


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ARTICLE

Brassinosteroid-enhanced phytoremediation for a sustainable strategy for mitigating vanadium contamination in agricultural soils

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ABSTRACT

Vanadium (V) contamination in soils, primarily from mining, industrial activities, and fossil fuel combustion, poses a significant ecological threat to plants, animals, and humans. While vanadium is an essential trace element in biological systems, excessive accumulation disrupts plant physiological processes, leading to oxidative stress, impaired growth, and reduced crop productivity. Brassinosteroids (BRs), a class of plant steroid hormones, have emerged as promising agents for mitigating heavy metal toxicity. This study explores the role of BRs, particularly 28-homobrassinolide (HBL) and 24epibrassinolide (EBL), in alleviating vanadium stress in plants. BRs enhance plant tolerance by modulating antioxidant defense mechanisms, regulating metal uptake, and activating stress-related signaling pathways such as MAPK and NADPH oxidase pathways. Additionally, BRs stimulate the production of reactive oxygen species (ROS) at controlled levels, inducing stress-adaptive responses while preventing oxidative damage. This review discusses vanadium speciation, soil contamination levels, plant uptake mechanisms, and the potential of BRs in assisted phytoremediation strategies. Understanding the molecular and physiological interactions between BRs and vanadium toxicity will provide insights into developing sustainable agricultural practices for improving crop resilience in contaminated environments.

1. Introduction

Vanadium (V), the fifth most prevalent element in the Earth's crust, is predominantly extracted in countries such as Russia, South Africa, the United States, and China (Imtiaz et al., 2015). In natural settings, vanadium can exist in oxidation states, including -3, -1, 0, +2, +3, +4, and +5, with V (V) being the most frequently encountered (Gan

et al., 2020). It is naturally found in titaniferous magnetites, sedimentary and igneous rocks, sandstone uranium deposits, and bauxite ores (Zhang et al., 2012). In addition to natural processes, the extensive use of vanadium in modern industries such as mining, fossil fuel combustion, fertilizer production, and byproducts from steel and petroleum industries serves as a significant source of anthropogenic emissions into the atmosphere (Shafer et al., 2012; Xiao et al., 2015; Liu et al., 2019). Approximately 1.32×10^8 kg of vanadium is deposited

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on land annually, contributing to the increasing detection of vanadium contamination in soils (Schlesinger et al., 2017). Vanadium concentrations in contaminated soils near mining and smelting areas in China have reached 938.4 mg/kg, 1500 mg/kg, and even 3600 mg/kg.

Due to the significant toxicity of vanadium (V) to aquatic and soil organisms and humans, its ecological risks have garnered considerable attention over the past decade (Zhang et al., 2020). Vanadium is a trace element that plays a crucial role in various biochemical processes. Low levels of vanadium (V) have a beneficial effect on plant growth and development. However, excessive amounts adversely affect plants by interfering with their essential functions (Imtiaz et al., 2017). Elevated levels of vanadium lead to stunted growth, chlorophyll breakdown, root deformities, reduced uptake and utilization of essential nutrients, inhibition, and disruption of critical enzyme activities, as well as impairment of various vital physiological processes in plants. These effects can ultimately threaten food security (Nawaz et al., 2018; Yang et al., 2017). Aihenmaiti et al., 2019; Garcia-Jimenze et al., 2018; Yang et al., 2014). Therefore, effective and economical strategies should undoubtedly be developed to reduce V stress and ensure sustainable agriculture productivity.

Brassinosteroids (BRs) are a group of plant steroidal hormones that regulate a plethora of physiological and developmental processes, such as cell division, elongation, morphogenesis, reproduction, and senescence, and have a pivotal role in strain management (Kour et al., 2021). Findings have presented that BRs help plants befitted metaltolerant, raising crop yield and quality. Brassinosteroids (BRs) minimize heavy metal uptake by modifying cell membrane permeability and activating a range of defensive enzymes, including superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), and glutathione reductase (GR). Nevertheless, the underlying mechanism by which BRs alleviate the V stress needs to be further clarified, which is the study's focus. Brassinosteroids (BRs) enhance plant metal tolerance, improving crop return and quality (Vriet et al., 2012). Among the bioactive BRs, 28-homobrassinolide (HBL) and 24epibrassinolide (EBL) play crucial roles in assisted phytoremediation by aiding plants detoxifying harmful metals. BRs limit heavy metal uptake by modifying cell membrane permeability and promoting the activity of cynical enzymes. They also encourage the synthesis of strain proteins by influencing anti-stress genetic material through increased ATPase representation. Exogenous solicitation of BRs triggers temporary H₂O₂ development, which activates MAPK pathways, leading to NADPH oxidase manufacture and the upregulation of stressrelated proteins and defensive enzymes, mitigating metal-induced stress (Jiang et al., 2012). Jiang et al. (2012) further observed that low concentrations of EBR (0.1-0.15 µM) reduced photosynthetic productivity. Similarly, Xia et al. (2014) reported that 0.1 µM EBR promoted stomatal opening, while a higher concentration of 1.0 µM caused stomatal closure.

The regulation of heavy metal toxicity by brassinosteroids (BRs) operates through several mechanisms: (a) stimulating the production of H_2O_2 , (b) reducing reactive oxygen species (ROS) via enhancement of the antioxidant defense system, (c) upregulating MAPK expression, and (d) mitigating metal toxicity by increasing levels of potassium and sodium ions, proline, antioxidants, and osmolytes (Rajewska et al., 2016). Research suggests that NADPH oxidase is a key apoplectic foundation of H_2O_2 , generated from the conversion of O_2^{-1} by

superoxide dismutase in plant cell plasma membranes. This process also elevates H+-ATPase activity by upregulating the CsHA gene (Jakubowska et al., 2017). While the uptake of toxic metals can damage plant cell membranes by promoting ROS-induced lipid peroxidation and protein oxidation, phytohormones like BRs enhance antioxidant and defensive enzyme levels, counteracting this damage and restoring normal osmoregulation. Additionally, the BR-specific inhibitor brassinazole (Brz) and the bioactive brassinosteroid 24-brassinolide (EBL) have been employed to mitigate metal toxicity and support recovery.

2. Vanadium uses and sources

Vanadium is naturally found in titaniferous magnetite, muddy and pyrogenic rocks, sandstone uranium formations, and bauxite deposits. In addition to this natural process, its emission to the atmosphere is dominantly anthropogenic due to its extensive use in modern industries, like mining, burning fossil fuels, fertilizer, and byproducts from steel and petroleum industries. Vanadium mineral sources are primarily in Russia, South Africa, China, and the United States. Until 2000, South Africa was the world's leading vanadium producer, contributing approximately 50% of global production (Moskalyk et al., 2003). However, China has taken the lead in recent years, producing 410,000 thousand tons of vanadium in 2014, accounting for 53% of global output. China is also the largest consumer of vanadium, driven by the fast expansion of its steel industry (Imtiaz et al., 2015). Significant amounts of vanadium are introduced into soils through human deeds such as mining, industrial waste incineration, using fertilizers and pesticides, and high-temperature industrial processes. (Figure. 1). The vanadium levels reached up 938.4mg/kg, 1500mg/kg, and 3600mg/kg in stained soils adjoining mining and smelting areas in China.

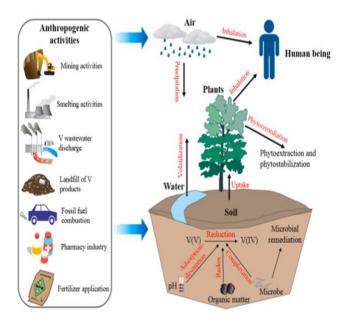


Figure 1. Vanadium within the soil-plant system

2.1 Maximum allowable levels of V in soil

The background levels of vanadium (V) in soils vary depending on the mineral alignment of the parent rocks. Globally, the average V concentration in soils is estimated at 108 mg kg⁻¹, although most regional studies report lower background values. Canadian scientists have established a soil V guideline value of 130 mg kg⁻¹ (CCME, 2007), which aligns with the optimal scale for soil, vascular plants and invertebrates. Similarly, China's Environmental Quality Standard for soil (GB-15618-2008) also recommends an acceptable V concentration of 130 mg kg⁻¹.In current years, V contamination in soils has been documented in several regions, particularly in China. Yang et al. (2017) reported that approximately 8.6% of soil trials across China exceeded the Canadian guideline value of 130 mg kg⁻¹, indicating that V contamination poses significant ecological dangers to plants, animals, and humans, especially near V-polluted mining sites. Teng et al. (2011) observed soil V levels of up to 532.1 mg kg⁻¹ around a smelting competence in Panzhihua, Sichuan Province, China. Aihemaiti et al. (2017) found V concentrations ranging from 129.8 to 754.4 mg kg⁻¹, with an average of 336.45 mg kg⁻¹, in a mining part in Shiyan City, Hubei Province, China. Similarly, Gummow et al. (2006) reported a standard soil V concentration of 622 mg kg⁻¹ near vanadium mines in South Africa, ahead to undue V collection in local wildlife and human populations.

2.2 Vanadium speciation in soil

The speciation of vanadium is crucial for assessing environmental risks and developing remediation approaches for V-contaminated soils and residues. In soils, the chemical form of vanadium influences its mobility, bioavailability, and toxicity within the soil-plant system (Tian et al., 2014; Xiao et al., 2015; Gustafsson et al., 2019). Soil pH is a key factor that regulates the chemical speciation of heavy metals in soil solutions (Reijonen et al., 2016). Studies have shown that increasing soil pH can enhance the mobilization and release of vanadium from soils (Tsadilas et al., 2010; Antoniadis et al., 2018). Furthermore, pH significantly impacts the retention of vanadium by soils, thereby influencing its chemical speciation and altering its mobility and bioavailability in soil-plant systems (Figure 2).

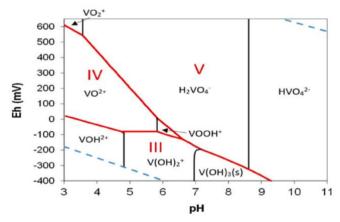


Figure 2. Eh-pH diagram of V chemical speciation formed in water (0.01 mM V concentration, 0.01 M NaCl, and 25 °C).

Soil organic matter (SOM) comprises both humic and non-humic substances and is vital for plant nutrient availability. Additionally, it significantly regulates the mobility and accessibility of vanadium (V) in soils (Reijonen et al., 2016). SOM typically acts as a carrier for vanadium through sorption processes under oxic conditions, suggesting a close relationship between the storage of V species and SOM in soil (Shaheen et al., 2019). The sorption behavior of SOM with vanadium is highly complex due to its intricate chemical nature. Furthermore, SOM can influence vanadium's behavior in soil by affecting its chemical speciation (Telfeyan et al., 2017).

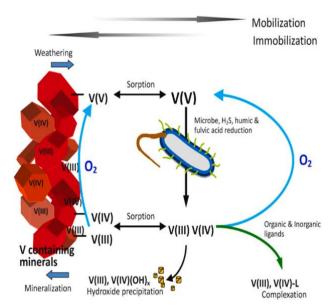


Figure 3. V biogeochemistry processes at the water-soil/sediment interference

Microorganisms are abundant in the soil-plant system and are crucial in maintaining soil productiveness and promoting plant growth. Cycling vanadium (V) through the weathering processes of V-rich minerals also influences its geochemical behavior in soil (Figure 3). Several microbial species with the ability to reduce V(V) have been recognized, incorporating Pseudomonas (Lyalkova et al., 1992), Acidithiobacillus ferrooxidans (Bredberg et al., 2004), Geobacter metallireducens, Methanosarcina, and Methanothermobacter thermautotrophicus (Zhang et al., 2014). Lactococcus and Enterobacter (Zhang et al., 2019), Rhodocyclus and Clostridium, and Proteobacteria (Uraguchi et al., 2009).

3. Related Study

Trace intensities of vanadium, typically below 2 ppm, are known to improve chlorophyll synthesis, nutrient uptake, potassium utilization, nitrogen metabolism, and overall plant development (García-Jiménez et al., 2018; Singh, 2017). In humans, vanadiumbased therapies are employed to cure conditions like cancer, diabetes tumors and hypertension. Additionally, bodybuilders, weightlifters, and shot putters often use vanadyl sulfate to boost implementation. In animals, vanadium deficiency below 0.1 ppm is associated with reproductive disorders, impaired red blood cell formation, disrupted iron metabolism, abnormal lipid profiles, and stunted growth in rats and chickens. Among goats, vanadium deficiency results in higher abortion rates, reduced milk production, swollen forefoot joints, and foreleg skeletal issues. Marine species like ascidians and tunicates

accumulate vanadium, reaching concentrations as high as 17 g/kg of body weight in their blood cells. This accumulation may function like iron in hemoglobin and protect against predators (Gustafsson, 2019). Vanadium also influences thyroid function, with evidence suggesting it regulates thyroid hormone levels. In nitrogen fixation, vanadium plays a key role for nitrogen-fixing bacteria, especially under molybdenum deficiency or low temperatures, aiding nitrogen fixation in temperate areas. Additionally, vanadium is an active component in haloperoxidases from certain marine algae, facilitating halide oxidation.

Vanadium levels exceeding 2 ppm in soil cause symptoms like chlorosis, necrosis, membrane destruction, reduced development, and root deformities such as coralloid structures. High vanadium levels hinder cell division, chlorophyll production, and protein synthesis. In growth media, elevated vanadium concentrations increase the absorption of metals like iron (Fe) and manganese (Mn), which can result in secondary metal toxicity. The vanadium toxicity threshold in plants varies based on species, vanadium type, and soil characteristics. In hydroponics, the half-utmost valuable concentration (EC50) and half-maximal inhibitory concentration (IC50) for vanadium range from 1 to 50 mg/L, while in soil, these values range between 18 and 510 mg/kg. For humans and animals, vanadium's toxicity threshold depends on species, age, and diet. Consuming over 3 ppm daily can lead to diarrhea, vomiting, tongue discoloration, anemia, and increased risks of uremia and lung cancer. In the U.S., the vanadium limit in drinking water is 0.33 mg/L. OSHA sets workplace exposure limits for vanadium pentoxide dust at 0.05 mg/m3 and fumes at 0.1 mg/m3. NIOSH classifies vanadium levels of 35 mg/m3 as life-threatening due to potential severe health effects or fatality. In animals, feed comprehending 10-300 mg/kg vanadium induces black diarrhea, lethargy, and spontaneous miscarriages.

The human body contains about 100 μg of vanadium, balancing intake and elimination. Familiar dietary sources include black pepper, mushrooms, parsley, dill seeds, cereals, leafy greens (e.g., lettuce and spinach), fruits (e.g., strawberries, apples, and pears), shellfish, and drinks like wine and beer (30–45 $\mu g/L$). These sources typically have vanadium levels from 0.02 to 2 mg/kg. Over 90% of ingested vanadium is excreted in urine, feces, and milk, showing low digestive absorption. Vanadium's urinary half-life ranges from 20 to 40 hours. Natural vanadium poisoning is rare, but excessive levels reduce microbial diversity and biomass. Based on respiration studies, the EC50 values for vanadium's impact on soil microbes, established on respiration studies, range from 200 to 580 mg/kg. Nitrogen and nitrification mineralization are prevented at 250 mg/kg.

Plants absorb vanadium and other metal ions primarily through root systems. Epidermal root cells stipulate a substantial surface area for absorbing nutrients but can also take in non-essential and toxic metals. The xylem transports toxic metals from roots to shoots, distributing them within tissues (Imtiaz et al., 2015). Vanadium dynamics in the soil-plant organization depend on its uptake and movement, which vary by plant species, vanadium form, and soil properties.

Table 1. The impact of V on plant growth and plant physiology.

Plant species	Growth parameters	V exposure level	
Rape	The stems, roots, and leaves	247 mg/kg V	
	biomass were decreased by	(NaVO ₃)	
	73.12%, 45.45% and 18.03%,	(Tian et	
	respectively.	al.,2015)	
		300 mg/kg V	
Chinese	The fresh weight was reduced	(NaVO ₃)	
cabbage	by 25.42%	(Liao et al.,	
		2020)	
	The fresh weight dealined by	130 mg/kg V	
Chickpea	The fresh weight declined by 49.58% in the shoots and	(NH_4VO_3)	
	29.68% in the roots.	(Imtiaz et al.,	
	29.08% III the 100ts.	2018)	
		100 mg/kg V	
Mustard	The development of shoots and	(NH_4VO_3)	
Mustard	roots is significantly diminished.	(Yang et al.,	
		2017)	
	The fresh weight of shoots,	250 mg/kg	
Soybean	roots, leaves, and beans showed	V(NaVO ₃)	
Soybean	a significant reduction.	(Gan et al.,	
	a significant reduction.	2020)	
Lettuce		265 mg/kg V	
	The germination and survival	(V_2O_5)	
	rates declined.	(Smith et al.,	
		2013)	
	The plant height, along with the	302 mg/kg	
Alfalfa	dry weight of shoots and roots,	V(NaVO ₃)	
	was significantly reduced.	(Gan et al.,	
	was significantly reduced.	2020)	

Low vanadium (V) concentrations promote plant growth and development, but excessive levels negatively impact plants by disrupting key physiological functions. The toxicity of vanadium in plants varies on factors such as plant species, the chemical form of vanadium, and its concentration. High levels of vanadium exposure can adversely affect plant development and physiological processes, incorporating seed germination, root and shoot development, nutrient absorption, and photosynthesis (Tables 1 and 2, Figure 4).

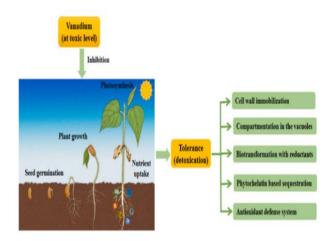


Figure 4. Vanadium toxicity to plants and tolerance machinery

Table 2. The impact of V on plant physiology.

Plant species	Growth factors	V exposure level
Watermelon	H ₂ O ₂ , MDA, and	50 mg/kg V
	chlorophyll levels	(NH_4VO_3)
	increased, while SOD	(Nawaz et al., 2018)
	and CAT activities	
	declined.	
Chickpea	Seedlings H ₂ O ₂ , MDA	120 mg/kg
	increased	$V(NH_4VO_3)$
		(Imtiaz et al., 2016)
Mustard	The SOD, POD, and	20-100 mg/kg V
	CAT activities in the	(Imtiaz et al., 2018)
	leaves were enhanced.	
Soybean	The concentrations of	0-500 mg/kg V
	chlorophylls a and b	(Yang et al., 2017)
	increased	
Chinese	The contents of	300 mg/kg V
cabbage	chlorophylls were	(NaVO ₃)
	increased by 60.42% for	(Liao et al., 2020)
	chlorophylls a and	
	83.33% for chlorophylls	
	b, respectively.	
Wheat	The chlorophyll a	350 mg/kg V
seedlings	content in the leaves	(NaVO ₃)
	decreased, whereas the	(Abeywardane et
	chlorophyll b content	al., 2019)
	increased.	
Rice seedlings	The levels of SOD, POD,	30 mg/L V
	CAT, and MDA were	(NaVO ₃)
	elevated.	(Yuan et al, 2020)

Excessive levels of vanadium are well-documented to trigger the overproduction of reactive oxygen species (ROS), including hydrogen peroxide (H_2O_2), superoxide (O^2), and hydroxyl radicals (OH), through Fenton and Haber-Weiss reactions (Figure 5). Nawaz et al. (2018) observed that applying mg L-1 V (NH₄VO₃) substantially elevated H_2O_2 levels in watermelon leaves associated with the control. Under normal conditions, these ROS are generated in several plant organelles, such as chloroplasts, mitochondria, and the endoplasmic reticulum, as derivatives of cellular metabolic methods. Additionally, ROS plays an active role in regulating several physiological processes in plants under non-stress conditions (Vriet et al., 2012).

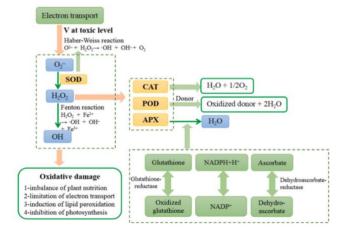


Figure 5. A diagram depicting the manufacture of reactive oxygen species (ROS) and the antioxidant defense arrangement in plants subjected to combined vanadium stress.

3.1 Plant vanadium accumulation and phytoremediation potentials

Plants utilize various strategies to manage exposure to toxic primarily through accumulation and exclusion mechanisms. In the accumulation process, harmful metals are confined within specific organs, tissues, or organelles, often forming insoluble complexes to prevent their dispersion into vital or sensitive areas. The exclusion strategy, on the other hand, involves the transport of metals from roots to shoots, thereby minimizing their concentration in root tissues (Hall, 2002; Wang et al., 2020). When plants are exposed to vanadium in their growing environment, accumulation serves as the primary defense against its toxicity. Typically, vanadium concentrates in the roots, with levels measured at 2 to 1000 times higher than those found in above-ground tissues (Ming et al., 2014; Yang et al., 2014). The extent of vanadium accumulation in roots corresponds to its concentration in the growth medium, up until reaching toxicity levels where visible symptoms emerge (Yang et al., 2017). Within these parameters, the vanadium concentration in the substrate plays a crucial role in determining root accumulation. Various plant species, including soybean, chickpea, bunny cactus, tomato, Chinese green mustard, rice, bush bean, alfalfa, corn, wheat, burning bush, green bean, and cabbage, display significant tolerance to vanadium and store considerable amounts in both roots and aerial parts. Among them, Chinese green mustard, chickpea, and bunny cactus exhibit the highest vanadium accumulation, with recorded concentrations of approximately 10,334, 8500, and 8640 mg/kg, respectively (Yang and Tang, 2015; Vachirapatama, 2011; Imtiaz et al., 2016).

Certain crops and vegetables, such as corn, tomato, rice, green bean, lettuce, and cabbage, also absorb substantial amounts of vanadium in both their roots and shoots, even under relatively low exposure levels (Saco et al., 2013). For example, hydroponically grown rice seeds exposed to a 20 mg/L vanadium solution accumulated 7.8 mg/kg of vanadium (Tham et al., 2001). Cultivating these crops in vanadium-enriched or contaminated soils may present potential health hazards for both humans and animals. In the context of large-scale in situ phytoremediation for moderately vanadium-contaminated soils, where biomass recovery for disposal or resale is practical, species such as dog tail grass, bunny cactus, alfalfa, chickpea, and Chinese green mustard are highly suitable due to their exceptional ability to accumulate vanadium.

3.2 Alleviation of Vanadium Toxicity and Enhanced Phytoremediation Strategies

Adjusting environmental conditions and soil factors can increase or reduce plant vanadium accumulation. For effective phytoremediation of highly vanadium-contaminated soils—where levels surpass plant tolerance it is critical to first lower its toxicity and bioavailability to enable standard germination, growth, and bioaccumulation in remediation plants. Methodologies such as

liming, using natural amendments, applying phosphate fertilizers, and introducing specific sorbents to heavily contaminated soils improve phytoremediation efficiency while enhancing soil quality.

In contrast, for mildly contaminated soils—where vanadium concentrations remain within plant tolerance—boosting vanadium mobility or bioavailability can increase plant uptake and improve phytoremediation outcomes. While EDTA can enhance vanadium solubility, its non-biodegradability risks secondary contamination (Tandy, 2004; Leštan et al., 2008). Zou et al. (2019a, 2019b, 2019c) discovered that fatty acids from food waste anaerobic digestion mobilize vanadium in mining-contaminated soils. Liquid digestate from food waste improved vanadium tolerance and uptake in dogtail grass (Aihemaiti et al., 2019a). Such biodegradable soil conditioners hold promise for enhancing the phytoremediation of vanadium-contaminated soils. Treatments using melatonin, caffeic acid, or polygalacturonic acid have also improved vanadium tolerance in watermelon and triticale (Nawaz et al., 2018; Garau et al., 2015).

Microorganisms from metal-polluted soils, particularly those exposed to high levels of toxic metals, demonstrate remarkable metal-resistance capabilities. These microbes remove high-valence poisonous metals from water through processes like bio-reduction and precipitation. As a redox-sensitive element, vanadium toxicity rises with its oxidation state, making microbial reduction from V(V) to V(IV) or lower states an effective detoxification strategy. When supported with appropriate electron donors, numerous microbes have achieved up to 100% removal efficiency for V(V). Notable microbial candidates for bioremediation of vanadiumpolluted wastewater and groundwater include Geobacter, Rhodocyclus, Pseudomonas, Bacillus, Clostridium, Methanothermobacter, and Thiobacillus thiooxidans.

Techniques such as soil washing and using amendments or sorbents have also been explored. For instance, vanadium removal from soils grasped 77.2% and 57.1% using 1.0 M oxalic acid solutions and volatile fatty acids (VFAs) derived from anaerobic digestion of food waste, respectively, as washing agents (Zou et al., 2019a). While soil washing efficiently extracts vanadium and other metals from highly contaminated soils, it generates wastewater rich in heavy metals, raising potential environmental concerns. Moreover, certain materials exhibit high vanadium removal efficiency in wastewater treatment. Examples include basic oxygen furnace steel slag (97.1% removal), ferric oxyhydroxides and similar compounds (91-94%), ceramics resulting from aminomodified municipal sludge (99.8%), residuals from ferric groundwater treatment (54%), and microbial fuel cell materials (67.9%). Combining phytoremediation with soil amendments and applying bioremediation to vanadium-polluted water are encouraging approaches for restoring contaminated sites, enabling their potential future reuse.

3.3 Role of BRs in Plants Under Heavy Metal Stress

Brassinosteroids (BRs) are vital plant hormones that play a key role in regulating growth and development. They are present in all actively growing tissues of higher plants, with exceptionally high levels found in fruits, seeds, and pollen. In Arabidopsis, the most biologically active form of BR, brassinolide (BL), is derived from the precursor campesterol (CR). CR is first converted into

campestanol (CN) and subsequently into castasterone (CS) through two distinct pathways: the early and late C-6 oxidation pathways. The enzyme DEETIOLATED 2 (DET2) catalyzes the conversion of 4-en-3-one to 3-one and 22-OH-4-en-3-one to 22-OH-3-one. Hydroxylation at the C-22 position is facilitated by DWARF4 (DWF4), whereas hydroxylation at C-23 is carried out by CONSTITUTIVE PHOTOMORPHOGENESIS AND DWARFISM (CPD). BR6ox mediates oxidation at the C-6 position. Furthermore, two P450 monooxygenases, CYP90C1 and CYP90D1, are involved in converting 22-OH-4-en-3-one, 22-OH-3-one, and 3-epi-6-deoxo CT into their respective 23-hydroxylated derivatives.

Brassinosteroids (BRs) are a group of plant steroidal hormones that regulate various physiological and developmental processes, including cell division, elongation, morphogenesis, reproduction, and senescence. They also significantly function in stress management (Kour et al., 2021). Research has demonstrated that BRs enhance plant tolerance to heavy metals, improving crop yield and quality. They achieve this by altering cell membrane permeability to reduce metal uptake and by inducing the production of defensive enzymes such as superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), and glutathione reductase (GR). However, the precise mechanisms through which BRs alleviate vanadium (V) stress require further investigation and are the focus of this study.

The bioactive brassinosteroids, 28-homobrassinolide (HBL) and 24-epibrassinolide (EBL), play a crucial role in supporting phytoremediation, aiding plants in removing toxic metals. BRs stimulate stress-protein production by activating anti-stress genes through increased ATPase expression. Externally applied brassinosteroids (BRs) induce temporary H₂O₂ production, which activates MAPK signaling pathways, resulting in NADPH oxidase generation and the upregulation of stress-related proteins and defending enzymes to alleviate metal-induced stress (Jiang et al., 2012). Low concentrations of 24-epibrassinolide (EBL) (0.1-0.15 µM) have been reported to suppress photosynthetic efficiency, while 0.1 µM EBL facilitates stomatal opening, and 1.0 µM triggers stomatal closure (Xia et al., 2014). BRs mitigate heavy metal toxicity through multiple mechanisms, including (a) stimulating H₂O₂ production, (b) scavenging reactive oxygen species (ROS) by advancing the antioxidant defense system, (c) upregulating MAPK pathways, and (d) alleviating metal toxicity by increasing the levels of potassium, sodium ions, proline, antioxidants, and osmolytes. NADPH oxidase has been identified as a key apoplastic source of H₂O₂, converting O2⁻ to H₂O₂ through the action of superoxide dismutase in the plasma membrane. This process also enhances H+-ATPase activity by upregulating the CsHA gene, thereby mitigating oxidative damage caused by toxic metals. The BR-specific inhibitor brassinazole (Brz) and 24epibrassinolide (EBL) have effectively reduced metal toxicity and restored photosynthetic function and defense mechanisms in Arabidopsis thaliana. BRs are crucial for maintaining cellular equilibrium in plants, restoring CO2 assimilation, and enhancing antioxidant capacity to combat heavy metal toxicity (Ahammed et al., 2012). The BR receptor BRI1 on the plasma membrane initiates a signaling cascade that activates transcription factors, increasing the expression of brassinosteroid-related genes. This upregulation elevates endogenous BR levels, further aiding in mitigating mental

stress, although the precise mechanism remains fully understood. Table 3 summarizes the roles of BRs in regulating the physiological and biochemical responses of plants under metal toxicity, highlighting their importance in mitigating stress and supporting plant growth and development in adverse conditions.

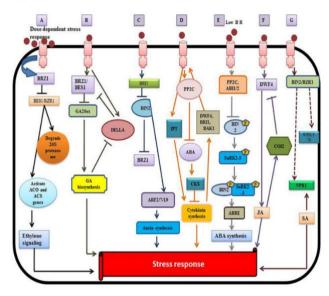


Figure 6. Brassinosteroids (BRs) regulate stomatal activity in a dose-dependent manner.

BRs stimulate the respiratory burst oxidase homolog (RBOH) at lower concentrations, increasing H₂O₂ production and facilitating stomatal opening (Figure 6). Conversely, at higher

concentrations, BRs lead to a buildup of H₂O₂ and reduce potassium (K+) ion uptake in guard cells. This reduction activates abscisic acid (ABA), ultimately causing the stomata to close. Brassinosteroids (BRs) show a critical and multifaceted role in controlling plant metabolism through their interaction with additional plant hormones, including auxin, cytokinins (CK), ethylene, polyamines (PA), gibberellins (GA), salicylic acid (SA), jasmonic acid (JA), and abscisic acid (ABA). Bioactive BRs, such as 28-homobrassinolide (HBL) and 24-epibrassinolide (EBL), help protect plants from toxic metals through assisted phytoremediation (Peres et al., 2019). They minimize toxic metal uptake by modifying cell membrane penetrability and mitigate damage by activating protective enzymes. The signaling pathways of BRs and their molecular interactions with further hormones are depicted in Figure 7 (Qi et al., 2012).

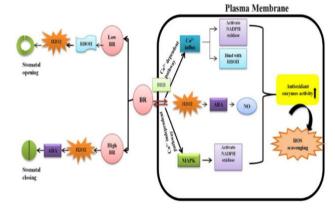


Figure 7. Crosstalk between BRs and other phytohormones

Table 3. Some of the reports studies on role of brassinosteroids under heavy metal stress

Plant species	Metal concentration	BER concentration	Effect	References
Brassica juncea L.	2 mM Pb	10 ⁻⁸ ERs	Mitigates Pb toxicity and enhances protein levels by decreasing H ₂ O ₂ and MDA concentrations.	(Dalyan et al., 2018)
Solanum lycopersicum	3 and 9 mg kg ⁻¹ Cd	10 ⁻⁸ ERs	Alleviates the harmful impact of Cd on Solanum seedlings by boosting the activity of photosystem II enzymes, as well as improving carbohydrate and nitrogen metabolism.	(Singh and Prakash, 2022)
Cucumis sativus	10 uM Cd (CdCl ₂)	10nM ERs	Boosts NADPH oxidase activity, leading to increased hydrogen peroxide accumulation and the activation of the antioxidant defense system to counter Cd stress.	(Jakubowska and Janicka, 2017)
Raphanus sativus L.	5 mM Zn (ZnSO ₄ 7H ₂ O)	2uM ERs	Upregulates expression of SOD, APOX, POD, GR, and CAT; increases proline and chlorophyll content; restore nitrate reductase level in radish plants	(Ramakrishna and Rao, 2015)
Pisum sativum	150 mg L ⁻¹ Pb	10 ⁻⁷ ERs	Decreases methylglyoxal and hydrogen peroxide; alleviates electrolyte leakage; enhances glyoxalase I content and nutrient uptake by roots and shoot	(Jan et al., 2018)

			Stimulates production of plant hormones, IAA and ABA, and	
Raphanus	0.2 mM Cr(VI) (K ₂ CrO ₄)	10 ⁻⁹ M BRs	antioxidant enzymes, GR, SOD, CAT, and GPOX; increases the	(Choudhary et
sativus L.			content of proline, sugars, phytochelatins, and pigments by	al., 2012a)
			decreasing MDA and H ₂ O	
Lycopersicon	0.5-1.5 nM	10-7,10-9	Enhances Cd tolerance by up-regulating antioxidant system and	(Sharma et al.,
esculentu			protein content; decreases PPO and GST activity	2014)
Eucalyptus	2.5 μM Fe (deficiency)	100nM BRs	Increases consumption, transport, and accumulation of iron (Fe)	
prophyll			and other micronutrients in roots, leaves, and stems	
Raphanus	1.0mM Ni	10 ⁻⁹ BRs	mitigates metal-induced oxidative damage and activates	
sativus L.	1.0IIIVI IVI		antioxidant enzymes	
Vigna	100 or 150 mg	10 ⁻⁶ BRs	Activates peroxidase, catalase, and superoxide dismutase; boosts	(Yusuf et al.,
radiata	kg-1 Ni	10 DKs	proline content for nodulation and growth	2012)
Chroimo man		Improves photosystem II; mitigates zinc stress by boosting	(Dos Santos et	
Glycine max L.	20 uM Zn	100nM BRs	antioxidant system and nutritional content; restores chloroplast	al., 2020)
L.			membrane	al., 2020)
Solanum	100 uM Ni	1 uM BRs	Raises Ni stress tolerance in Solanum by enhancing SOD	(Soares et al.,
nigrum			activity; but can cause down-regulation of APOX and CAT	2016)

4. Conclusion

Vanadium contamination in soil and water has become an increasing environmental concern due to its toxic effects on plants, animals, and human health. While vanadium is an essential trace element in biological systems, excessive accumulation leads to oxidative stress, impaired nutrient uptake, and disrupted physiological functions in plants. This study highlights the potential of brassinosteroids (BRs) as effective plant hormones in mitigating vanadium toxicity. BRs regulate metal uptake, enhance antioxidant defence systems, and activate stress-responsive pathways such as MAPK and NADPH oxidase, ultimately improving plant growth and resilience under vanadium stress. Furthermore, BRs play a crucial role in phytoremediation strategies, enabling plants to detoxify and accumulate vanadium in a controlled manner. By modifying cell membrane permeability and enhancing enzyme activity, BRs minimize heavy metal uptake while promoting stress tolerance. The integration of BR-based treatments with traditional phytoremediation techniques can provide an eco-friendly and cost-effective approach to rehabilitate vanadium-contaminated soils. Future research should focus on understanding the molecular mechanisms of BR-mediated vanadium stress tolerance, optimizing BR application methods, and exploring the synergistic effects of BRs with other plant hormones and soil amendments. By advancing our knowledge of BRs in plant-metal interactions, we can develop sustainable agricultural practices that ensure crop productivity environmental health in contaminated regions.

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