Phytoremediation-a sustainable remedial method for soil contaminated by vanadium

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Abstract. Vanadium amassing in the soil increased with its widespread usage in multi-field. Elevated soil vanadium confers adverse effects on living organisms involved in plants, animals, and microorganisms. Moreover, vanadium can enter the human body through the food chain and lead to potential health risks stemming from its toxicity and carcinogenicity. Therefore, the remediation of soil contaminated by vanadium is imperative. Phytoremediation, a clean phytotechnology, is gaining increasing grace in modern society that prefers spirit-enjoy pursing. However, due to the blemishes of the remediation plants per se, the remediation efficiency relying on plants alone is not attractive. Therefore, the strengthened screening of vanadium accumulator and hyperaccumulator plants should step forward. Simultaneously, it is necessary to improve phytoremediation efficiency by some complementary measures, such as inoculating plant growth-promoting bacteria, vanadium reducing bacteria, and the proper application of plant growth regulators. Overall, microbe-assisted and moderate usage of plant growth-promoting factors are promising for the phytoremediation of vanadium-contaminated soil.

1. Introduction

Vanadium is a known metal element exhibiting high significance in physiology, environment, and industry[1]. It ranks 5th among the transition metal in the soil, exceeding the content of the metal present in the Universe by 135 times[2]. Vanadium in the environment derives from natural sources and anthropogenic activities[3]. Anthropogenic activities, e.g., the mining and smelting of vanadium-containing ore, extensive usage of vanadium-bearing products, and combustion of fossil fuel, have led to substantial vanadium enter the environment[4]. A survey showed that global vanadium production, mainly by mining, had more than doubled during the past two decades[5]. More people will be affected by vanadium pollution, particularly in American, South Africa, China, and Russia[6]. Therefore, vanadium becomes a re-emerging environmental hazard[7]. High levels of vanadium are toxic to plants and animals[8], and sometimes it even endangers human health[4]. Intake of high levels of vanadium can result in severe diseases, including renal lesions and potential pulmonary tumors[4,8].

Vanadium can exhibit in several valence states, out of which pentavalent vanadium (V(V)) peaks in toxicity and mobility[10]. Vanadium has been counted as a potentially harmful pollutant comparable to mercury, lead, and arsenic[11,12]. Similar to other metals, vanadium has no biodegradability and tends to concentrate in the environment, and has a biological amplification effect in the food chain[13]. Out of
the consideration of environmental and healthy risks attributed to the vanadium contaminants, the remediation of soil contaminated by vanadium is pretty necessary.

2. Phytoremediation application of vanadium-contaminated soil

The remediation technology of soil contaminated by vanadium primarily includes physio-chemical and biological methods\cite{14}. Physical-chemical pathways like adsorption and precipitation are often used to remove vanadium from the soil despite their questionable cost-effectiveness\cite{15}. Phytoremediation is a contaminated environment cleanup method by using plants and their associated microbes\cite{16}. Phytoremediation of environmental pollutants exhibits many potential merits, e.g., minimal disruption, aesthetic pleasure, high public acceptance\cite{17}. Revegetation of soil contaminated with vanadium, especially in mining areas, in one aspect, restrains the diffusion of vanadium to the adjacent environment; in another aspect, it cleanses the soil by harvesting the aerial parts and simultaneously improves the soil properties\cite{14}.

Phytoextraction and phytostabilization are two critical mechanisms used in the phytoremediation of soil contaminated by vanadium\cite{18}. Phytoextraction is one of the most effective phytotechniques to remove vanadium pollutants from the soil. In general, phytoextraction relies heavily on hyperaccumulators to efficiently transport vanadium from plant roots to their aboveground parts. Some (potential) vanadium hyperaccumulators, such as dog tail grass (\textit{Setaria viridis}), \textit{Phaseolus vulgaris} L., \textit{Thuja} (\textit{Cupressaceae}), and \textit{Zea mays} L, have been screened out\cite{18}. Phytostabilization mainly declines the bioavailability of soil vanadium and thus suppresses the transport toward the surrounding environment, which plays the role of temporarily immobilize vanadium pollutants even though it does not remove soil vanadium pollutants\cite{19}. Due to the limited number of (potential) vanadium accumulator and hyperaccumulator plants identified at present, and therefore the screening works should be further strengthened.

3. Effect conferred by vanadium on plant growth

Vanadium is undoubtedly essential to some algae (e.g., \textit{Scenedesmus obliquus}) growth\cite{20}. Nevertheless, the essentiality of vanadium for the higher plant is still an open question even though minor quantities have exhibited a conducive effect for some plants’ growth and development\cite{21}. The toxicity concentrations of vanadium on plants are plant- and vanadium species-dependent and influenced by soil conditions\cite{14}. Vanadium in trace quantities is essential for normal cell growth, but high dosages (e.g., > 1 mg L$^{-1}$) become toxic\cite{22}. Low dosages of vanadium can promote chlorophyll synthesis, nutrient absorption, nitrogen assimilation, potassium usage, and plant growth\cite{14}. In contrast, excessive vanadium results in negative influences on plant growth, such as declined seed germination percentage, stunted (leaf, stem, and root) growth, chlorophyll degradation, attenuated photosynthesis, root distortion, water imbalance, poor absorption and use of essential elements, suppression and disruption of some pivotal enzymes activities, declined biomass and yield, and abnormality of other significant physiological functions in plants\cite{14,23}.

4. Rethinking of plant translocation and bioconcentration factors

$$TF = \frac{C_l}{C_r}$$ \hspace{1cm} (1)  \\
$$BF = \frac{C_l}{C_m}$$ \hspace{1cm} (2)

where $TF$ is the metal translocation factor, and $BF$ is the metal bioconcentration factor; $C_l$ indicates metal concentration in plant leaf ($C_{l}$), stem ($C_{s}$), and aboveground part ($C_{a}$); $C_r$ indicates metal concentration in plant root; $C_{l}$ indicates metal concentration in plant leaf ($C_{l}$), stem ($C_{s}$), root ($C_{r}$), and aboveground part ($C_{a}$); $C_m$ indicates metal concentration in the matrix.

Metal translocation factor ($TF$) and bioconcentration factor ($BF$) are two nontrivial parameters in evaluating plants' capability to translocate and accumulate pollutants. Especially for hyperaccumulator
plants, their TF and BF should be > 1\(^{[18]}\). It can be seen from formulas 1 and 2 that different transfer coefficients and bioaccumulation coefficients can be obtained according to metal concentrations in various parts of plants used in the formulas.

Furthermore, different plants have specific (roots, stems, and leaves) structural characteristics, thereby the biomass allocation undergoes the change in their growth, and correspondingly plants exhibit various contaminant accumulation characteristics. Therefore, a more detailed assessment of metal transfer and enrichment coefficients based on plant different tissues concentration is conducive to understand the distribution of accumulated metal by plants.

5. Vanadium detoxification mechanism
Plants absorb nutrients and heavy metals by the transmembrane of their roots and transfer them to various organelles\(^{[24]}\). Vanadium is mainly stored in roots after entering plants\(^{[14,25]}\). Furthermore, it is usually contended that vanadium exists as CaVO\(_3\) in plant\(^{[23]}\). Vanadium concentration in plant tissues is generally ordered as root > stem > leaf\(^{[25,26]}\). Thereby, vanadium translocation capability from root to aboveground organs is relatively weakened for the majority of plants. The bio-transformation of V(V) to V(IV) undergoing during plant vanadium intake is also a vital plant tolerance mechanism against vanadium\(^{[12]}\). From the perspective of subcellular level, vanadium binding with some components (like pectin, cellulose) of cell wall lowers vanadium toxicity efficacy exhibited on plants\(^{[24]}\). In addition, compartmentalization of vanadium by vacuoles in roots and stems declines the translocation of vanadium from root to aerial parts\(^{[14]}\).

6. Enhanced phytoremediation by microorganism
Since the 1970s, various microorganisms for bacterial, eukaryotic, or archaeal domains have shown the capability of reducing V(V) to V(IV)\(^{[27]}\). For example, vanadium-reducing bacteria (VRB), a community with the vanadium reduction function, may play a pivotal action in the vanadium-reducing process\(^{[4]}\). Many microorganisms are strongly resistant to vanadium. e.g., Pseudomonas and Thiobacilli are competent to tolerate 5000 mg L\(^{-1}\) V\(^{[28]}\). Nowadays, microbial V(V) reduction gains increasing concerns. It is reviewed as a promising strategy for remediating V(V) pollution, as a variety of microorganisms own the ability to reduce V(V) to V(IV)\(^{[29]}\). For plants, vanadate is also the most available vanadium speciation\(^{[28]}\). Moreover, V(V) is an electron acceptor used by microorganisms in their anaerobic metabolism, and it will be reduced\(^{[29]}\). Therefore, microbial reduction of V(V) descends the toxic effects of vanadium on plants.

7. Conclusion and prospect
Phytoremediation is a clean and purifying technology to remove environmental pollutants, attracting the increasing attention of researchers. Some comforting achievements have been made in the phytoremediation of soil contaminated by vanadium, and increasing researches are undergoing. It is necessary to explore further (potential) vanadium hyperaccumulator plants for phytoremediation is largely dependent on hyperaccumulator plants. In addition, intercropping is also an available pathway to enhance phytoremediation efficiency. Consequently, its remediation effect can be further explored in vanadium contaminated soil by plants through their intercropping. Microbes can actively participate in the transformation of vanadium and thereby play a critical role in situ decontaminating vanadium contaminants. Proper inoculation of plant growth-promoting bacteria and vanadium-resistance endophytes to remedial plants will reinforce plant growth and increase plant vanadium accumulation through microbial detoxification. In addition, considering that the mining area environment is harsh and the remediation plants are often faced with a variety of stressors, screening indigenous plants from the mining area is more conducive to the remediation operation.

The deeper bioreduction mechanism of vanadium from V(V) to V(IV) or lower valences needs to be further probed to strengthen vanadium detoxification by plant per se. Plant growth regulators, such as auxins, cytokines, gibberellins, jasmonates, and salicylic acid, have exhibited positive action in increasing plant biomass and compromising the negative influences of contaminants accumulated in
plants. Proper application of these regulators is an available pathway to elevate phytoremediation efficiency. Microbial-assisted phytoremediation had shown a positive effect in strengthening plant vanadium tolerance in the laboratory trial, thereby further researches in the outdoor or contaminated site in mining area are imperative to test their actual remediation efficacy. Noteworthily, for assessing vanadium accumulation capability of remediation plants, it is of high importance to clarify the variations of vanadium accumulation amounts in various portions (leaf, stem, root, shoot) of plants, and the corresponding percentage changes of tissue intake amount to total uptake amount of the whole plants. Doing this can provide a more comprehensive assessment of the vanadium enrichment capacity of different plants, which is also applicable to evaluating the accumulative ability of other heavy metal pollutants. Additionally, integrated multidisciplinary exploration orchestrated plant physiology, biochemistry, microbiology, soil science, transcriptomics, metabolomics, genetic engineering, lipidomics, and others are required to enhance phytoremediation efficiency more.

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References
[1] Kiosseoglou, E., Petanidis, S., Gabriel, C., Salifoglou, A. (2015) The chemistry and biology of vanadium compounds in cancer therapeutics. Coord. Chem. Rev., 301–302: 87–105.
[2] Del Carpio, E., Hernández, L., Ciangherotti, C., Villalobos Coa, V., Jiménez, L., Lubes, V., Lubes, G. (2018) Vanadium: History, chemistry, interactions with α-amino acids and potential therapeutic applications. Coord. Chem. Rev., 372: 117–140.
[3] Sun, X.X., Qiu, L., Kolton, M., Häggblom, M., Xu, R., Kong, T.L., Gao, P., Li, B.Q., Jiang, C.J., Sun, W.M. (2020) V V\textsuperscript{V} Reduction by Polaromonas spp. in vanadium mine tailings. Environ. Sci. Technol., 54: 14442–14454.
[4] Wang, S., Zhang, B.G., Li, T.T., Li, Z.Y., Fu, J. (2020) Soil vanadium(V)-reducing related bacteria drive community response to vanadium pollution from a smelting plant over multiple gradients. Environ. Int., 138: 105630.
[5] Schlesinger, W.H., Klein, E.M., Vengosh, A. (2017) Global biogeochemical cycle of vanadium. Proc. Natl. Acad. Sci. U.S.A.,114: E11092–E11100.
[6] Yang, J.Y., Tang, Y., Yang, K., Rouff, A.A., Elzinga, E.J., Huang, J.H. (2014) Leaching characteristics of vanadium in mine tailings and soils near a vanadium titanomagnetite mining site. J. Hazard. Mater., 264: 498–504.
[7] Watt, J.A.J., Burke, I.T., Edwards, R.A., Malcolm, H.M., Mayes, W.M., Olszewska, J.P., Pan, G., Graham, M.C., Heal, K.V., Rose, N.L., Turner, S.D., Spears, B.M. (2018) Vanadium: a re-emerging environmental hazard. Environ. Sci. Technol., 52: 11973–11974.
[8] Chételat, J., Nielsen, S.G., Auro, M., Carpenter, D., Mundy, L., Thomas, P.J. (2021) Vanadium stable isotopes in biota of terrestrial and aquatic food chains. Environ. Sci. Technol., 55: 4813–4821.
[9] Chen, G.D., Liu, H.Z. (2017) Understanding the reduction kinetics of aqueous vanadium(V) and transformation products using rotating ring-disk electrodes. Environ. Sci. Technol., 51: 11643–11651.
[10] Zhang, B.G., Qiu, R., Lu, L., Chen, X., He, C., Lu, J.P., Ren, Z.J. (2018) Autotrophic vanadium(V) bioreduction in groundwater by elemental sulfur and zerovalent iron. Environ. Sci. Technol., 52: 7434–7442.
[11] Yang, J., Teng, Y.G., Wu, J., Chen, H.Y., Wang, G.Q., Song, L.T., Yue, W.F., Zuo, R., Zhai, Y.Z. (2017a). Current status and associated human health risk of vanadium in soil in China. Chemosphere, 171: 635–643.
[12] Tian, L.Y., Yang, J.Y., Alewell, C., Huang, J.H. (2014) Speciation of vanadium in Chinese cabbage (Brassica rapa L.) and soils in response to different levels of vanadium in soils and cabbage growth. Chemosphere 111: 89–95.

[13] Fazio, F., Saoca, C., Sanfilippo, M., Capillo, G., Spanò, N., Piccione, G. (2019) Response of vanadium bioaccumulation in tissues of Mugil cephalus (Linnaeus 1758). Sci. Total Environ., 689: 774–780.

[14] Aihemaiti, A., Gao, Y.C., Meng, Y., Chen, X.J., Liu, J.R., Hu, W.F., Gao, J., Yang, J.Y. (2021) Vanadium in soil-plant system: Source, fate, toxicity, and bioremediation. J. Hazard. Mater., 405:124200.

[15] Shah, V., Daverey, A. (2020) Phytoremediation: A multidisciplinary approach to clean up heavy metal contaminated soil. Environ. Tech. Innov., 18: 100774.

[16] Pilon-Smits, E. (2005) Phytoremediation. Annu. Rev. Plant Biol. 56: 15–39.

[17] Cary, T.J., Rylott, E.L., Zhang, L., Routsong, R.M., Palazzo, A.J., Strand, S.E., Bruce, N.C. (2021) Field trial demonstrating phytoremediation of the military explosive RDX by XplA/XplB-expressing switchgrass. Nat. Biotechnol. doi: 10.1038/s41587-021-00909-4

[18] Chen, L., Liu, J.R., Hu, W.F., Gao, J., Yang, J.Y. (2021) Microbial reduction and precipitation of vanadium (V) in groundwater: Interactions with coexisting common electron acceptors and analysis of microbial community. Environ. Pollut., 231: 1362–1369.

[19] Yang, J.Y., Wang, M., Jia, Y.B., Gou, M., Zeyer, J. (2017b) Toxicity of vanadium in soil on soybean at different growth stages. Environ. Pollut., 231: 48–58.

[20] Hou, M., Huo, Y., Yang, X.H., He, Z.C. (2020) Absorption, transport, content, and subcellular distribution of vanadium in the polysaccharide fraction of cell wall in corn seedlings. Plant Physiol. Biochem. 149: 153–168.

[21] Wu, Z.Z., Yang, J.Y., Zhang, Y.X., Wang, C.Q., Guo, S.S., Yu, Y.Q. (2021) Microbial reduction and precipitation of vanadium (V) in groundwater by immobilized mixed anaerobic culture. Bioresour. Technol., 192: 410–417.

[22] Huang, J.H., Huang, F., Evans, L., Glassauer, S. (2015) Vanadium: Global (bio)geochemistry. Chem. Geol. 417: 68–89.

[23] Hao, L.T., Zhang, B.G., Tian, C.X., Liu, Y., Shi, C.H., Cheng, M., Feng, C.P. (2015) Enhanced microbial reduction of vanadium (V) in groundwater with bioelectricity from microbial fuel cells. J. Power Sources 287: 43–49.