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A Systemacic Review of Vanadium and Derivates : Distribution of Coordination Complex and Application

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ABSTRACT

Vanadium is a metal that has unique characteristics both in the form of free elements, ions, and in the form of complex compounds. In common with other minerals, essential and non-essential, vanadium has a wide range of usual dietary intakes, levels of least observed adverse effects, measures of toxicological exposure, and potential therapeutic effects, with concentration ranges that may be disease specific. This review aims to summarize and evaluate the distribution and interactions between vanadium communities in aquatic, soil, and biological chemical systems. In the aquatic environment, vanadium can be distributed directly by marine microorganisms and marine biota, as well as sediments, which at certain concentrations are very toxic, and several studies have even equated the toxicity of vanadium with other heavy metals such as arsenic, lead, mercury and chromium. In soil, vanadium contamination can originate from parent rocks and anthropogenic activities such as mining, the textile industry, the burning of fossil fuels, and the effects of pesticide use. High concentrations of vanadium can interfere with energy metabolism and matter cycles; inhibits the action of enzymes, protein synthesis, ion transport, and other important physiological processes. However, it is unique because vanadium provides an advantage in plant growth process at low levels. On the other hand, the coordination of vanadium with various types of ligands to make complex compounds significantly enhances the significance of vanadium in various applications such as catalysis in polymerization reactions, and therapeutic agents and drug candidates. Ultimately, although vanadium has demonstrated cytotoxicity in testing as a therapeutic agent, several studies have shown promising opportunities for designing effective and safe vanadium derivates-based antiviral or COVID-19 drug candidates in the future.

Keywords: Coordination Compelxes, Distribution, Drug Candidate, Vanadium

I. INTRODUCTION

Vanadium, the second-most abundant transition metal in seawater and the 20th-most abundant element in the continental crust, is a common trace metal on earth [1,2]. In recent years, vanadium has been classified as a potentially toxic element in the same category as lead, arsenic, and mercury, according to the United States Environment Protection Agency (USEPA) [3,4]. However, there is still disagreement around the requirements and essential functions of vanadium in living organisms. Vanadium is supported by nontoxic bioaccumulation in three groups of species [3,5,6] biological processes like the bacterial vanadium-dependent nitrogenases or haloperoxidases [7] or respiration, and nontoxic bioaccumulation. In the plant growth process, vanadium plays an important role in optimum concentrations [8]. Low levels of vanadium enhance plant height, root length, and biomass output through enhanced chlorophyll biosynthesis, seed germination, critical element intake, and nitrogen assimilation. However, high vanadium levels damage crucial enzymes involved in generating energy, assembling proteins, moving ions, and other crucial physiological activities, which causes growth inhibition, anomalies in the roots and shoots, and even plant mortality [9].

Apart from being involved in the plant growth processes, based on several research reports, vanadium, which is a group of transition metal elements, also plays a very important role in chemical-biological processes. Some metal ions play a crucial role in balancing proteins and negatively charged metabolites, maintaining biomolecules in a state relevant to cellular functions. When linked to biomolecules, vanadium metals and transition metals frequently serve structural or catalytic purpose (Jasińska et al., 2022; Sgarbossa et al., 2013; Szklarzewicz et al., 2020; Szklarzewicz et al., 2019; Szklarzewicz, Jurowska, Matoga, 2020). Like any heavy metal in general, vanadium has a threshold concentration value that is considered toxic. Several reviews shown that the threshold level of vanadium metal in water is 0.05 mg/m^3 (Li et al., 2022; Xi et al., 2021). However, the interesting thing about vanadium metal is its ability to coordinate interactions with various ligands to form complex compounds which have a very vital role in various applications such as catalysis of polymerization reactions and its potential as a therapeutic agent and drug candidate (Abd-Elaziz et al., 2020; Sakurai, Katoh, and Yoshikawa, 2006; Strianese et al., 2013).

This is inseparable from the characteristics of vanadium, which is a reactive element when in an oxidized or reduced state (in a redox state) so that vanadium can form cationic and anionic complexes under certain pH conditions known in several studies. Most of the vanadium complexes that have been studied and tested both as reaction catalysts and as disease therapy agents are dominated by complexes in oxide reduction (redox) states IV and V (vanadyl and vanadate) which can interact with various kinds of ligands such as oxo, non- oxo, sulfate ligands, and can even interact with ligands derived from natural materials (Abd-Elaziz et al., 2020; Gao et al., 2011; Mirdarvatan et al., 2021; Nunes et al., 2021; Patel et al., 2020; Sakurai et al., 2006; Szklarzewicz et al., 2019; Thompson and Orvig, 2001).

Therefore, this review describes in detail the characteristics of vanadium and the distribution of vanadium in various systems such as soil systems, aquatic systems, and of course biological systems. And finally, the author will review in great depth the vanadium coordination complex and its potential for various applications, especially in health and disease treatment applications.

II. METHODS

Online databases like PubMed, Science Direct, MDPI, Google Scholar, Springer Link, Web of Science, and Scopus were used to conduct the literature search for this review. The search approach is centered on the principal keywords that are utilized in different combinations, such vanadium, vanadium complexes, distribution of vanadium, bioactive compounds, therapeutic agent for Covid-19, and anti-bacterial. Full-length publications on the topic were published between 2001 and 2023 in peer-reviewed journals.

III. RESULTS AND DISCUSSION

Vanadium and Its Characteristic

Vanadium is an element in Group 5B. Vanadium exhibits some biological functions and, like most transition metals, may exist in a variety of oxidation states, with the most frequent valence levels in nature falling between vanadium (III) and vanadium (V). The most common forms of vanadium in living organisms are vanadyl (IV, VO^{2+}, V^{4+}) and vanadate (V, VO_4^{3-}, V^{5+}), both of which have significant biological functions (Gao et al., 2011; Jasińska et al., 2022; Thompson and Orvig, 2001; Zahirović et al., 2023). Vanadium in lower oxidation states is seldom discovered in the biosphere, except in some marine organisms like ascidians and tunicates. Vanadate's high structural similarity to phosphate has led to the hypothesis that it enters people, plants, and other organisms through anionic channels or phosphate transportation systems, while vanadyl cations enter through passive transport or diffusion (Shi et al., 2021; Wang et al., 2021; Zhang et al., 2019).

According to Szklarzewicz et al. (2019), pure vanadium is a bright silver-white, ductile metal with an atomic weight of 50.95 g/mol and a melting point of 1890 °C. The manufacturing of sulfuric acid and SCR catalysts both need vanadium. Approximately 80% of the vanadium produced is used in the steel industry to produce high-strength steel. The most widely utilized vanadium compounds are sodium orthovanadate, ammonium metavanadate, sodium metavanadate, and vanadium pentaoxide (V_2O_5). Pentavalent vanadium predominated in polluted soils found in vanadium mining and smelting regions, making up around 50% of the total vanadium content that could be extracted with aqua regia. Vanadate V(V) is strongly retained at low pH when hydroxide surfaces are positively charged, much like other oxyanions such as phosphate, molybdate, and arsenate. Long-lasting in soil, water, and the atmosphere, vanadium has the capacity to interact with nearby substances and can also function alone.

One of the most redox active elements, vanadium can form both cationic and anionic complexes in the pH range that is likely to be encountered physiologically (pH 2–8). The two oxidation states coexist in equilibrium both inside and outside of cells in vivo, and this redox interplay is mostly between V(V) and V(IV) (González-Baró et al., 2017; Kazek et al., 2019; Mangundu et al., 2022). Vanadium's redox balance in living organisms is controlled by oxygen tension, acidity, and the presence of endogenous reducing substances such ascorbate acid, glutathione, and catecholamines. Although Na^+, K^+-ATPase inhibition and the in vivo regulation of cell metabolism by vanadium have been proposed, vanadium's biochemical function in mammals has not yet been proven. Vanadium is a necessary cofactor for certain haloperoxidases in some marine organism (Sakurai et al., 2006; Szklarzewicz et al., 2020; Matoga et al., 2019; Matoga et al., 2020). Extremely low dietary vanadium combined with excessive dietary iodine causes obvious abnormalities in the metabolism of thyroid hormones in rats. Vanadium has a variety of effects on different intracellular signaling cascade elements in vitro. Vanadium has also been adequately shown to exhibit insulin-like stimulatory or inhibitory effects at higher doses (1–5 mM) on particular glucose- and lipid-related enzyme systems (Jurowska et al., 2022).

Distribution of Vanadium in Various System

Numerous researches have looked into the presence of vanadium in diverse systems in both qualitative and quantitative ways. Vanadium can be found in soil, water bodies, organisms and plants. Vanadium is also distributed in microorganisms in soil, waters, and biological systems (see **Figure 1**). In the soils system, vanadium is a major contaminant in source rock (Imtiaz et al., 2018; Liu et al., 2023; Mandiwana and Panichev, 2004). In contrast, distributing vanadium through human activity including mining, factories, burning fossil fuels, applying fertilizer and pesticides, and recycling household trash can potentially damage soils (Tian et al., 2014). Vanadium has a strong compatibility and attraction with organic matter so it is rich in peat soils. In addition, vanadium is also widely distributed into clay materials and iron oxides due to rock weathering residue. Much literatures show that vanadium is widely distributed and bound to many minerals (about 65 types of minerals). Still carbon-containing deposits have a higher vanadium content than these minerals. The distribution of vanadium in the soil is highly dependent on the geochemical characteristics which are determined by two factors, namely the oxidation state and pH. In its high oxidation state, vanadium is very soluble but in its reduced state it tends to be immobile (Fei et al., 2022; Hu, Yue, and Peng, 2018; Lu et al., 2019; Teng et al., 2011; Wang et al., 2020). Depending on the kinds of soil and their chemical properties, average vanadium amounts in numerous soils range from 10 to 220 mg kg-1 dry weight. Vanadium is found in substantially higher concentrations in soils used directly by people (1510 to 3600 mg kg-1) and in mining sites (738 mg kg1 and 3505 mg kg-1). Earlier research showed that peat soils did not contain as much vanadium as limestone soils and that soils close to factories have more vanadium as a result of human activity (Aihemaiti et al., 2020; Ceci et al., 2012; Wang et al., 2023).

In aquatic systems, vanadium is a heavy metal, a very important pollutant for groundwater and surface water. In the aqua sphere, vanadium is a highly prevalent transition metal, with a common proportion approximately to that of zinc. Additionally, vanadium pollution has been found in rivers, lakes, and oceans. Vanadate predominates in oxic waters while vanadyl, which tends to hydrolyze, is the most stable diatomic ion known to exist in reducing environments and has been identified. In reducing sediments, Vanadyl is likely to be sunk inorganically by adsorption and subsequent assimilation of vanadium (IV) as a solid solution (Tulcan et al., 2021). Vanadium in drinking water has an acknowledged acceptable limit of 0.33 (Wang et al., 2022). Although vanadium has a fairly vital role in groundwater and surface air systems, high concentrations of vanadium in aquatic environments (in this case the sea) can be a problem for living organisms there. Vanadium contamination in the sea can originate from various activities such as burning fossil fuels, industrial activities, and urban environments (Gustafsson, 2019; Mato-López et al., 2022; Park et al., 2016). The distribution of vanadium into wastewater and into the sea can be seen in Figure 1. According to (Tulcan et al., 2021) that vanadium exposure >1.8 mg daily can lead to health issues like kidney and liver damage. High blood V(III) levels are linked to breast cancer risk, etc. The concentration of vanadium in marine organism is presented in Table 1.

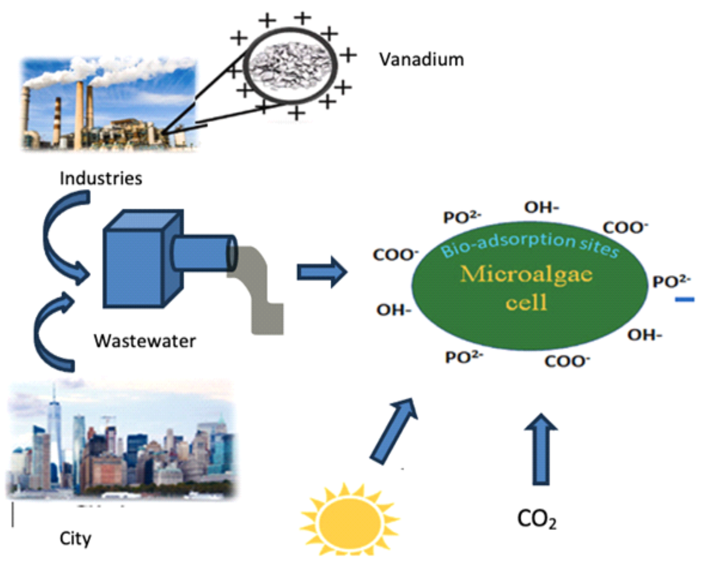

Figure 1. Distribution of Vanadium in Aquatic System from Industries and The City

Table 1. Structure of Anti-Bacterial peptides Compounds From Marine Bacteria.

Name of organism	Concentration of vanadium	Effect of high concentration of vanadium	Ref.
Phytoplankton	1.5 to 4.7	metabolism is impaired, and there are interactions with ATP, glutathione, amino acids, nucleic acids, and lipids.	[3]
Zooplankton	0.07 to 290	reactivate phosphorylase in the muscles from their dormant state. increased phospholipid oxidation in specific liver tissues.	[6]
Macroalgae	0.4 to 8.9	Enhance the production of fresh and dry biomass and chlorophyll	[43]
Ascidians	25 to 10,000	contribute to the defense system	[26]
Annelids	0.7 to 786	impact on the respiration and urinary systems	[33]
Other invertebrates	0.004 to 45.7	Obstacles to growth and reproduction	[34]
Fish	0.08 to 3	affects the liver, renal, respiratory, and reproductive systems.	[35]
Mammals	0.01 to 1.04 (fresh weight)	The liver's functioning are also impacted by renal and kidney disorders.	[39]

Vanadium has a trifecta of complex chemical properties controlled by pH, redox, and coordination chemistry (Zhao et al., 2006). Vanadium may be present in one of three oxidation states after being introduced to an aquatic environment (Wang et al., 2022). Oxo- and oxyhydroxide-V molecules are the most prevalent and physiologically accessible in surface and oxygenated porewater. Some examples include (1) vanadates, $H_3V(V)O_4$, $H_2V(V)O_4^{-}$, $HV(V)O_4^{2-}$, and $V(V)O_4^{3-}$; (2) oxyhydroxides, $V(V)O_2(OH)^{2-}$, $V(IV)OOH^{+}$; and vanadyl, $V(IV)O^{+2}$ (Gillio Meina, Niyogi, and Liber, 2020; Tulcan et al., 2023). Due to its anionic nature, vanadate is considered the most poisonous and labile species, especially in alkaline and oxic conditions. Although lower oxidation states (V(IV), V(III) are primarily found in sediment phases, they may be quickly converted to aqueous vanadate by hydrolysis or oxidation. Vanadyl can also be harmful to organisms when dissolved (Chen et al., 2022; Liu et al., 2017).

According to Meina et al. (2020) vanadium is a transition metal with numerous oxidation states, which could be variable in their toxicity due to an ionic or oxidative imbalance". Their research investigated how vanadium affects Daphnia magna and Oncorhynchus mykiss organisms found in aquatic systems. In another study, Liu et al (2017) reported the distribution of heavy metals in organisms in aquatic systems such as fish, crabs, and shellfish in Laizhou bay. Their investigation results showed that the vanadium concentration in the three organisms was higher than that of arsenic and mercury. Likewise, several other studies in various regions showed that the distribution of vanadium in organisms in aquatic environments was higher than that of arsenic and mercury. However, arsenic in several other areas showed a higher distribution. According to isotope correlation analysis as reported by (Liu et al., 2017), the vanadium and other heavy metals transport have a biodilution and a biomagnification effect in marine food web systems.

Application of Vanadium Complexes

Apart from V(V) and V(IV), vanadium complexes can also be formed in the V(III) oxidation state as shown in the study by (Bottini et al., 2022) who used vanadium (III) complexes as catalysts for the ethylene polymerization process. In the process of polymerization of ethylene into polyethylene using vanadium catalysis, it has been reported in many studies that both vanadium metal-based catalysts with V (III), V(IV), and V(V) are covalently coordinated with many ligands.

Apart from being a catalyst in the process of polymerization reactions and the conversion of organic compounds, another role of vanadium coordination complexes which are very dominant and promising is shown in the focus of research on drug candidates and disease therapeutic agents (see **Table 2**). From the various studies that have been developed to date, the use of vanadium complex compounds in the field of health and medicine has been widely applied in anti-diabetic, anti-tumor and anticancer, antiviral, anti-inflammatory, and antihyperglycemic. According to the earlier explanation, vanadium, which is absorbed through food and water, positively effects organisms, including plants and people, in modest amounts. As a cofactor in the functioning of enzymes, vanadium has the potential to catalyze, which gives it a crucial role. Additionally, vanadium metal has drawn attention from researchers due to its capacity to coordinately bond with a variety of ligands to form coordination complexes, particularly for use in the medical and health industries.

Simple vanadium salts and coordination complexes with different organic metals that coordinate with oxo, nitro, and sulfate groups have been investigated and put through a variety of tests both in vitro and in vivo for drug potential in the treatment of diabetes (Sakurai et al., 2006)[16], tropical diseases, bacterial and viruses' infections, cardiovascular dysfunction, spinal trauma, and anticancer drug candidates, even though they are still in the early stages (in vitro) (Costa Pessoa et al., 2015; Rehder, 2017; Ścibior et al., 2020)[66,70]. In fact, as will be shown later, new research has also indicated that vanadium complexes may be utilized to treat problems brought on by Covid-19. Vanadyl sulfate and other organic vanadium (Figure 3) have been shown to improve insulin sensitivity, reduce insulin resistance, and control blood sugar levels.

Additionally, a recent study found that diabetes-related kidney impairment can be improved by vanadium's antihyperglycemic action. Another study also revealed that peroxyvanadate compounds boost insulin sensitivity and activate insulin signaling cascades (Sakurai et al., 2006). According to (Chen et al., 2014) the antidiabetic effect of the vanadyl (IV) folic acid–amino acid complex in an animal model of diabetes. Other research indicates that the oxidovanadium complex is capable of binding to the active site of dipeptidyl peptidase IV (DPP-IV), which is the target of recently developed antihyperglycemic therapies to manage and inhibit type 2 diebetes (T2D). In animal models of diabetes, vanadium compounds have been found to be successful in preventing the onset of type 2 diabetes (Szklarzewicz et al., 2021). In addition to vanadium compounds, one of the vanadium complexes that is actually active in in-vivo conditions is the vanadate complex ($H_2VO_4^-$) which exerts a hypoglycemic effect given orally to diabetic rats. Vanadates can enter the intracellular space through phosphate channels built into the cell membrane and interact with (and subsequently lock in) protein tyrosine phosphatase, blocking the dephosphorylation of the intracellular tyrosine phosphate bound to the insulin receptor.

Table 1. Vanadium Complexes and its Application

Type of Coordination Complexes Vanadium	Redox State	Ligand	Application	Ref
minopyrrolylvanadium(III) complexes	V(III)	Iminopyrrolyl (N-Donor Ligand) (Tridentate)	Ethylene polymerization	(Igarashi et al., 2016)
$[(L^2)V^{IV}O](ClO_4)$	V (IV)	ClO_4	Direct Conversion of Alcohols and Aldehydes	(Mali et al., 2023)
bis(salicylaldiminato) vanadium(III)	V(III)	bis(salicylaldiminato)	Ethylene polymerization	(Igarashi et al., 2016)
(imido)vanadium(IV) dichlorides	V(IV)	Imido	Ethylene polymerization	(Igarashi et al., 2016)
Aroylhydrazone vanadium (V)	V(V)	Ligan Aroylhydrazone	selective oxidation of toluene	(Sutradhar et al., 2022)
l-Phenylalanine derived tripodal vanadium complexes		l-Phenylalanine	the asymmetric reductive coupling of benzaldehyde	(Teixeira et al., 2020)
vanadium complexes of 2-(benzimidazolyl, benzothiazolyl, and benzoxazolyl) pyridine		Pyridine ligand	ethylene polymerization	(Elagab and Alt 2015a)
vanadium complexes with 1,1-bis(benzothiazolyl)		bis(benzothiazolyl) ligand	ethylene polymerization	(Elagab and Alt 2015b)
adamantylimido)vanadium(V) dialkyl complexes	V (V)	aryloxo ligands	catalyst precursors for metathesis polymerization	(Suzuki, Matsumoto, and Nomura 2011)
(Imido)Vanadium(V) Dichloride Complexes	V (V)	Imido ligand	Ethylene Polymerization	(Elagab and Alt 2015c)
Vanadyl sulfate	V(IV)	Sulfato ligand	Antidiabetic	(Costa Pessoa et al., 2015)
Sodium orthovanadate	V(V)	Sodium ligand	Antidiabetic	
Peroxovanadium complex	V(V)	Ligan oxo	Antidiabetic	
Bis(maltolato)oxovanadium(IV)	V(IV)	methil-maltolate	Antidiabetic	(Semiz 2022a)
Bis(ethil-maltolato)oxovanadium(IV)	V(IV)	Ethil-maltolate	Antidiabetic	
hydrogenvanadate $H_2VO_4^-$	V(V)	Ligan aquo	Anti-tumor and anticancer	
cyclopentadienide(1-) vanadyl	V(IV)	cyclopentadienide(1-) ligand	Anticancer	

IV. CONCLUSION

The metal vanadium is exceptional. Like heavy metals in general, vanadium can be harmful at large doses. Yet, in specific amounts, it plays an extremely important function in biological and chemical processes in animals, plants, and even human beings. Vanadium is a crucial component of photosynthesis and other processes important to plant growth and development. However, because vanadium can function as a cofactor in the enzyme production process, vanadium is essential for humans. Vanadium compounds may also be a novel possible treatment for diabetes, cancer, atherosclerosis, and other disorders, according to vanadium's capacity to coordinate with diverse ligands. Additionally, vanadium compounds have non-toxic, broad-spectrum activity against RNA viruses, making them intriguing candidates for the treatment of acute respiratory illnesses treatment. Because of vanadium compounds' beneficial antiviral, antihyperglycemic, insulin-boosting, and anti-inflammatory abilities as well as the strong link between COVID-19 and diabetes, they can be considered an additional therapy for the COVID-19 indicated treatment.

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