Leaching of vanadium from waste V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst catalyzed by functional microorganisms

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HIGHLIGHTS
• Bioleaching of waste V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst was performed using five methods.
• The S-mediated way was demonstrated as a promising method to extract vanadium.
• Direct and indirect mechanisms worked to leach vanadium effectively.
• The direct vanadium bioleaching mechanism of the S-mediated way was first reported.

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ABSTRACT
Solid wastes are currently produced in large amounts. Although bioleaching of metals from solid wastes is an economical and sustainable technology, it has seldom been used to recycle metals from abandoned catalyst. In this study, the bioleaching of vanadium from V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst were comprehensively investigated through five methods: Oligotrophic way, Eutrophic way, S-mediated way, Fe-mediated way and Mixed way of S-mediated and Fe-mediated. The observed vanadium bioleaching effectiveness of the assayed methods was follows: S-mediated > Mixed > Oligotrophic > Eutrophic > Fe-mediated, which yielded the maximum bioleaching efficiencies of approximately 90%, 35%, 33%, 20% and 7%, respectively. The microbial community analysis suggested that the predominant genera Acidithiobacillus and Sulfobacillus from the S-mediated bioleaching way effectively catalyzed the vanadium leaching, which could have occurred through the indirect mechanism from the microbial oxidation of S. In addition, the direct mechanism, involving direct electron transfer between the catalyst and the microorganisms that attached to the catalyst surface, should also help the vanadium to be leached more effectively. Therefore, this work provides guidance for future research and practical application on the treatment of waste V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst.

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1. Introduction
Selective catalytic reduction catalyst (SCR catalyst) has been extensively used in fossil fuel combustion plants (Kim et al., 2015). V$_2$O$_5$-WO$_3$/TiO$_2$ is a traditional commercial SCR catalyst, containing approximately 1–5% V$_2$O$_5$ and 10% WO$_3$ (Castellino et al., 2008; Kim et al., 2015; Kompio et al., 2012). Both vanadium and tungsten are toxic to human and environmental health but play a pivotal role in industrial applications, such as in the metallurgy and aerospace industries (Amiri et al., 2011; Li et al., 2014; Nikiforova et al., 2016; Zhang et al., 2007). However, this catalyst has a limited life with 2–3 years due to...
inactivation (Benson et al., 2005; Li et al., 2016; Madia et al., 2002; Nova et al., 2001). In China, it is estimated that 38,000 t/y of catalyst becomes solid wastes (Li et al., 2014). Therefore, extracting metals from waste catalyst would alleviate the national demand for metals and mitigate damage to the environment.

Hydrometallurgy, pyrometallurgy and bioleaching are the general methods used for metal recovery from solid wastes. Both hydrometallurgical and pyrometallurgical processes can contribute to metal mixtures being rapidly and efficiently obtained, resulting from high acid or alkali and high temperature conditions, respectively (Arabikaragani et al., 2010; Havlík et al., 2010; Huo et al., 2015). However, these two processes produce environmental pollutants, such as dioxins, furans and highly acidic wastewater (Gu et al., 2017). Bioleaching of metals from solid wastes is a promising and economical technology with low-cost and environment-friendly benefits (Fonti et al., 2017). Bioleaching has been widely applied to solubilize metals from solid wastes such as swine manure and electronic wastes (Wei et al., 2018; Xiang et al., 2010), but few studies have concentrated on waste catalysts. Unlike printed circuit boards (PCBs, the classic electronic waste), in which the metals are primarily in the form of elementary substances (Hong and Valix, 2014; Li et al., 2015), the elements in the V₂O₅-WO₃/TiO₂ catalyst exist as oxides. In addition, TiO₂ is anatase polymorphic, while monomeric vanadyls and wolframyls and polymeric WWO₅ are observed for V₂O₅ and WO₃ (Alemany et al., 1995). Thus, there are markedly different physicochemical structures and properties between PCBs and V₂O₅-WO₃/TiO₂ catalyst, which may lead to different bioleaching mechanisms.

Therefore, in this study, we investigated five different bioleaching pathways to extract vanadium and tungsten from waste V₂O₅-WO₃/TiO₂ catalyst, including a simple carbon-mediated pathway (Oligotrophic way), rich carbon-mediated pathway (Eutrophic way), reduced sulfur-mediated pathway (S-mediated way), iron-mediated pathway (Fe-mediated way) and a mixed of sulfur- and iron-mediated pathway (Mixed way) (Brandl et al., 2001; Chi et al., 2011; Choi et al., 2004; Wang et al., 2009; Wang et al., 2016). The most important distinction among these five methods was the diverse lixiviant produced by different functional microorganism communities that grew on different electron donors. To understand the bioleaching mechanism, the microbial community structure was investigated using amplification sequencing. Accordingly, the major objective of this study was to fully explore the feasibility of using different bioleaching methods for V₂O₅-WO₃/TiO₂ catalyst recycling to identify an economical and eco-friendly method.

2. Materials and methods

2.1. Waste V₂O₅-WO₃/TiO₂ catalyst

The industrial waste catalysts used in the experiment were kindly provided by Prof. Jinsheng Chen (Institute of Urban Environment, Chinese Academy of Sciences, China). After peeling off the flat, non-catalytic outer layer, the catalysts were mashed by a pestle and then shattered using a multi-function disintegrator (Xiaobao, China) at a speed of 31,000 rpm for 10 min. The powders were sieved and particle sizes below 80-mesh were collected. The final catalyst powders were dried in a vacuum oven at 75 °C to a constant weight before they were used in experiments. The metal determination of spent catalysts was performed according to a previously described method (Wang et al., 2016). The vanadium and tungsten contents are shown in Table S1 (Supporting information). The titanium was not detected, as it barely solubilized.

2.2. Microorganisms and culture medium

Experimental microbial communities were enriched from aerobic activated sludge (supplied by the Jimei sewage treatment plant in Xiamen, Fujian province, China). The bacteria were cultivated in M9, LB, Starkey, 9K and Fe+S media, containing glucose (Oligotrophic way), peptone (Eutrophic way), S⁰ (S-mediated way), Fe²⁺ (Fe-mediated way) and Fe²⁺+S⁰ (Mixed way) as energy sources. The components of M9 medium (g/L): NaCl, 0.5; NH₄Cl, 1; K₂HPO₄, 3; Na₂HPO₄, 6. The medium pH was approximately 7.0 without adjustment and was sterilized under 121 °C for 20 min. Then 1 mL each of 1 M MgSO₄·7H₂O and 0.1 M CaCl₂·2H₂O which have been autoclaved at 121 ºC for 20 min were added to the solution in a sterile environment. Finally, the glucose was added to the solution to a final concentration of 4 g/L after autoclaved at 115 ℃ for 15 min (Reeve et al., 1984). The LB medium contained the following (g/L): Peptone, 10; Yeast extract, 5; NaCl, 5. After the pH was adjusted to 7.2 using NaOH, the medium was autoclaved at 121 ºC for 20 min. Filter sterilized glycine solution was added to the solution to a final concentration of 5 g/L in a sterile environment before inoculation (Brandl et al., 2008). The Starkey medium was composed of (g/L): MgSO₄·7H₂O, 0.5; (NH₄)₂SO₄, 0.4; CaCl₂·2H₂O, 0.25; K₂HPO₄, 3; FeSO₄·7H₂O, 0.01; Yeast extract, 0.5. The pH was adjusted to 2.0 using sulfuric acid and was autoclaved at 121 ºC for 20 min. 10 g/L sulfur was added to the medium in the clean bench after intermittent sterilization (Findley et al., 1974; Wang et al., 2009). The 9 K medium contained the following (g/L): KCl, 0.1; (NH₄)₂SO₄, 3; MgSO₄·7H₂O, 0.5; K₂HPO₄, 0.5; Ca(NO₃)₂·2H₂O, 0.01; Yeast extract, 0.5. Before autoclaved at 121 ºC for 20 min, adjusting the medium pH to 2.0 using sulfuric acid. Filter sterilized FeSO₄·7H₂O solution was added to the solution to a final content of 44.7 g/L in the clean bench before inoculation (Wang et al., 2009). The Fe+S medium contained the following (g/L): KCl, 0.1; (NH₄)₂SO₄, 2; MgSO₄·7H₂O, 0.25; K₂HPO₄, 0.1; Yeast extract, 0.5; Sulfur, 5; FeSO₄·7H₂O, 22.35 (Wang et al., 2009). The medium pH was 2.0, and the sterilization method was the same to Starkey and 9K.

To obtain the functional microbial communities, 10 mL of sludge and a specific amount of catalyst powders were added into 250 mL flasks containing 90 mL of M9, LB, Starkey, 9K and Fe+S media, respectively. The flasks were incubated at 30 ºC in a shaking incubator at 150 rpm for 7 days, after which 10 mL of culture was transferred to fresh M9, LB, Starkey, 9K and Fe+S media with different amounts of catalyst powder.

2.3. Bioleaching experiments

To identify the most economical and eco-friendly bioleaching method, the experiments were conducted to assess the above-mentioned five bioleaching pathways. After two months of acclimation, five types of microbial communities were used in the bioleaching experiments, and the initial content of catalyst was 10 g/L. Abiotic experiments were conducted under the same conditions. To investigate the influence of different initial amounts of catalyst powder on bioleaching efficiency, a series of flasks were arranged with various amounts of catalyst powders. Each experiment was carried out in triplicate, and the average data were reported.

2.4. Analytical methods

During the experiment, portions of the bioleaching solutions were periodically taken to test the pH and the concentrations of soluble V, W and Fe²⁺. Each sample was firstly filtered through a 0.22 μm membrane to remove cell debris and precipitates prior to measurements. The pH was measured using a pH meter (UB-7, Denver, USA) and the concentration of Fe²⁺ was determined using a previously described ferrozine assay (Panda et al., 2017). Next, a certain amount of filtrate was diluted to an appropriate concentration range with 2% HNO₃, after which the concentration of soluble V and W were determined by inductively coupled plasma-optical emission spectrometry (Optima 7000DV, PerkinElmer, USA).
were provided. These three pathways showed notable differences with respect to vanadium bioleaching.

The Fe-mediated way involves two steps, where soluble Fe\(^{2+}\) serves as electron donor to iron-oxidizing bacteria and is oxidized to Fe\(^{3+}\), after which the solid metals are oxidized to soluble forms by donating electrons to Fe\(^{3+}\). According to the bioleaching of Cu from PCBs under Fe-mediated way, Fe\(^{3+}\) can oxidize Cu\(^0\) to Cu\(^{2+}\), and the leaching efficiency of Cu through Fe-mediated process is higher than that observed for the S-mediated way (Wang et al., 2016). Thus, we anticipated to obtain a rapid and high vanadium leaching when iron-oxidizing bacteria participated in the bioleaching process. However, the Fe-mediated way showed a much less ability than S-mediated way to leach vanadium, which was just about 7%. The relatively lowest V bioleaching efficiency for the Fe-mediated pathway among the tested conditions might be ascribed to the following reasons: (1) the vanadium in V\(_2\)O\(_5\) cannot be oxidized to a higher valence by the oxidant Fe\(^{3+}\) (the highest valence of vanadium is +5) (Imtiaz et al., 2015); and (2) the reaction between Fe\(^{3+}\) and V\(_2\)O\(_5\) was greatly inhibited by the production of Fe(III)-precipitates, which was indicated by the decrease of the total Fe concentration (Fig. S1(a) in supporting information) (Pradhan et al., 2008).

Theoretically, two carbon-mediated pathways can be achieved through the reaction between microbial metabolites and solid metals via complexation or chelating. The major difference between Oligotrophic way and Eutrophic way was the different bioleaching agent that producing from microbial metabolism. The microbial metabolite of Eutrophic way should be cyanide, which generated from the glycine. Glycine is a direct precursor of cyanide (Brandl et al., 2008). While the leaching agent of Oligotrophic way should be organic acids (citrate, oxalate and glucose) (Brandl et al., 2001). During 10 days of operation, the V bioleaching rate under the Oligotrophic way increased to about 33% on the second day. However, the V bioleaching efficiency under the Eutrophic way had a steady and slow-growing performance, increasing to approximately 20% from 0. The relatively low bioleaching rate may have resulted from the use of ordinary sludge, or perhaps the carbon substrate provided was not able to promote the growth of functional bacteria or produce the useful microbial metabolites (Brandl et al., 2001). It can be concluded that the Oligotrophic way was more feasible than the Eutrophic way because of the higher V bioleaching rate and the lower associated cost.

The co-cultures of sulfur-oxidizing and iron-oxidizing bacteria have been shown to result in more efficient bioleaching of Cu\(^0\) from PCBs than the sulfur-oxidizing bacteria or iron-oxidizing bacteria alone (Wang et al., 2009). Therefore, Fe\(^{2+}\) and S\(^0\) were used as electron donors in the Mixed process. However, the results suggested that it was not necessary to utilize FeSO\(_4\)-7H\(_2\)O and S\(^0\) as energy sources during V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) recycling. The bioleaching rate of vanadium from the Mixed way was between that of the S-mediated and Fe-mediated ways. After four days of operation, the vanadium extraction efficiency was about 35% and then had no obvious change. The usage of S\(^0\) under Mixed way was half of that under S-mediated process, resulting in a higher pH, so it was reasonable to have a lower vanadium bioleaching efficiency than S-mediated way (Fig. S1(b)). Although the Fe\(^{2+}\) was almost oxidized after two days (Fig. S1(b)), the existence of iron-oxidizing bacteria did not act as a positive factor under Mixed way.

The highest V bioleaching rate was achieved under the S-mediated way, reaching approximately 90%, where the pH decreased from 2.0 to about 0.5 (Fig. 1b). The increase in the vanadium bioleaching efficiency showed a good correspondence to the decrease in pH, both of them exhibited a significant change in the first 6 days. There should be a close relationship between pH and vanadium leaching rate. It has been reported that the oxidation of S\(^0\) is catalyzed by sulfur-oxidizing bacteria, producing several intermediate sulfur species among which the sulfate ion is the uppermost, and H\(_2\)SO\(_4\) is the final product (Eqs. (1) and (2)) (Panda et al., 2017).

\[
\text{S}^0 + \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}
\]  
(1)
Vanadium from solid wastes, such as carbonaceous shale, can be decomposed by sulfuric acid (Eq. (3)) (Zhou et al., 2009). Therefore, it can be speculated that the production of H$_2$SO$_4$ or the release of H$^+$ decomposed by sulfuric acid (Zhou et al., 2009). Therefore, it can be speculated that the production of H$_2$SO$_4$ or the release of H$^+$ was not the only factor for efficient vanadium leaching, the participation of bacteria was necessary.

It was previously reported that SO$_3^{2-}$ generated from microbial oxidation of SO$_2$ has strong reducing properties, and that the vanadium(V) of solid compound V$_2$O$_5$ can be reduced by SO$_3^{2-}$ to soluble vanadium(IV) (Bredberg et al., 2004; Mishra et al., 2007). However, the SO$_3^{2-}$ is quickly oxidized by O$_2$ to SO$_4^{2-}$, and vanadium(IV) from V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst is differ to that from pure compound V$_2$O$_5$, which can result in a low effect of SO$_3^{2-}$ on vanadium(IV) reduction. Importantly, the microorganisms themselves could help to extract the vanadium more effectively, which could benefit from the direct contact with the surface of SCR catalyst powder (Brandl, 2008). This promotion would increase with the growth of microbes. Finally, abandoned V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts does not always solely contain vanadium in the form of V$_2$O$_5$, and V$_2$O$_3$ or V$_2$O$_5$ may also be present (Li et al., 2014). Different forms of vanadium may result in a higher biotic leaching rate than abiotic leaching rate. From the above results, it was observed that the sulfur-oxidizing bacterial community of the S-mediated process played a key role in vanadium leaching. Compared with the other reported methods that concentrated on hydrometallurgy (Aarabi-Karasgani et al., 2010; Huo et al., 2015; Li et al., 2014; Zhou et al., 2009), the S-mediated approach for vanadium recovery has the following advantages: low temperature, normal pressure, low energy consumption and environmental-friendly.

There were diverse responses to leach vanadium from V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst under five bioleaching pathways. Instead of the Fe-mediated process which was the major bioleaching way of Cu from PCBs, the S-mediated way was a quite promising method to leach vanadium. However, the tungsten was hardly to be leached in any of the five biological pathways, with all the extraction rates lower than 10% (Fig. S2 in supporting information). Little is known regarding the tungsten recovery from spent SCR catalyst through biotechnology, but it was reported that the fungus *Penicillium simplicissimum* helps to leach solid W from spent hydrocracking catalyst through the production of gluconic acid (Amiri et al., 2011). Compared to the growth substrate containing 100 g/L sucrose and 1.6 g/L yeast extract for *P. simplicissimum*, the use of 4 g/L glucose or 5 g/L yeast extract may not be very beneficial to the production of a useful lixiviant, especially for the Oligotrophic way. The Eutrophic way may be a potential method to leach vanadium by optimizing the culture medium.

### 3.2. Response of microbial community to the five bioleaching methods

The microbial community structure is strongly associated with its corresponding environmental role. Bioleaching of solid wastes is primarily controlled by the predominant functional microorganisms, including organic acid-producing fungi, reduced sulfur-oxidizing bacteria and iron-oxidizing bacteria. Therefore, the microbial community compositions from the five bioleaching processes were analyzed to discuss the possible vanadium bioleaching mechanisms.

There is no known bioleaching mechanism for V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst, and the study of vanadium bioleaching from other solid wastes is concentrated on the influencing factors. In this study, the "indirect" and "direct" mechanisms proposed for the bioleaching of metal sulfide are quoted for the S-mediated way (Brandl, 2008), although the direct mechanism is still in dispute. For S-mediated bioleaching process, *Acidithiobacillus* and *Sulfobacillus* genera were the dominant bacteria (Fig. 3). *Acidithiobacillus* species are one of the best-known bacteria from acidic environment and are the most extensively used in bioleaching, especially the species *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. As chemautotrophic bacteria, both *A. thiooxidans* and *A. ferrooxidans* can feed on reduced sulfur (Brandl, 2008). Many *Sulfobacillus* species are applied in metals bioleaching through the oxidation of Fe$^{2+}$ and S$^0$, such as *Sulfobacillus thermostosulfidooxidans* (Stott et al., 2000). Thus, one of the vanadium bioleaching mechanisms under the S-mediated way was further demonstrated by the existence of these genera. When grown with S$^0$, S$^0$ was oxidized by *Acidithiobacillus* and *Sulfobacillus* genera to produce SO$_3^{2-}$ and H$_2$SO$_4$, and then the solid V$_2$O$_5$ reacted with SO$_3^{2-}$ and H$_2$SO$_4$ to extract vanadium into ionic state. Therefore, the bioleaching of vanadium via the S-mediated way can be achieved through an indirect mechanism from the microbial oxidation of S$^0$.

For the direct mechanism, direct electron transfer occurs between metal sulfide and the cells attached to the mineral surface (Vera et al., 2013). For example, the bacteria can obtain electrons directly from the pyrite through a direct mechanism (Eq. (4)).

### References

**Equation (2)**

\[2H^+ + SO_3^{2-} + 0.5O_2 \rightarrow H_2SO_4\]

**Equation (3)**

\[V_2O_5(s) + H_2SO_4 \rightarrow (VO_2)^2SO_4 + H_2O\]

**Equation (4)**

\[2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4\]
During the direct bioleaching process, cells would attach to the mineral surface, as a close contact is needed (Brandl, 2008). Extracellular polymeric substances (EPS) mediate the contact between the bacteria and the mineral, having an important role in the organic film formation and the bacterium-mineral interactions (Gehrke et al., 1998). EPS primarily consists of proteins, lipids and sugars (Zeng et al., 2010), and the redox active components have been reported to facilitate U(VI) reduction (Cao et al., 2011). There are two levels for microbes to contact with mineral surface: the physical sorption and chemical sorption (Brandl, 2008; Zeng et al., 2010). It was previously reported that the bacteria can attach to the mineral surface within minutes or hours (Brandl, 2008). Therefore, a two-step bioleaching process should be more favorable for vanadium bioleaching. First, the functional bacteria were cultivated in the absence of catalyst powder. Subsequently, when the microbes were in the exponential growth stage, the catalyst was added, and the culture was incubated for an additional period of time, enabling the direct mechanism to play a greater role. However, the specific direct bioleaching process between microorganisms and V2O5-WO3/TiO2 catalyst still requires additional researches.

The two additional genera, Alicyclobacillus and Acidiphilium, were also the predominant bacteria in the Fe-mediated way, in addition to the Acidithiobacillus and Sulfobacillus genera. Members of these genera can grow on Fe2+ and play an important role in bioleaching (Jiang et al., 2010). However, the bacteria of Fe-mediated process did not effectively promote the extraction of vanadium. The Fe(III)-precipitates would coat the surface of the catalyst, resulting in inhibition of direct mechanism. For the Mixed way, the predominant bacteria were the same as those for the S-mediated way.

For two carbon-mediated ways, the fungal and bacterial community structures at genus level were analyzed. The well-known fungi Penicillium simplicissimum and Aspergillus niger are known to produce organic acid to leach metals form solid wastes (Brandl et al., 2001), while the abundance of functional genus Aspergillus declined dramatically after the treatment of V2O5-WO3/TiO2 by Oligotrophic and Eutrophic processes (Fig. S3 in Supporting information). It was notable that no dominant functional fungal species were only observed from the Eutrophic process or Oligotrophic process. The family unclassified_f_Trichocomaceae contains some of the most familiar bioleaching fungi, such as Penicillium and Aspergillus (Peterson, 2012). Although the abundance of unclassified_f_Trichocomaceae from the Eutrophic way was higher than that from the Oligotrophic way, the vanadium bioleaching ability of Eutrophic way was lower than that of Oligotrophic way. Therefore, the fungi of these two carbon-mediated ways may not play a vital role in enhancing V2O5-WO3/TiO2 recycling. The bacterial diversity of Eutrophic way was clearly higher than that of Oligotrophic way, and they had distinct predominant bacteria (Fig. 3). Notably, some Pseudomonas species have been found to excrete cyanide when mobilizing silver and gold from solid wastes ([Au(CN)2]− and [Ag(CN)2]−) (Brandl et al., 2008), this genus may play a leading role in vanadium bioleaching under Oligotrophic way. Citrobacter species are known for accumulating uranium from contaminated wastewaters (Bonthrone et al., 2000). Bacillus and Lysinibacillus should be the functional bacteria of Eutrophic way, some species of these two genera have been used for biological metallurgy (Arshadi and Mousavi, 2015; Ghosh et al., 2017; Styriakov et al., 2003).

3.3. Effect of the initial content of V2O5-WO3/TiO2 catalyst on vanadium bioleaching under the S-mediated pathway

To optimize the appropriate solid to liquid ratio, the effect of the initial content of V2O5-WO3/TiO2 catalyst powders on vanadium bioleaching under S-mediated pathway was studied. The pH was measured to assess the possible trend of the V bioleaching rate. With an increasing content of the catalyst, the rate of decrease in pH became
slower (Fig. 4a). On the one hand, the bioactivity of bacteria could be restrained by the toxic effect of plentiful SCR catalysts, resulting in inhibiting the oxidation of $S^0$. The toxic effect of other types of solid waste on microorganisms has been shown (Brandl et al., 2001). On the other hand, the SCR catalyst would lead to a little increase in pH (Fig. 1b).

For vanadium extraction, the change in bioleaching rate was in response to the change in pH (Fig. 4b). The V bioleaching rates at 10 and 20 g/L catalyst were almost same after 6 days of operation. Apparent decreases were observed at 40 and 60 g/L catalyst, with the maximum bioleaching rates of approximately 65% and 45% on day 7, respectively. At an initial content of 80 and 100 g/L of catalyst, the bioleaching efficiencies were even lower, approximately 22% and 18%, respectively. However, when converting the vanadium bioleaching rate into the dissolved vanadium concentration, it increased with SCR catalyst range from 10 to 60 g/L, and then decreased at an initial content higher than 60 g/L (Fig. 4c). According to the bioleaching mechanism of the S-mediated process, the more $H^+$ that accumulated would increase the vanadium leaching. Moreover, a negative effect of abundant catalyst powder occurred on the direct mechanism, resulting from the toxic effect on bacteria growth. Finally, it was believed that high solid waste dosage resulted in lower metal leaching, partly because of a limitation in oxygen mass transfer and air distribution (Xiang et al., 2010). These results indicated that an initial 20 g/L of SCR catalyst was more appropriate for vanadium bioleaching when taking into account the treatment cost.

4. Conclusions

This study provides insight into the extraction of vanadium and tungsten from spent $V_2O_5$-WO$_3$/TiO$_2$ catalysts driven by functional microorganisms, the results of which should aid in the development of research and practical application for $V_2O_5$-WO$_3$/TiO$_2$ recycling. For vanadium bioleaching, the S-mediated process should be studied further, as the direct and indirect mechanisms due to the existence of Acidithiobacillus and Sulfobacillus genera can cooperate to catalyze the vanadium leaching. For simultaneous and effective extraction of vanadium and tungsten to be more economical and environmental, the top priority should be combining Eutrophic way and Oligotrophic way based on the optimization of electron donors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.168.

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