

Vanadium in the Environment and Its Bioremediation

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Abstract Vanadium is an element with symbol V and atomic number 23. The vast majority of vanadium demand is from the steel industry, and the rest for titanium alloy and catalyst in chemical factory. Air pollution and water pollution by vanadium were recognized from early twentieth century. Increasing information on the toxicity and medicinal use enhanced the development of bioremediation of vanadium. In this chapter, the author would like to overview the history of pollution of vanadium, vanadium toxicity, bioaccumulation and bioremediation of vanadium.

Keywords Heavy metal • Bioremediation • Vanadium • Ascidiaceans

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1 Introduction

Vanadium is an element with symbol V and atomic number 23. It is the 19th most abundant element in the earth's crust (0.015–0.016 %, 150–160 ppm) (Emsley 1998; WHO 2000). Metallic vanadium is not found in nature, but its compounds can be obtained as minerals such as vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) (Fig. 1), a lead vanadate ore from which vanadium was first discovered by a Mexican, Andrés Manuel del Río. In 1831, Nils Gabriel Sefström rediscovered this element and he called the element vanadium after Vanadis, an additional name of the Norse goddess Freyja, which represented beauty and fertility, because of beautifully colored chemical compounds of this element (Sefström 1831). Mine production including slag products increased year by year up to 75,000 tons in the world, about half of which is produced in China, followed by South Africa and Russia (Brown et al. 2014).

The vast majority (92 %) of vanadium demand is from the steel industry (Parles 2012). Vanadium is mainly used to produce high speed and high alloy tool steels. Vanadium is also used in the production of titanium alloys for aerospace and industrial purposes. Titanium alloys account for about 4 % of consumption in 2012 (Parles 2012). Vanadium pentoxide is used as a catalyst in sulfuric acid production and in the manufacture of ceramics. About 3 % of global vanadium consumption is in petrochemical, catalyst and pollution control applications as well as ceramic pigments, special glasses and other chemical industry applications.

In 2012, about 1 % of vanadium consumed was used in energy storage applications. Vanadium redox flow battery (Rychcik and Skyllas-Kazacos 1988) systems for grid energy storage applications and lithium battery systems incorporating vanadium for mobility applications are under development today with potential to have a significant impact on future vanadium demand (Parles 2012).

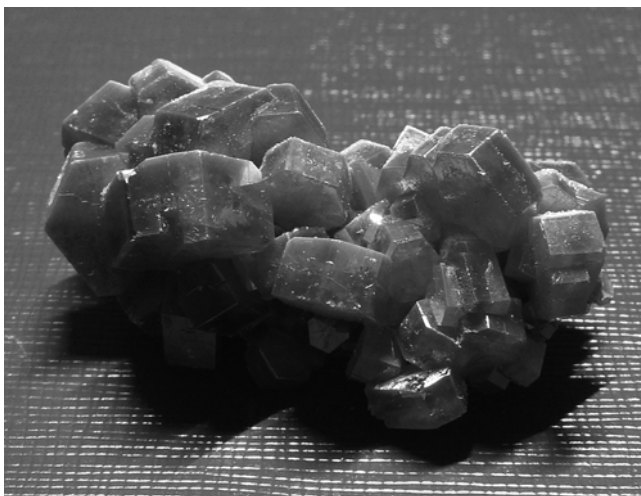


Fig. 1 Vanadinite, Mibladen Atlas Mountain, Morocco. *Dark orange color*

In this chapter, the author would like to overview the history of studies on pollution, toxicity, bioaccumulation and bioremediation of vanadium.

The readers may refer to a recent book on biological and biochemical aspects on vanadium edited by Dr. Michibata (2012). Bioinorganic and chemical topics can be found in a book by Dr. Rehder (2008).

2 Pollution of Vanadium

From early twentieth century, vanadium is regarded as a pollutant. Dutton was the first to describe vanadium poisoning, and produced a word “vanadiumism”, which means a chronic intoxication caused by ingestion or absorption of some forms of vanadium, either industrially, medicinally, or accidentally (Dutton 1911). In his recognition, anemia is an early symptom, and the cough is a prominent and characteristic one. He also noted that some workers using vanadium are susceptible to tuberculosis. Anorexia, nausea and diarrhea indicated gastrointestinal involvement.

2.1 Air Pollution

Four principal oxides are known for vanadium: vanadium monoxide (VO), vanadium trioxide (V_2O_3), vanadium dioxide (VO_2) and vanadium pentoxide (V_2O_5), which ranges +2 to +5 oxidation states. Vanadium pentoxide dust is known to be one of hard metal irritants that affect the upper respiratory tract, producing tracheitis, bronchitis, pneumonia and pulmonary oedema (WHO 2014).

Experimental poisoning in animals indicated that accumulation does not occur and that acute and chronic symptoms are similar (Daniel and Lillie 1938). Studies in early 1900s on experimental administration of vanadium on animal models are well summarized in a review by Wyers (1946).

Stocks reported the relationship between atmospheric pollution in urban area and cancer, bronchitis and pneumonia (Stocks 1960). He especially noted the correlation between trace elements and lung cancer. Vanadium's action as respiratory irritant is significant.

Recent research on pollution of vanadium mainly focuses on the global movement of small particles. The United States of America and the European Union determined their own environmental baseline in 1971 and 1980, respectively, for PM10 and PM2.5. WHO first determined a guideline in Europe, and then extended it in 2005 as a global guideline (WHO 2005). In Japan, original guideline was first released in 1972, and the baseline for PM2.5 was determined in 2009.

Since vanadium is the major trace metal in fossil fuels (Filby and Branthaver 1987; Jacks 1976; Sundararaman et al. 1988), combustion of these materials provides an appreciable source of vanadium in the environment and can be a source for this heavy metal in particular materials in the air (Chen and Duce 1983; Duce and

Hoffman 1976; Weisel et al. 1984). Crude oil contains vanadium as high as 1580 ppm, and it varies depending on the source (Barwise 1990).

2.2 *Water Pollution*

Vanadium can either be dissolved in water as ions or may become adsorbed to particulate matter. The concentration of vanadium in water is largely dependent on geographical location and ranges from 0.2 to more than 100 ppb in freshwater, and from 0.2 to 29 ppb in seawater (WHO 2000). Typical average value of vanadium is recognized as 1.8 ppb (35 nM) (Cole et al. 1983; Collier 1984). Concentrations of vanadium in drinking water may range from about 0.2 to more than 100 µg/L (Nordberg et al. 2011). The concentration of vanadium in drinking-water depends significantly on geographical location.

World health organization (WHO) formulated no guidelines for vanadium in drinking water. US Environmental Protection Agency (EPA) did not formulate the limit, but designated vanadium as hazardous substances. The ministry of Health, Labor and Welfare, Japan, also does not determine the limit for vanadium in tap water, although those for other trace metal elements such as Fe, Zn, Al, Pb, Cd, Hg, Se, and Cr are determined.

A lot of toxicological studies on aquatic animals can be found in literatures for assessment of both acute and chronic toxicity on freshwater and marine fishes (e.g., Knudtson 1979; Perez-Benito 2006; Stendahl and Sprague 1982). A study using rainbow trout suggested that hardness did not exert a major effect, and the authors supposed that it was because vanadium is present in water as various anions (Stendahl and Sprague 1982).

3 **Toxicity of Vanadium**

The toxicity of vanadium, as vanadate anions, have been published from early twentieth century. Studies on rodent and avian models precedes the studies on aquatic animals, as mentioned in the previous section.

Moxon et al. published several papers on the toxicity of oxy anions including vanadate on rats (Franke and Moxon 1936, 1937; Moxon and DuBois 1939). It was revealed that arsenic and molybdenum were slightly toxic, tellurium and vanadium were moderately toxic, and selenium was very toxic as they were compared at the 50-ppm level.

Chicks were also used as test animals for vanadium toxicity by adding vanadium to the diets (Berg 1963, 1966; Hathcock et al. 1964; Nelson et al. 1962; Romoser et al. 1961). Nelson et al. showed that diets containing less than 20 ppm of vanadium were safe for young chicks (Nelson et al. 1962). Hathcock et al. examined the toxicity of vanadium with a diet added by 25-ppm vanadium for 2-weeks, which caused a significant decrease in growth rate and 90 % death in chicks (Hathcock et al. 1964).

Acute toxicity of vanadium compounds, both +5 and +4 oxidation states (NaVO_3 and VOSO_4), were examined by oral or intraperitoneal administration for rats and mice (Llobet and Domingo 1984), and LD_{50} (up to 14 days) were determined. The dose of vanadium was 39–845 mg/kg body weight. As a result, LD_{50} for V^{5+} was 2.2–3.0 times lower than that for V^{4+} after oral administration, as well for intraperitoneal administration where the factor was 1.2–1.9 times. Reproductive toxicity of vanadium was also examined in mice and rats (Elbetieha and Al-Hamood 1997; Jain et al. 2007; Llobet et al. 1993; Morgan and El-Tawil 2003) by using several different salts and compounds.

Later, more detailed studies using cell culture were conducted. Cytotoxic effects of vanadium on rabbit alveolar macrophages (RAM) was assessed *in vitro* with exposure to particulate forms of vanadium oxides in +5 or +4 oxidation state (V_2O_5 , V_2O_3 and VO_2) (Waters et al. 1974). Cell viabilities after 20-h exposure were reduced to 50 % by 13–33 ppm vanadium, depending on chemical species.

Toxicity of vanadium is related to the production of reactive oxygen species (ROS) that cause several damages on nucleic acids, proteins and lipids. Exposure to air pollution particles also cause such damages (Kadiiska et al. 1997).

4 Bioaccumulation of Vanadium

Humans usually consume 10–60 μg of vanadium through foods daily. The mean vanadium concentration in the diet was reported to be 32 $\mu\text{g}/\text{kg}$ and the mean daily intake was estimated to be 20 $\mu\text{g}/\text{day}$ (WHO 2000). The human body is estimated to contain 50–200 μg of vanadium. In each organ, vanadium is present at very low concentrations (Underwood 2012). High levels of vanadium are found in marine organisms, such as ascidians and fan worms. On dry weight base, the vanadium level in a genus *Ascidia* reaches 4,000–20,000 ppm dry weight (Michibata et al. 1986). The fly agaric mushroom (*Amanita muscaria*) also contain relatively high levels of vanadium (120 ppm dry weight) (Michibata 2012). Comprehensive survey of vanadium levels in marine organisms suggested that around 20 ppm dry weight were found in sea weeds (Fukushima et al. 2009).

Approximately 100 years ago, the German physiological chemist Dr. Martin Henze discovered high levels of vanadium in the blood (coelomic) cells of the ascidian *Phallusia mammillata* collected from the Bay of Naples, Italy (Henze 1911). His discovery attracted the inter disciplinary attention of chemists, physiologists, and biochemists.

The greatest concentration was found in blood cells of the ascidian *Ascidia gemmata*, at up to 350 mM (Michibata et al. 1986, 1991), which is 10^7 times that in seawater (35 nM) (Cole et al. 1983; Collier 1984); this is believed to be the highest degree of accumulation of a metal in any living organism. Vanadium ions are mostly accumulated in the vacuole of signet ring cells, which are a type of blood (coelomic) cell and called “vanadocytes” (Michibata et al. 1987; Ueki et al. 2002).



Fig. 2 Amino acid sequences of the five Vanabins from *Ascidia sydneiensis samea* and the two from *Ascidia gemmata*. Conserved amino acid residues are boxed, and the 18 cysteines in the core region are numbered. Positively and negatively charged amino acids are shaded in gray (Reproduced from Samino et al. 2012)

Ongoing research during the last two decades has identified many proteins involved in the process of accumulating and reducing vanadium in vanadocytes, blood plasma, and the digestive tract of ascidians. Among the proteins identified so far, the vanadium-binding proteins (Vanabins) are most prominent.

Vanabins were first purified from blood cells of *Ascidia sydneiensis samea*, which contained 12.8 mM vanadium in the blood cells, by anion-exchange column chromatography (Kanda et al. 1997). The related proteins and genes were identified by ion exchange chromatography, metal ion affinity chromatography and a expressed sequence tag (EST) analyses from the same species (Ueki et al. 2003a; Yoshihara et al. 2005, 2008; Yamaguchi et al. 2004). In this species, the Vanabin family consists of at least five closely related proteins, Vanabins1–4 and VanabinP. All five Vanabins possess 18 cysteine residues, and the intervals between cysteines are well-conserved (Fig. 2).

A homology search of public DNA and protein databases, using both Vanabin1 and Vanabin2 amino acid sequences, revealed no proteins with striking similarities, other than those from two ascidian species, *Ciona intestinalis* and *A. gemmata*. We identified five Vanabins (CiVanabin1 to CiVanabin5) from *C. intestinalis* (Trivedi et al. 2003) and two Vanabins (AgVanabin1 and AgVanabin2) in *A. gemmata* (Fig. 2) (Samino et al. 2012). Thus, Vanabins appear to be ubiquitous among the vanadium-accumulating ascidians and may hold the key to resolving the mechanism underlying the highly selective and extremely high-level accumulation of vanadium ions.

More detailed review of the molecular mechanism of vanadium accumulation in ascidians can be found in publications from our research group (Michibata and Ueki 2010; Michibata et al. 2003, 2007; Ueki and Michibata 2011; Ueki et al. 2014).

The accumulation of vanadium is also revealed in the fan worms *Pseudopotamilla ocellata* (Ishii et al. 1993) and *Perkinsiana littoralis* (Fattorini et al. 2010). In these fan worms, the concentration of vanadium is as high as 60 mM. Fan worms belong to the phylum Polychaeta, which is phylogenetically distant from ascidians (Chordata). Unlike the chordates, in fan worms, the highest level of vanadium is found not in blood (coelomic) cells but in the epithelial cells of the branchial crown.

5 Bioremediation of Vanadium

The decontamination of soil and water containing heavy metals from industrial activity is a troublesome problem. Natural or synthetic organic materials are useful to absorb heavy metals. Bioremediation strategies, using microorganisms or plants with metal-binding ability, have been proposed as attractive methods, because these are effective at low metal concentrations and are less expensive and more efficient than physicochemical methods of removing heavy metals.

5.1 Organic Materials

Efforts have been made from 1970s in order to process industrial waste waters by activated sludge. An early study succeeded in absorbing vanadium from a solution at the concentration of 30–40 mg/L, but it was not very efficient (Kunz et al. 1976). Metal sludge was also tested for removal of vanadium but, as compared with other heavy metal ions, vanadium removal efficiency was low (Namasivayam and Sangeetha 2007). One reason could be the behavior of vanadium in ambient environment as an anion (protonated forms of VO_4^{3-}) (Fig. 3) (Crans et al. 2004; Ueki et al. 2014).

Chitosan is very efficient at removing vanadium from dilute solutions (Guzman et al. 2002; Jansson-Charrier et al. 1996; Niu and Volesky 2003). Anionic metal complexes such as anions as VO_4^{3-} , CrO_4^{2-} , SeO_4^{2-} are very effectively bound by biomass types like chitosan that contains abundant amine groups (Niu and Volesky 2003). In contrast, cationic form of vanadium (VO^{2+}) is also absorbed by chitosan (Jansson-Charrier et al. 1996). Adsorption of other cationic heavy metal ions such as Fe^{3+} , Cu^{2+} and Cd^{2+} using chitosan is also reported (Juang et al. 1999; Namdeo and Bajpai 2008; Prakash et al. 2012). Thus, chitosan is both effective for anions and cations.

By using plant materials, lead and vanadium were efficiently absorbed from a real industrial wastewater onto *Pinus sylvestris* sawdust (Kaczala et al. 2009). Removal of V^{3+} and Mo^{5+} from model wastewater using dried and re-hydrated biomass of a sea grass *Posidonia oceanica* is reported (Pennesi et al. 2013).

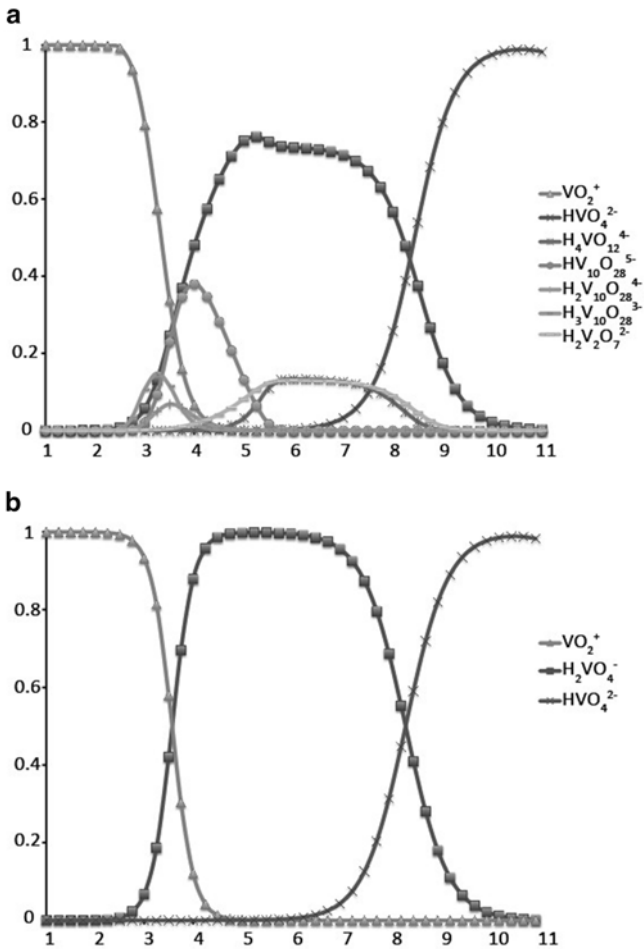


Fig. 3 Speciation diagram for aqueous vanadate solutions calculated by Visual MINTEQ ver. 3 based on MINTEQA2 (Allison et al. 1989). Data are normalized to total concentration and expressed as molar fraction x_V vs. pH. Ionic strength: 0.45 M. Vanadium concentration and species: 1 mM V^V (a) or 1 μM V^V (b). Temperature: 25 °C. Species that comprised less than 3 % are not shown. As compared with experimentally determined speciation diagrams (Rehder 2008), the ratios of polymeric vanadate species are relatively low (Modified from Ueki et al. 2014)

5.2 Biotechnological Approaches

To recover heavy metals, one possible approach is the biotechnological use of metal-binding peptides with the ability to bind heavy metals in various living organisms to improve the metal-binding abilities of microorganisms via heterologous expression.

Table 1 Bioremediation of heavy metals by *E. coli* cells expressing Vanabins from an ascidian *Ascidia sydneiensis samea*

	Vanabin1	Vanabin2	MBP	TB1
V(IV)	3.9	7.3	4.1	3.5
Cu(II)	876 ± 215**	882 ± 136**	87.5 ± 22.4	43.2 ± 20.9

Values are given as ng mg⁻¹ dw.

***P* < 0.005

Table 2 Bioremediation of heavy metals by *E. coli* cells expressing Ag Vanabins from an ascidian *Ascidia gemmata*

	AgVanabin1	AgVanabin2	MBP	TB1
Vanadium	6.25 ± 0.48	10.12 ± 0.95*	6.92 ± 0.16	7.47 ± 0.54
Iron	203,303 ± 4,192	251,586 ± 73,094	299,422 ± 26,428	239,257 ± 16,521
Copper	550.79 ± 6.50	2360.91 ± 462.05*	559.81 ± 64.19	173.62 ± 43.06
Cobalt	4.33 ± 0.64	4.88 ± 0.57	3.97 ± 0.20	8.23 ± 2.50
Nickel	25.04 ± 1.08	26.64 ± 1.53	25.12 ± 1.97	20.46 ± 1.16
Zinc	151.10 ± 19.45	158.72 ± 39.41	159.48 ± 17.68	145.56 ± 31.64

Values are given as ng mg⁻¹ dw.

**P* < 0.05

Many studies have focused on metallothioneins, which are small, cysteine-rich proteins that are widely distributed from prokaryotes to eukaryotes. When metallothioneins are expressed in the cytoplasm (He et al. 2014; Pazirandeh et al. 1995; Singh et al. 2008; Yoshida et al. 2002), periplasm (Mauro and Pazirandeh 2000; Pazirandeh et al. 1995, 1998) or outer membrane (Lin et al. 2010) of *Escherichia coli*, the cells remove heavy metal ions, such as Cd²⁺, Hg²⁺, Pb²⁺, Cu²⁺ and As³⁺ from the culture media and accumulate them.

Phytochelatin(PCs) are also metal-binding cysteine-rich proteins found in plants and fungi, and heterologous expression of PC-synthase enhanced Cd²⁺, Cu²⁺ and As³⁺ accumulation in bacteria (Sauge-Merle et al. 2003). Several studies have sought novel synthetic small peptides that enhance the bioaccumulation of specific metals (Kotrba et al. 1999; Mej re et al. 1998; Samuelson et al. 2000).

It is well known that porin channels (exclusion size, 600 Da) exist on the outer membrane of gram-negative bacteria, including *E. coli*, and small molecules including heavy metal cations and anions can diffuse through this type of channel in a rather non-specific manner (Benz 1988; Benz et al. 1985; Nikaido and Rosenberg 1983).

In my research group, it was intended to express Vanabin genes in bacteria to construct bioremediation system for vanadium. First study was done by using two Vanabin genes from *Ascidia sydneiensis samea*. But unfortunately, *E. coli* cells expressing these Vanabins in the periplasm could not accumulate VO²⁺ significantly but absorption of Cu²⁺ was around 20-fold enhanced (Table 1) (Ueki et al. 2003b). A following study using two Vanabins from another ascidian species *A. gemmata* was performed. When AgVanabin2, was expressed in the periplasm of *E. coli*, absorption of both VO²⁺ and Cu²⁺ were enhanced significantly (Table 2) (Samino et al. 2012).

6 Conclusion and Future Prospective

From early twentieth century, vanadium is regarded as a pollutant, especially in air exhausted from industry. Waste water management for vanadium is also recognized. Bioremediation of vanadium is mainly intended to manage waste water, since natural water does not contain hazardous level of vanadium. Cost effective method is to use organic non-living materials such as chitosan. Biotechnological applications may provide much more specific method to remove vanadium, but it must need to improve both absorption activity and the cost-efficiency. Once these problems are solved, biotechnological methods may surpass the other technologies.

References

- Allison JD, Brown DS, Novo-Gradac KJ (1989) MINTEQA2/PRODEFA2, A geochemical assessment model for environment system: version 3.0. US EPA, Office of Research and Development, Washington, DC, 20460
- Barwise AJG (1990) Role of nickel and vanadium in petroleum classification. *Energy Fuels* 4:647–652
- Benz R (1988) Structure and function of porins from gram-negative bacteria. *Annu Rev Microbiol* 42:359–393
- Benz R, Schmid A, Hancock RE (1985) Ion selectivity of gram-negative bacterial porins. *J Bacteriol* 162:722–727
- Berg LR (1963) Evidence of vanadium toxicity resulting from the use of certain commercial phosphorus supplements in chick rations. *Poult Sci* 42:766–769
- Berg LR (1966) Effect of diet composition on vanadium toxicity for the chick. *Poult Sci* 45:1346–1352
- Brown TJ, Idoine N, Raycraft ER, Shaw RA, Deady EA (2014) World mineral production 2008–12. British Geological Survey, pp 1–115
- Chen L, Duce RA (1983) The sources of sulfate, vanadium and mineral matter in aerosol particles over Bermuda. *Atmos Environ* 17:2055–2064
- Cole PC, Eckert J, Williams K (1983) The determination of dissolved and particulate vanadium in sea water by x-ray fluorescence spectrometry. *Anal Chim Acta* 153:61–67
- Collier RW (1984) Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* 309:441
- Crans DC, Smee JJ, Gaidamauskas E, Yang L (2004) The chemistry and biochemistry of vanadium and the biological activities exerted by vanadium compounds. *Chem Rev* 104:849–902
- Daniel EP, Lillie RD (1938) Experimental vanadium poisoning in the white rat. *Pub Health Rep* (1896–1970) 53:765–777
- Duce RA, Hoffman GL (1976) Atmospheric vanadium transport to the ocean. *Atmos Environ* 10:989–996
- Dutton WF (1911) Vanadiumism. *J Am Med Assoc* LVI:1648
- Elbetieha A, Al-Hamood MH (1997) Long-term exposure of male and female mice to trivalent and hexavalent chromium compounds: effect on fertility. *Toxicology* 116:39–47
- Emsley J (1998) The elements (Oxford chemistry guides). Oxford University Press, Oxford
- Fattorini D, Notti A, Nigro M, Regoli F (2010) Hyperaccumulation of vanadium in the Antarctic polychaete *Perkinsiana littoralis* as a natural chemical defense against predation. *Environ Sci Pollut Res* 17:220–228

- Filby RH, Branthaver JFE (1987) Metal complexes in fossil fuels: geochemistry, characterization, and processing. In: Presented at the ACS National meeting in New York. American Chemical Society, Washington, DC
- Franke KW, Moxon AL (1936) A comparison of the minimum fatal doses of selenium, tellurium, arsenic and vanadium. *J Pharmacol Exp Ther* 58:454–459
- Franke KW, Moxon AL (1937) The toxicity of orally ingested arsenic, selenium, tellurium, vanadium and molybdenum. *J Pharmacol Exp Ther* 61:89–102
- Fukushima M, Suzuki H, Saito K, Chatt A (2009) Vanadium levels in marine organisms of Onagawa Bay in Japan. *J Radioanal Nucl Chem* 282:85–89
- Guzman J, Saucedo I, Navarro R, Revilla J, Guibal E (2002) Vanadium interactions with chitosan: influence of polymer protonation and metal speciation. *Langmuir* 18:1567–1573
- Hathcock JN, Hill CH, Matrone G (1964) Vanadium toxicity and distribution in chicks and rats. *J Nutr* 82:106–110
- He Y, Ma W, Li Y, Liu J, Jing W, Wang L (2014) Expression of metallothionein of freshwater crab (*Sinopotamon henanense*) in *Escherichia coli* enhances tolerance and accumulation of zinc, copper and cadmium. *Ecotoxicology* 23:56–64
- Henze M (1911) Untersuchungen über des Blut der Ascidien. I. Mitteilung. Die Vanadiumverbindung der Blutkörperchen. *Hoppe-Seyler's. Z Physiol Chem* 72:494–501
- Ishii T, Nakai I, Numako C, Okoshi K (1993) Discovery of a new vanadium accumulator, the fan worm *Pseudopotamilla ocellata*. *Naturwissenschaften* 80:268–270
- Jacks G (1976) Vanadium in an area just outside Stockholm. *Environ Pollut* 11:289–295
- Jain GC, Pareek H, Sharma S, Bhardwaj M, Khajja BS (2007) Reproductive toxicity of vanadyl sulphate in male rats. *J Health Sci* 53:137–141
- Jansson-Charrier M, Guibal E, Roussy J, Delanghe B (1996) Vanadium (IV) sorption by chitosan: kinetics and equilibrium. *Water Res* 30:465–475
- Juang RS, Wu FC, Tseng RL (1999) Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents. *Water Res* 30:2403–2409
- Kaczala F, Marques M, Hogland W (2009) Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto *Pinus sylvestris* sawdust. *Biores Technol* 100:235–243
- Kadiiska MB, Mason RP, Dreher KL, Costa DL, Ghio AJ (1997) *In vivo* evidence of free radical formation in the rat lung after exposure to an emission source air pollution particle. *Chem Res Toxicol* 10:1104–1108
- Kanda T, Nose Y, Wuchiyama J, Uyama T, Moriyama Y, Michibata H (1997) Identification of a vanadium-associated protein from the vanadium-rich ascidian, *Ascidia sydneiensis samea*. *Zool Sci* 14:37–42
- Knudtson BK (1979) Acute toxicity of vanadium to two species of freshwater fish. *Bull Environ Contam Toxicol* 23:95–99
- Kotrba P, Dolecková L, de Lorenzo V, Ruml T (1999) Enhanced bioaccumulation of heavy metal ions by bacterial cells due to surface display of short metal binding peptides. *Appl Environ Microbiol* 65:1092–1098
- Kunz RG, Giannelli JF, Stensel HD (1976) Vanadium removal from industrial wastewaters. *J Water Pollut Control Fed* 48:762–770
- Lin K-H, Chien M-F, Hsieh J-L, Huang C-C (2010) Mercury resistance and accumulation in *Escherichia coli* with cell surface expression of fish metallothionein. *Appl Microbiol Biotechnol* 87:561–569
- Llobet JM, Domingo JL (1984) Acute toxicity of vanadium compounds in rats and mice. *Toxicol Lett* 23:227–231
- Llobet JM, Colomina MT, Sirvent JJ, Domingo JL (1993) Reproductive toxicity evaluation of vanadium in male mice. *Toxicology* 80:199–206
- Mauro JM, Pazirandeh M (2000) Construction and expression of functional multi-domain peptides in *Escherichia coli*: expression of the *Neurospora crassa* metallothionein gene. *Lett Appl Microbiol* 30:161–166

- Mejáre M, Ljung S, Bülow L (1998) Selection of cadmium specific hexapeptides and their expression as OmpA fusion proteins in *Escherichia coli*. *Protein Eng* 11:489–494
- Michibata H (2012) Vanadium. Springer, Dordrecht
- Michibata H, Ueki T (2010) Advances in research on the accumulation, redox behavior, and function of vanadium in ascidians. *Biomol Concepts* 1:97–107
- Michibata H, Terada T, Anada N, Yamakawa K, Numakunai T (1986) The accumulation and distribution of vanadium, iron, and manganese in some solitary ascidians. *Biol Bull* 171:672–681
- Michibata H, Hirata J, Uesaka M (1987) Separation of vanadocytes: determination and characterization of vanadium ion in the separated blood cells of the ascidian, *Ascidia ahodori*. *J Exp Zool* 244:33–38
- Michibata H, Iwata Y, Hirata J (1991) Isolation of highly acidic and vanadium-containing blood cells from among several types of blood cell from Ascidiidae species by density-gradient centrifugation. *J Exp Zool* 257:306–313
- Michibata H, Yamaguchi N, Uyama T, Ueki T (2003) Molecular biological approaches to the accumulation and reduction of vanadium by ascidians. *Coord Chem Rev* 237:41–51
- Michibata H, Yoshinaga M, Yoshihara M, Kawakami N, Yamaguchi N, Ueki T (2007) Genes and proteins involved in vanadium accumulation by ascidians. In: ACS symposium series. American Chemical Society, Washington, DC, pp 264–280
- Morgan AM, El-Tawil OS (2003) Effects of ammonium metavanadate on fertility and reproductive performance of adult male and female rats. *Pharm Res* 47:75–85
- Moxon AL, DuBois KP (1939) The influence of arsenic and certain other elements on the toxicity of seleniferous grains three figures. *J Nutr* 18:447–457
- Namasivayam C, Sangeetha D (2007) Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from *Jatropha Husk*, an agro-industrial solid waste. *Process Saf Environ Prot* 85:181–184
- Namdeo M, Bajpai SK (2008) Chitosan–magnetite nanocomposites (CMNs) as magnetic carrier particles for removal of Fe(III) from aqueous solutions. *Colloid Surf A Physicochem Eng Asp* 320:161–168
- Nelson TS, Gillis MB, Peeler HT (1962) Studies of the effect of vanadium on chick growth. *Poult Sci* 41:519–522
- Nikaido H, Rosenberg EY (1983) Porin channels in *Escherichia coli*: studies with liposomes reconstituted from purified proteins. *J Bacteriol* 153:241–252
- Niu H, Volesky B (2003) Characteristics of anionic metal species biosorption with waste crab shells. *Hydrometallurgy* 71:209–215
- Nordberg GF, Fowler BA, Nordberg M, Friberg L (2011) Handbook on the toxicology of metals. Academic, Waltham
- Parles T (2012) Vanadium market fundamentals and implications. Presented at the metal bulletin 28th international ferroalloys conference. Berlin, Germany.
- Pazirandeh M, Chrisey LA, Mauro JM, Campbell JR, Gaber BP (1995) Expression of the *Neurospora crassa* metallothionein gene in *Escherichia coli* and its effect on heavy-metal uptake. *Appl Microbiol Biotechnol* 43:1112–1117
- Pazirandeh M, Wells BM, Ryan RL (1998) Development of bacterium-based heavy metal biosorbents: enhanced uptake of cadmium and mercury by *Escherichia coli* expressing a metal binding motif. *Appl Environ Microbiol* 64:4068–4072
- Pennesi C, Totti C, Beolchini F (2013) Removal of vanadium(III) and molybdenum(V) from wastewater using *Posidonia oceanica* (Tracheophyta) biomass. *PLoS One* 8:e76870
- Perez-Benito JF (2006) Effects of chromium(VI) and vanadium(V) on the lifespan of fish. *J Trace Elem Med Biol* 20:161–170
- Prakash N, Sudha PN, Renganathan NG (2012) Copper and cadmium removal from synthetic industrial wastewater using chitosan and nylon 6 – Springer. *Environ Sci Pollut Res* 19: 2930–2941
- Rehder D (2008) Bioinorganic vanadium chemistry. Wiley, Chichester
- Romoser GL, Dudley WA, Machlin LJ, Loveless L (1961) Toxicity of vanadium and chromium for the growing chick. *Poult Sci* 40:1171–1173

- Rychcik M, Skyllas-Kazacos M (1988) Characteristics of a new all-vanadium redox flow battery. *J Power Sources* 22:59–67
- Samino S, Michibata H, Ueki T (2012) Identification of a novel Vanadium-binding protein by EST analysis on the most vanadium-rich ascidian, *Ascidia gemmata*. *Mar Biotechnol* 14:143–154
- Samuelson P, Wernérus H, Svedberg M, Ståhl S (2000) Staphylococcal surface display of metal-binding polyhistidyl peptides. *Appl Environ Microbiol* 66:1243–1248
- Sauge-Merle S, Cuine S, Carrier P, Lecomte-Pradines C, Luu DT, Peltier G (2003) Enhanced toxic metal accumulation in engineered bacterial cells expressing *Arabidopsis thaliana* phytochelatin synthase. *Appl Environ Microbiol* 69:490–494
- Sefström NG (1831) Ueber das Vanadin, ein neues Metall, gefunden im Stangeneisen von Eckersholm, einer Eisenhütte, die ihr Erz von Taberg in Småland bezieht. *Ann Phys Chem* 97:43–49
- Singh S, Mulchandani A, Chen W (2008) Highly selective and rapid arsenic removal by metabolically engineered *Escherichia coli* cells expressing *Fucus vesiculosus* metallothionein. *Appl Environ Microbiol* 74:2924–2927
- Stendahl DH, Sprague JB (1982) Effects of water hardness and pH on vanadium lethality to rainbow trout. *Water Res* 16:1479–1488
- Stocks P (1960) On the relations between atmospheric pollution in urban and rural localities and mortality from cancer, bronchitis and pneumonia, with particular reference to 3:4 benzopyrene, beryllium, molybdenum, vanadium and arsenic. *Br J Cancer* 14:397
- Sundararaman P, Biggs WR, Reynolds JG (1988) Vanadylporphyrins, indicators of kerogen breakdown and generation of petroleum. *Geochim Cosmochim Acta* 52:2337–2341
- Trivedi S, Ueki T, Yamaguchi N, Michibata H (2003) Novel vanadium-binding proteins (vanabins) identified in cDNA libraries and the genome of the ascidian *Ciona intestinalis*. *Biochim Biophys Acta* 1630:64–70
- Ueki T, Michibata H (2011) Molecular mechanism of the transport and reduction pathway of vanadium in ascidians. *Coord Chem Rev* 255:2249–2257
- Ueki T, Takemoto K, Fayard B, Salomé M, Yamamoto A, Kihara H, Susini J, Scippa S, Uyama T, Michibata H (2002) Scanning x-ray microscopy of living and freeze-dried blood cells in two vanadium-rich ascidian species, *Phallusia mammillata* and *Ascidia sydneiensis samea*. *Zool Sci* 19:27–35
- Ueki T, Adachi T, Kawano S, Aoshima M, Yamaguchi N, Kanamori K, Michibata H (2003a) Vanadium-binding proteins (vanabins) from a vanadium-rich ascidian *Ascidia sydneiensis samea*. *Biochim Biophys Acta* 1626:43–50
- Ueki T, Sakamoto Y, Yamaguchi N, Michibata H (2003b) Bioaccumulation of copper ions by *Escherichia coli* expressing vanabin genes from the vanadium-rich ascidian *Ascidia sydneiensis samea*. *Appl Environ Microbiol* 69:6442–6446
- Ueki T, Yamaguchi N, Isago Y, Tanahashi H (2014) Vanadium accumulation in ascidians: a system overview. *Coord Chem Rev* 301–302:300–308. doi:10.1016/j.ccr.2014.09.007
- Underwood E (2012) Trace elements in human and animal nutrition, 4th edn. Elsevier, Amsterdam
- Waters MD, Gardner DE, Coffin DL (1974) Cytotoxic effects of vanadium on rabbit alveolar macrophages *in vitro*. *Toxicol Appl Pharmacol* 28:253–263
- Weisel CP, Duce RA, Fasching JL, Heaton RW (1984) Estimates of the transport of trace metals from the ocean to the atmosphere. *J Geophys Res* 89:11607
- WHO (2000) Vanadium air quality guidelines, WHO Regional Office for Europe, Copenhagen, Chapter 6.12, pp 1–9
- WHO (2005) Air quality guidelines – global update 2005. WHO, Copenhagen
- WHO (2014) Dust: definitions and concepts, Hazard prevention and control in the work environment: airborne dust (WHO, 1999). WHO, Chapter 1, pp 1–96
- Wyers H (1946) Some toxic effects of vanadium pentoxide. *Br J Ind Med* 3:177–182
- Yamaguchi N, Kamino K, Ueki T, Michibata H (2004) Expressed sequence tag analysis of vanadocytes in a vanadium-rich ascidian, *Ascidia sydneiensis samea*. *Mar Biotechnol* 6:165–174

- Yoshida N, Kato T, Yoshida T, Ogawa K, Yamashita M, Murooka Y (2002) Bacterium-based heavy metal biosorbents: enhanced uptake of cadmium by *E. coli* expressing a metallothionein fused to beta-galactosidase. *Biotechniques* 32:551–558
- Yoshihara M, Ueki T, Watanabe T, Yamaguchi N, Kamino K, Michibata H (2005) VanabinP, a novel vanadium-binding protein in the blood plasma of an ascidian, *Ascidia sydneiensis samea*. *Biochim Biophys Acta* 1730:206–214
- Yoshihara M, Ueki T, Yamaguchi N, Kamino K, Michibata H (2008) Characterization of a novel vanadium-binding protein (VBP-129) from blood plasma of the vanadium-rich ascidian *Ascidia sydneiensis samea*. *Biochim Biophys Acta* 1780:256–263