



Oral bioaccessibility and health risk assessment of vanadium(IV) and vanadium(V) in a vanadium titanomagnetite mining region by a whole digestive system in-vitro method (WDSM)

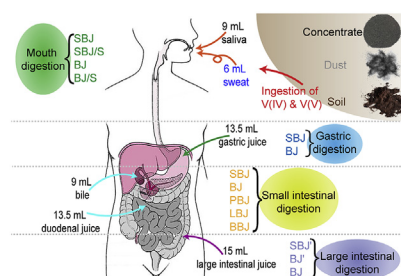
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HIGHLIGHTS

- Determine vanadium bioaccessibility (VB) by a whole digestive system in-vitro model.
- Sweat had insignificant influence ($p > 0.05$) on VB in mouth.
- Most bioaccessible vanadium was observed in stomach and small intestine.
- Digestive enzymes had opposite effect on VB in different digestive phases.
- Bioaccessible vanadium(IV) was lower than vanadium(V) in digestive system.

GRAPHICAL ABSTRACT



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ABSTRACT

Oral bioaccessibility of vanadium(IV) and vanadium(V) in soil, dust and concentrate fines from a vanadium titanomagnetite mining region was assessed by a whole digestive system in-vitro scheme. The scheme including the addition of sweat and the large intestinal digestion was used to estimate the oral bioaccessibility of vanadium(IV) and vanadium(V) in the whole digestive system for the first time. Higher oral bioaccessibility of vanadium(IV) and vanadium(V) was determined in gastric and small intestinal phases demonstrating that their major roles for vanadium digestion and absorption. The decreasing order of the oral bioaccessibility of vanadium(IV) and vanadium(V) in each digestive phase was stomach, small intestine, large intestine and mouth. Higher oral bioaccessibility of vanadium(V) in the whole digestion indicated its higher risk potential for human than vanadium(IV). Lower oral bioaccessibility of vanadium(IV) and vanadium(V) determined in bionic digestion illustrated detoxicity potential of human body for ingested vanadium. Compared with soil and dust, higher digestion rate of vanadium in vanadium titanomagnetite concentrate fines indicated its higher risk for human, especially for mining workers. Based on vanadium oral bioaccessibility, hazard quotients of the vanadium were much less than the critical level suggested for no non-carcinogenic risks to the populations surrounding the sampling sites. Indeed, compared with the estimations based on total vanadium content, the incorporation of oral vanadium bioaccessibility into risk assessments could give more realistic information.

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Abbreviations in the present study

V(IV)	tetravalent vanadium
V(V)	pentavalent vanadium
SBJ	semi-bionic digestive juices
SBJ/S	mixture of semi-bionic digestive juices and artificial sweat
BJ	bionic digestive juices
BJ/S	mixture of bionic digestive juices and artificial sweat
PBJ	mixture of semi-bionic digestive juices and the pancreatin
LBJ	mixture of semi-bionic digestive juices and the lipase
BBJ	mixture of semi-bionic digestive juices and the bile
'	analysis of the pellet after small intestinal digestion by the first step of sequence extraction of Tessier et al. (1979)
WDSM	whole digestive system in-vitro method

1. Introduction

Vanadium, which occurs in soil at a mean concentration of about 90 mg kg^{-1} in global, has been recognized as potentially dangerous pollutant in the same class as mercury, lead and arsenic (Wisawapipat and Kretzschmar, 2017; Teng et al., 2011). Interest in vanadium in the environment is growing continuously because of the rapid increasing anthropogenic vanadium pollution caused by mining activities, fossil fuel combustion, petrochemical refining, metal industry, automotive traffic and domestic heating (Wisawapipat and Kretzschmar, 2017). High levels of vanadium can exert substantial toxic effects (Tian et al., 2014). For human, excess vanadium can increase the risk of morphological and functional lesions in kidneys, liver, spleen, bones and leukocytes (Ghosh et al., 2015).

Multi oxidation states ($-III$, $-I$, 0 , $+I$, $+II$, $+III$, $+IV$ and $+V$) and various coordination compounds of vanadium in environment and in living organisms put forth its chemical and toxic complexity (Nedrich et al., 2018; Tracey et al., 2007). Vanadium(V) and vanadium(IV) are the predominant redox forms in environment generally (Baken et al., 2012). Vanadium(IV) in-vivo can undergo spontaneous oxidation to vanadium(V) (Li et al., 1996), and the in-vivo vanadium in its anionic form [vanadate(V), H_2VO_4^-] has been observed to be absorbed at much higher amount (about 5 times more than the cationic form [vanadyl (IV), VO^{2+}]) through anionic transport system (Hirano and Suzuki, 1996). Therefore, compared with the tetravalent form, the pentavalent one has been reported more stable and toxic (Mthombeni et al., 2016).

Exposure refers to the contact process between visible boundary of human and environmental pollutants (Duan, 2012). Therefore, the human environmental exposure study is important to assess the contaminant toxicity. Generally, the local population exposure can be estimated by comprehensive consideration of oral, inhalation and dermal routes (Yang et al., 2017). Therefore, vanadium in environment, which may be ingested by hand-to-mouth behavior, food chain and contaminated water via oral ingestion, plays an important role in human health (Zhang et al., 2014; Luo et al., 2011). However, the toxicity of ingested vanadium in different media is dependent on the mineral forms, particle types and solubility of vanadium and the specific media chemistry (Ruby et al., 1993). Thus, equal ingested doses of total vanadium may not be of equal

health concern. Considering the inappropriate toxic estimation by total vanadium content, the oral bioaccessibility which indicates the amount of metal that is dissolved in the gastrointestinal fluid (Ruby et al., 1993) was introduced to evaluate the vanadium toxicity via oral intake pathway more accurately. Anke (2004) has proposed that fecal excretion of the nutritional vanadium intake amounts to 96% in men and non-lactating women and that to 79% in lactating women. Although the vanadium digestion in gastric and small intestinal phases has been reported (Palmer et al., 2014; He et al., 2012), the systematic digestion in the whole digestive system, especially in the large intestinal phase remains unclear. Besides, the effect of sweat on oral bioaccessibility of vanadium by hand-to-mouth pathway is an interesting facet remaining to be studied. Further studies on the oral bioaccessibility of vanadium from various environmental media are still needed. Though preliminary investigations on the vanadium occupational exposure to mining workers have been reported (Kawai et al., 1989), thorough researches still need to be undertaken. Therefore, it is necessary to investigate the digestion and absorption of oral intake vanadium in each phase of the whole digestive system, and give more accurate health risk estimations of vanadium in different environmental media.

Recently, Yang et al. (2017) reported that about 26.49% of the soils was contaminated by vanadium in southwest of China. Pan-zhihua region was the most important vanadium base in southwest of China, and the environment has been impacted severely by extensive mining, smelting and processing activities of vanadium titanomagnetite (Teng et al., 2011). Thus, the mining workers were the main occupational vanadic exposed population here. Besides, the unconscious oral intake of the roadside dusts and soils played an important role in vanadium ingestion by urban population except for the inhalation and dermal pathways. Therefore, the aims of this study are to (1) develop a whole digestive system in-vitro method (WDSM) to simulate the behavior of vanadium(IV) and vanadium(V) in mouth, stomach, small and large intestine, (2) use the WDSM to measure the oral bioaccessibility of vanadium(IV) and vanadium(V) in soils, dusts and vanadium titanomagnetite concentrate fines collected from a vanadium contaminated area in Panzhihua region, (3) investigate the influence of digestive enzymes that was normally ignored by previous studies on the oral bioaccessibility of vanadium(IV) and vanadium(V), and (4) estimate the human health risk of vanadium(IV) and vanadium(V) to the occupationally exposed population and general population around the sampling area based on the oral bioaccessibility. Results of this study can provide insights into the toxicity and health risk of vanadium from different sources in environment, which therefore may make a contribution for controlling and decreasing the hazards caused by vanadium to human to some degree.

2. Materials and methods**2.1. Sample preparation**

To investigate the potential health risks posed by intensive vanadium mining activities, a total of 9 samples was collected from 9 sampling sites (Table 1) in Panzhihua region, Sichuan province, SW-China, at an elevation of 1200 m above sea level at $101^\circ 08' - 102^\circ 15' \text{ E}$, $26^\circ 05' - 27^\circ 21' \text{ N}$. Sites that are either densely populated or the most influenced by mining activities were selected for the health risk assessments of the general population and occupationally exposed population, respectively. The soil samples were all collected at top 0–15 cm depths from each sampling point and the road dust samples were collected according to Zheng et al. (2010). The concentrate fines were collected from the mining area in Baima concentrating plant. Samples were all stored in separate sealed

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