Sustainable Selective Recovery of Sulfuric Acid and Vanadium from Acidic Wastewater with Two-Step Solvent Extraction

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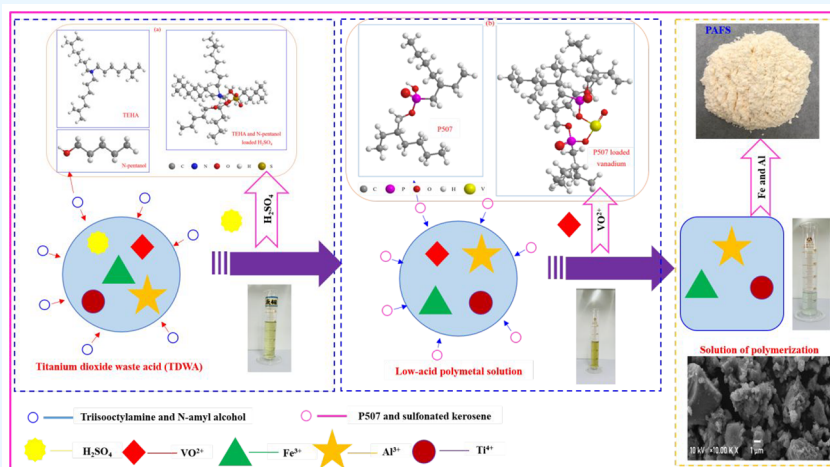
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ABSTRACT: A two-stage extraction process was proposed to recover sulfuric acid and vanadium from simulated acid solution and titanium dioxide waste acid (TDWA). Some extractants were compared and studied, in which the enthalpy changes (ΔH) of the extraction process and the extracted complex were analyzed by using thermodynamics. The microscopic characteristics of the loaded organic phase were compared and investigated by infrared spectroscopy (FT-IR), where the extraction mechanism was described. The extraction efficiency of sulfuric acid was more than 99% by three-stage countercurrent extraction with 60% triisooctylamine (TEHA) and 35% N-pentanol, in which ΔH was −61.31 kJ/mol and the extracted complex of $H_2SO_4 \cdot TEHA \cdot 2 \cdot N$-pentanol was obtained. The extraction efficiency of vanadium was above 98% by using 20% bis-2-ethylhexyl phosphate (P507) and 80% sulfonated kerosene, where ΔH was 14.69 kJ/mol and the extracted complex of $VO \cdot 2A$ (vanadium as VO^{2+} and P507 as HA) was obtained. The stripping efficiencies of sulfuric acid and vanadium were more than 90% and 98%, respectively. The extraction effect of used organic phase after regeneration was equivalent to that of the new organic phase with cycle numbers of less than 10. The real waste acid of TDWA was operated to extract and separate sulfuric acid and vanadium with the same parameters, in which the characteristics of high extraction efficiency and good selectivity were obtained. The technique may provide a new thinking for the separation and recovery of valuable components from TDWA.

1. INTRODUCTION

Titanium dioxide waste acid (TDWA) is a highly acidic wastewater in the preparation of titanium white from vanadium−titanomagnetite by leaching with concentrated sulfuric acid and hydrolysis precipitation.[1−3] The waste acid of 5−6 m³ with a concentration of 20% and the acid wastewater of 50−80 m³ with a concentration of 2%−6% would be discharged per ton of titanium dioxide.[4] TDWA also contains metal ions such as iron, vanadium, titanium and aluminum besides sulfuric acid. Vanadium (V) is a rare metal that can also cause serious heavy metal pollution to the wastewater due to its toxicity. The chronic toxicity threshold of V in fresh water should be less than 20 mg/L, and the acute
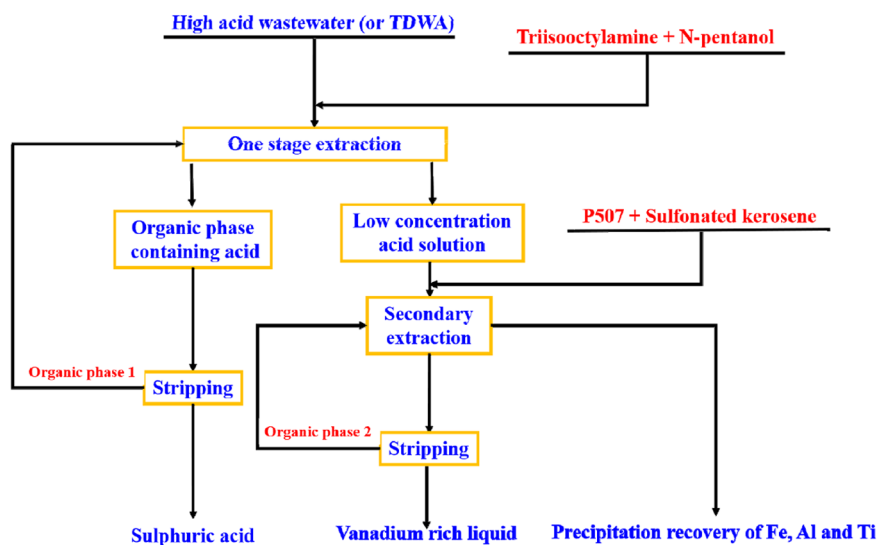
toxicity threshold of V is less than 300 mg/L.[5,6] Therefore, the problem of water pollution, soil acidification and deterioration of ecological environment still exists without treatment of TDWA. It may seriously endanger the lives of nearby residents, in due to which a serious waste of resources also exists.[7]

Figure 1. Process of continuous extraction and separation of acid and vanadium.

The solvent extraction methods by using bis(2-ethylhexyl) phosphate (P204), 2-ethylhexyl phosphate mono-2-ethylhexyl ester (P507), tri(octyl decyl) alkyl tertiary amine (N235), secondary carbon primary amine extraction agent (N1923), etc. were promoted for the recovery of V from the acid solution containing a variety of metal ions.[8−11] Due to the fact that TDWA was a waste liquid generated from the production of TiO_2, the titanium was no longer the main recycling object with solvent extraction from TDWA. Titanium could be recovered together with metal ions such as iron and aluminum, in which aluminum, iron, titanium and silicon in the acid solution could also be prepared into polymeric aluminum iron flocculants by a polymerization reaction.[12] The flocculants could be used for the treatment of wastewater with high turbidity, color and organic matter. However, a high pH value was required while recovering the above valuable metals. For example, the pH value usually needed to be more than 1.5 for the recovery of V. The appropriate pH value for the polymerization process of aluminum and iron needed to be more than 3.5.[13,14] The usual method of adjusting the pH value was to add alkaline substances such as ammonia, lime and sodium hydroxide for neutralization pretreatment.[15,16] However, the problems of high reagent cost and a large number of solid wastes (containing valuable metals) would exist in this process. These solid wastes were defined as "hazardous wastes", in which the recoverable residual sulfuric acid was not fully utilized. Therefore, the separation and recovery of sulfuric acid prior to recovering valuable metals from TDWA has important economic value and theoretical significance.

Electrodialysis, diffusion dialysis and solvent extraction were usually applied for the separation of H_2SO_4.[17] Electrodialysis and diffusion dialysis could make the cation and anion in the waste acid pass through the ion exchange membrane with selective permeability by using direct current and osmotic pressure. The recovery of sulfuric acid was significant, but there were also problems such as large investment and small processing capacity.[18] Solvent extraction has been widely used for continuous recovery production of H_2SO_4.[19] The extraction reagents mainly included the system of trioctylamine (Alamine 336), isodecanol, and kerosene; the system of Alamine 336 and

tributyl phosphate (TBP); the triisooctylamine (TEHA) system; and the trialkyl phosphine oxide (Cyanex 923) system.[20] The extraction efficiency of the acid was low with a single stage with the Alamine 336 system, but it could reach more than 90% with multistage extraction. Furthermore, the stripping process was difficult to operate, and the stripping efficiency was usually less than 30%.[21] The extraction efficiency of the acid could reach more than 80% by using the TEHA system or the Cyanex 923 system, in which the TEHA system was obviously superior to the Cyanex 923 system due to the fewer extraction stages and higher extraction efficiency.[22] The TEHA system was more suitable for the H_2SO_4 recovery. However, there were still several problems to be solved in the process of extracting sulfuric acid with TEHA. First, the coextractants (isotridecanol, N-pentanol, sec-octanol, etc.) in the TEHA extraction system were obviously different, in which the existence of emulsification of the organic phase may result in difficulties of the two-phase separation.[23] Second, the extraction selectivity of the TEHA system was not thoroughly studied and analyzed. Third, it was not clear whether the method could be applied for further separation of V from the raffinate of the TEHA system. Fourth, the separation mechanism of sulfuric acid and vanadium was indeterminate with solvent extraction.

Therefore, a continuous solvent extraction technology was proposed to treat TDWA for the separation of H_2SO_4 and V. The effects of three coextractants on the separation of H_2SO_4 were investigated, in which the separation selectivity of H_2SO_4 was also analyzed. The effects of several extractants on the selective extraction of V were investigated from the raffinate of the organic phase system with TEHA. The micro-ion morphology, solution thermodynamics and extraction thermodynamics were systematically studied by using simulation software and microdetection. The investigation could provide experimental and theoretical basis for the efficient separation and comprehensive utilization of acid, vanadium and valuable metals from TDWA.

2. MATERIALS AND EXPERIMENTAL SECTION

2.1. Reagents. Triisooctylamine (TEHA, >99%), N-pentanol (>99%), dearomatic solvent (Exxsol D110)
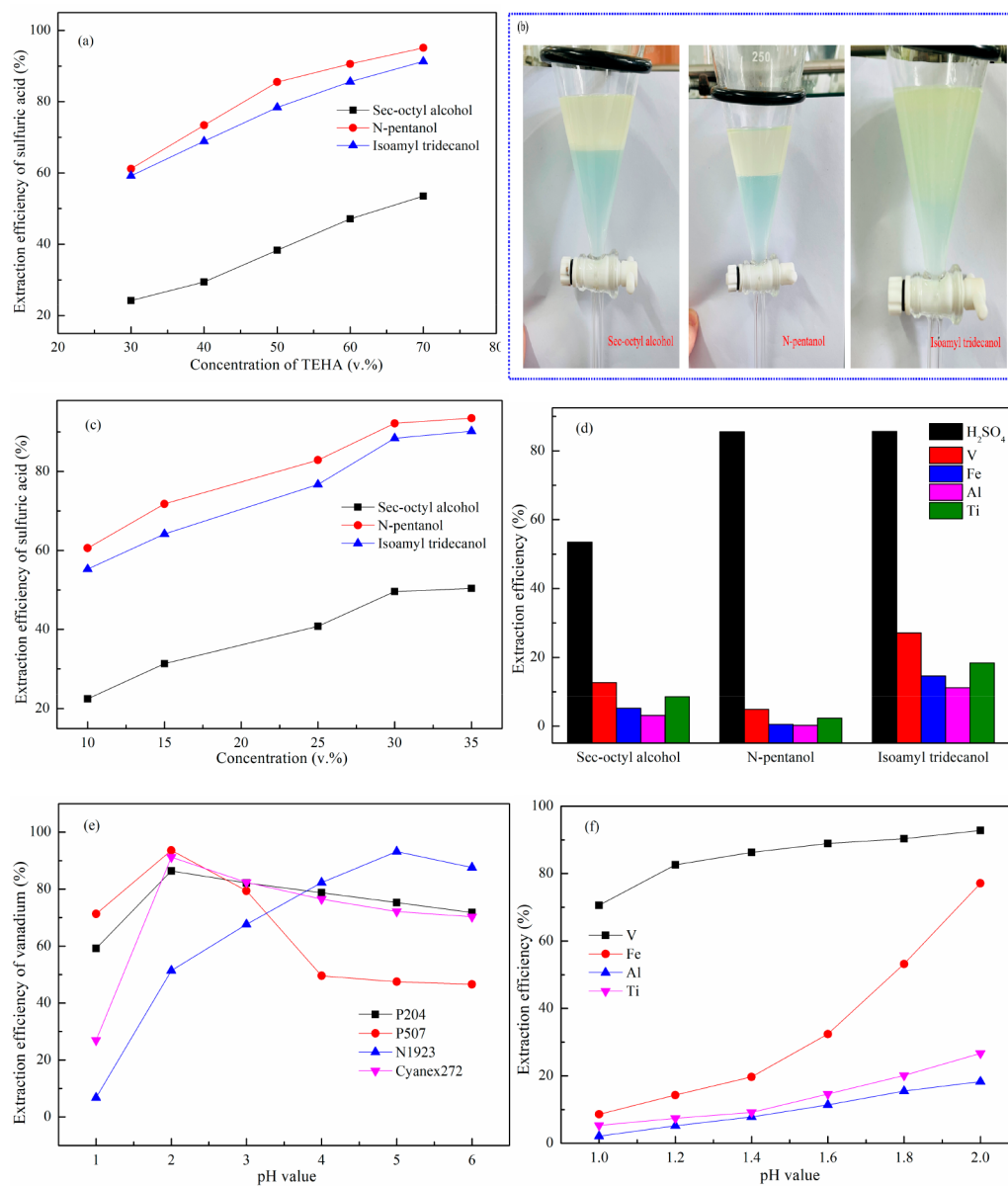
Figure 2. Influence of extractant type, concentration and pH value: (a) concentration of TEHA; (b) photos of extracted acid; (c) concentration of extractant for recovery of sulfuric acid; (d) kinds of extractant for recovery of sulfuric acid, V, Fe, Al and Ti; (e) effect of extractant for recovery of V at different pH values; and (f) effect of pH value for recovery of metals.

(>99%), 2-ethylhexyl phosphate mono-2-ethylhexyl ester (P507, ≥99%) and sulfonated kerosene (>99%) were bought from Tianjin Keda Technology Co., Ltd. (China). Vanadium-(IV) oxysulfate (VOSO$_4$, >99.5%), ferrous (II) sulfate (FeSO$_4$, >99.5%), sulfuric acid (>99%) and sodium hydroxide were also collected from Tianjin Keda Technology Co., Ltd. (China). Distilled water was used for the various prepared solutions.

2.2. Batch Extraction Experiments. The stock solution of 196 g/L H$_2$SO$_4$, 4 g/L VOSO$_4$, 5 g/L FeSO$_4$, 3 g/L Al$_2$(SO$_4$)$_3$, and 6 g/L Ti(SO$_4$)$_2$ was prepared with the distilled water. Organic phase one for acid extraction was composed of TEHA, N-pentanol and Exxsol D110, in which the stripping agent of the acid was the deionized water. Organic phase two for extracting vanadium was composed of P507 (main extractant) and sulfonated kerosene (diluent), in which the 2 mol/L H$_2$SO$_4$ solution was applied as the stripping agent. Twenty mL of the simulated solution was taken into a 250 mL

beaker, and then a certain amount of organic phase one was added according to different O/A values. The mixture was shaken for 3 min in a shaker at the required temperature. The mixture was then taken into a 250 mL separatory funnel for static stratification, in which raffinate one was discharged from the fluid outlets. The second-stage extraction was carried out for raffinate one without adjusting its pH value. Raffinate one was directly poured into a 250 mL beaker, in which a certain amount of organic phase two was added according to different O/A values. The mixture was shaken in an oscillator shaker for 5 min. The mixture was then taken into a separating funnel for static stratification, in which raffinate two was also discharged from the fluid outlets. Raffinate two contained a large amount of iron and aluminum ions, which could be prepared for aluminum iron polymeric flocculants like the sulfuric acid solution containing aluminum and iron.[24] The process of

continuous extraction and separation of acid and vanadium is indicated in Figure 1.

In the two-stage extraction process, the concentrations of V and Fe in the raffinate were detected with ICP-OES. The concentration of hydrogen ions in raffinate one was titrated with acid−base titration. The distribution ratio (D) and extraction efficiency (E) of the extraction process can be expressed and calculated by the following formula.

$$D = \sum [A_i]_o / \sum_i [A_i]_{aq} \tag{1}$$

$$E = ([A_i]_o V_o) / ([A_i]_o V_o + [A_i]_{aq} V_{aq}) \tag{2}$$

where $[A_i]_o$ represents the substance concentration in the organic phase (g/L), $[A_i]_{aq}$ represents the substance concentration in the raffinate (g/L), V_o represents the organic phase volume (mL), V_{aq} represents the raffinate volume (mL), and A_i represents the different extracted substances (hydrogen ion, vanadium or iron).

2.3. Competitive Selective Extraction Experiment. In order to investigate the selectivity of the organic phase for acids and vanadium, a competitive extraction experiment was carried out by adding 0.5 g/L of a solution containing sodium, magnesium and aluminum to the simulated solution. Then the two-stage extraction was carried out according to the above batch extraction experiment. The ICP-OES was operated to detect the concentration of these metal ions.

2.4. Stripping and Reuse of Organic Phase. Organic phase one loaded with acid continued with the intermittent acid extraction experiment until it was saturated. Then the saturated organic phase one was taken into a 250 mL beaker, in which the corresponding volume of deionized water was added at different O/A values. The H_2SO_4 solution was obtained by oscillating stripping at 50 °C for 8 min. Finally, organic phase one can be reused after repeatedly shaking and washing with deionized water for five times. Organic phase two loaded with vanadium continued to extract vanadium until it was saturated. Then the saturated organic phase two was taken into a 250 mL beaker, in which the 2 mol/L H_2SO_4 solution was added under different conditions of O/A value. The V-rich solution was obtained after stripping for 6 min at room temperature. Organic phase two was washed with 0.5 mol/L Na_2CO_3 solution for three times. Finally, it was regenerated and reused.

2.5. Extraction of Acid and Vanadium from Titanium Dioxide Waste Acid. A strong acid wastewater, namely, titanium dioxide waste acid (TDWA), was collected from a local titanium dioxide plant. The concentrations of H_2SO_4, V, Fe, Al and Ti in TDWA were 2.5 mol/L, 116 mg/L, 21.2 g/L, 3.4 g/L and 4.7 g/L, respectively. The TDWA was directly operated without any treatment by using organic phase one (60% TEHA + 35% N-amyl alcohol + 5% Exxsol D110) for the extraction of H_2SO_4. Raffinate one was obtained with an O/A of 1:1, shaking intensity of 200 r/min, and shaking time of 3 min at room temperature. The V was extracted from raffinate one with organic phase two (80% P507 + 20% sulfonated kerosene). Raffinate two was obtained by shaking with an O/A of 1:1 and shaking intensity of 150 r/min at 5 min. The concentrations of these metal ions in raffinate one and raffinate two were detected and analyzed with ICP-OES. The concentration of hydrogen ion was detected by using the acid−base titration with sodium carbonate and phenolphthalein, in which the concentration of sulfuric acid was

obtained according to the result of hydrogen ion concentration.[25]

3. RESULTS AND DISCUSSION

3.1. Influence of Extractant Type, Concentration and pH Value. TEHA was used as the main extractant to separate and recover H_2SO_4, in which the synergistic effects of *sec*-octyl alcohol, N-pentanol and isoamyl tridecanol were investigated, and the results are indicated in Figure 2. Figure 2(a) shows that the increase of TEHA concentration was conducive to acid extraction, while the three coextractants of *sec*-octyl alcohol, N-pentanol and isoamyl tridecanol were used. When TEHA concentration increased from 30% to 70%, the extraction efficiency of acid could increase by 15% (with *sec*-octyl alcohol), 29% (with N-pentanol) and 25% (with isoamyl tridecanol), respectively. The results also show that the synergistic extraction effect of N-pentanol and isoamyl tridecanol was more obvious at the low concentration of TEHA (30%), where the extraction efficiency of sulfuric acid (more than 60%) was higher than that of *sec*-octyl alcohol (26%). Figure 2(b) indicates that there was a significant difference in the layering effect between the two phases with the three coextractants. *sec*-Octyl alcohol and N-pentanol had obvious layering effects. The extraction phase of isoamyl tridecanol had the problems of insignificant two-phase layering and organic phase emulsification, which made the subsequent process difficult to operate.

Figure 2(c) shows that the increase of the three coextractants' concentrations could promote the recovery increase of H_2SO_4. Among them, the effect of N-pentanol was the most obvious, in which the extraction efficiency of H_2SO_4 reached 92% with 35% N-pentanol. At this time, the recoveries of H_2SO_4 by using *sec*-octyl alcohol and isoamyl tridecanol were 49% and 88%, respectively. Figure 2(d) shows that the lowest recovery of H_2SO_4 was obtained with *sec*-octyl alcohol. N-Pentanol and isoamyl tridecanol had the same effect on the recovery of H_2SO_4, but the isoamyl tridecanol had relatively poor extraction selectivity. The recoveries of V and Ti were more than 20%, in which the recoveries of Al and Fe were more than 10% by using isoamyl tridecanol. The recoveries of several other ions were less than 10% with N-pentanol, where the recoveries of Al and Fe were even less than 5%. The selective separation of sulfuric acid was better realized by using N-pentanol. Therefore, it is more suitable to select the system of TEHA + N-pentanol for the extraction and separation of sulfuric acid. The effects of the extractants on the recovery of metal ions from the raffinate of the extraction system with TEHA + N-pentanol were compared and studied (Figure 2(e) and (f)). The pH value was the key factor affecting the effects of various extractants. The influences of P204, P507, Cyanex 272 and N1923 on vanadium extraction were mainly divided into two sections. The extractants of P507, Cyanex 272 and P204 showed strong extraction efficiencies under strongly acidic conditions (pH value <2.0). Among them, P507 was more appropriate for the recovery of vanadium under these conditions, in which the extraction efficiency of vanadium increased from 70% to 93% with increasing pH value from 1.0 to 2.0. The extraction efficiencies of vanadium with P507, Cyanex 272 and P204 showed a downward trend under weakly acidic conditions (pH value of 3.0−6.0). However, the extraction performance of N1923 was more obvious, in which the recovery of vanadium increased from 67% to 93% with increasing pH value from 3.0 to 6.0.
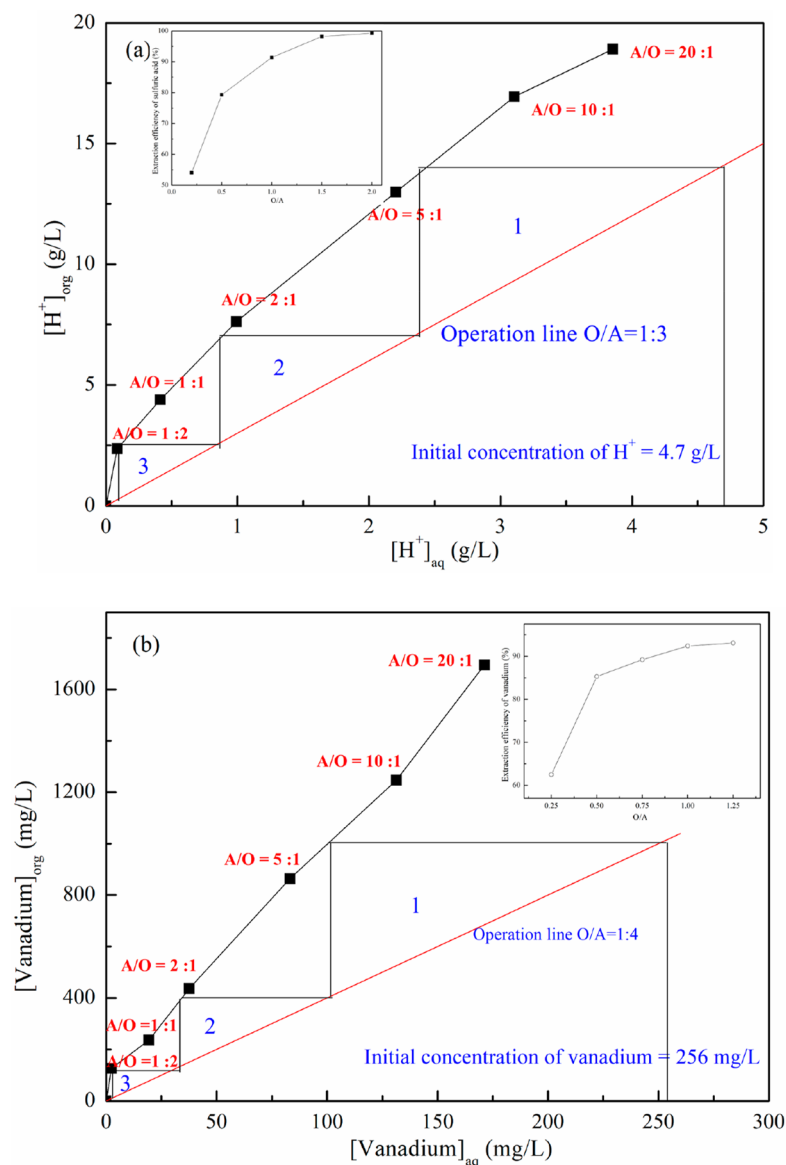
Figure 3. Multistage extraction of acid (a) and vanadium (b) with different O/A values.

There were two main reasons for this phenomenon. First, the functional groups of these extractants were different, and their exchange capacities at different pH values were also different.[26] Second, vanadium ions could exist in a variety of complex forms (including cations and anions) under solution conditions with different pH values, in which the vanadium-(IV) could exist as VO^{2+} at pH < 2.0 and anions such as $HV_2O_5^-$ could exist at pH > 5.0 (see Figure 6), and this was consistent with the description in the literature.[27] It was also the main factor leading to the difference of extraction effects with different extractants. The organic phosphine of extractant P507 used for the recovery of vanadium was a cation extraction, in which the exchange mechanism between P507 and VO^{2+} was easier to occur than that with $HV_2O_5^-$ under weakly acidic or neutral conditions. Therefore, the extraction efficiency of vanadium by P507 could decrease with increasing pH value from 2.0 to neutral. Regarding the acidic phosphate extractants such as P507 and P204 for the recovery of metal ions such as vanadium, aluminum, iron, and titanium in sulfuric acid media, a large number of studies show that

vanadium(IV) exhibited excellent extraction selectivity under lower pH conditions. As the pH value of the solution increased, the influence of iron ions was most significant, which was consistent with the results of this study.[28,29] The extraction effects of aluminum and titanium were not significant, which may be related to the existing forms of various metal ions in the sulfuric acid medium. Generally, the extraction and separation of titanium were mostly carried out using extractants such as N1923 and Cyanex 923.[30,31] Therefore, P507 was chosen as the extractant for the recovery and separation of vanadium in this study.

3.2. Influence of O/A. The solvent extractions of acid and vanadium were investigated with different O/A values, for which the results are indicated in Figure 3.

Figure 3(a) shows that the O/A could obviously affect the extraction efficiency of acid. The recovery of acid increased from 54% to 92% with increasing O/A from 0.2 to 1.0. The recovery of acid was close to 100% with increasing O/A from 1.5 to 2.0. Considering the recovery of acid and the reagent consumption of the organic phase, the multistage counter-

current extraction experiment has been operated with an O/A of 1:3. The theoretical extraction order of H_2SO_4 was three stages with the McCabe−Thiele diagram at 4.7 g/L hydrogen ion. The concentration of hydrogen ion was lower than 0.1 g/L (pH value of more than 1.0) in the raffinate after three-stage countercurrent extraction, which could be conducive to the further recovery of vanadium from the raffinate. Figure 3(b) shows that O/A could also obviously affect the recovery of vanadium. The recovery of vanadium increased from 62% to 87% by increasing the O/A from 0.25 to 0.5, in which the recovery of vanadium increased to 95% with a further increase of O/A to 1.25. The theoretical extraction order of vanadium was also three stages according to the McCabe−Thiele diagram. The recovery of vanadium was more than 98%, and the concentration of vanadium in the two-stage raffinate was lower than 5 mg/L after the three-stage countercurrent extraction.

3.3. Influence of Extraction Temperature and Thermodynamics.

The influence of temperature on the recovery of acid and vanadium was investigated, and the results are indicated in Figure 4.

The effect of temperature on the recovery of H_2SO_4 was very obvious (Figure 4(a)). The recovery of H_2SO_4 decreased from 92% to 68% with increasing temperature from 30 to 50 °C. According to previous scientific research, the relationship of the distribution ratio and temperature is as follows under certain conditions.[32]

$$\log D = -\Delta H/(2.303RT) + A \tag{3}$$

where D is the distribution ratio, ΔH is the reaction enthalpy change (kJ/mol), R is the universal gas constant (J/(mol·K)), T is the temperature (K), and A is a constant.

The ΔH of the extraction reaction could be obtained by plotting between $\log D$ and $1/T$, in which the extraction reaction was endothermic with $\Delta H > 0$ and exothermic with $\Delta H < 0$. Therefore, the relationship between $\log D$ and temperature (T) in Figure 4(a) was linearly fitted, in which the relationship of $y = 3.202x − 9.5906$ was obtained with R^2 of 0.9985. The ΔH of −61.31 kJ/mol was obtained by calculation, which indicates that an exothermic reaction was carried out in the recovery of acid with extraction by using TEHA + N-pentanol. The results of the extraction reaction of sulfuric acid show that the enthalpy change of the extraction process was less than 0, which was consistent with the results obtained in ref 20. The increase of temperature would be detrimental to the recovery of acid extraction. However, the effect of temperature on the recovery of vanadium was relatively gentle (see Figure 4(b)), where the recovery of vanadium increased from 92.7% to 94.6% with increasing temperature from 30 to 50 °C. Therefore, the relationship of $y = −0.7149x + 0.9945$ with R^2 of 0.9945 was obtained by linear fitting of the relationship between $\log D$ and $1/T$. A ΔH of 14.69 kJ/mol could be obtained by calculation, which indicates that the extraction process of vanadium was an endothermic reaction. However, the extraction of vanadium was less affected by temperature due to the low ΔH value. The recovery of vanadium could be operated in a wide temperature range, in which the operation can be operated at different temperatures without special control.

3.4. Verification of Extracted Complex.

According to previous scientific research, the recovery of H_2SO_4 by using TEHA and N-pentanol was a process of molecular extraction. The formula of the extraction reaction is shown as follows, according to refs 17, 19, 20, 22, and 23.

$$H_2SO_4 + mA + nO = (H_2SO_4)A_mO_n$$
$$(A_mO_nH_2(SO_4) \text{ or } A_mO_nH(HSO_4)) \tag{4}$$
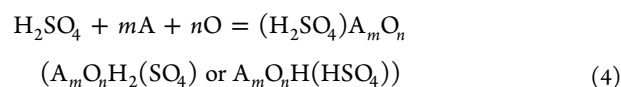
where A is TEHA and O is N-pentanol. However, the specific values between sulfuric acid and TEHA and N-pentanol (i.e., m and n) were still uncertain and needed to be further investigated. The formula was further derived as follows.

$$K = [(H_2SO_4)A_mO_n]/([H_2SO_4][A]^m[O]^n)$$
$$= D/([A]^m[O]^n) \tag{5}$$

$$\log(D) = \log(K) + m\log[A] + n\log[O] \tag{6}$$

The $\log K$ was constant when the extraction process was carried out at a constant temperature. While the concentration of an organic phase TEHA or N-pentanol was unchanged, the linear relationship of $\log(D)$, $\log[A]$ and $\log[O]$ was investigated to determine the specific values of m and n (see Figure 5).

Figure 5 indicates that $m = 1$ and $n = 2$ was obtained, in which the extracted complex was preliminarily determined as $H_2SO_4·TEHA·2N$-pentanol. TEHA and N-pentanol were extracted with sulfuric acid in the form of 1:1 and 2:1,
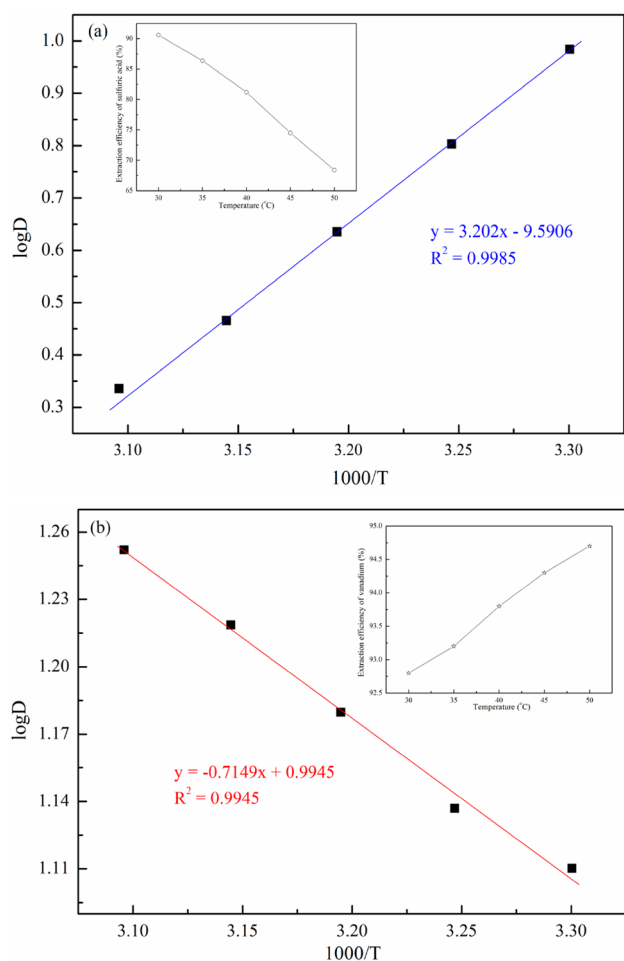
Figure 4. Influence of extraction temperature on acid (a) and vanadium (b).
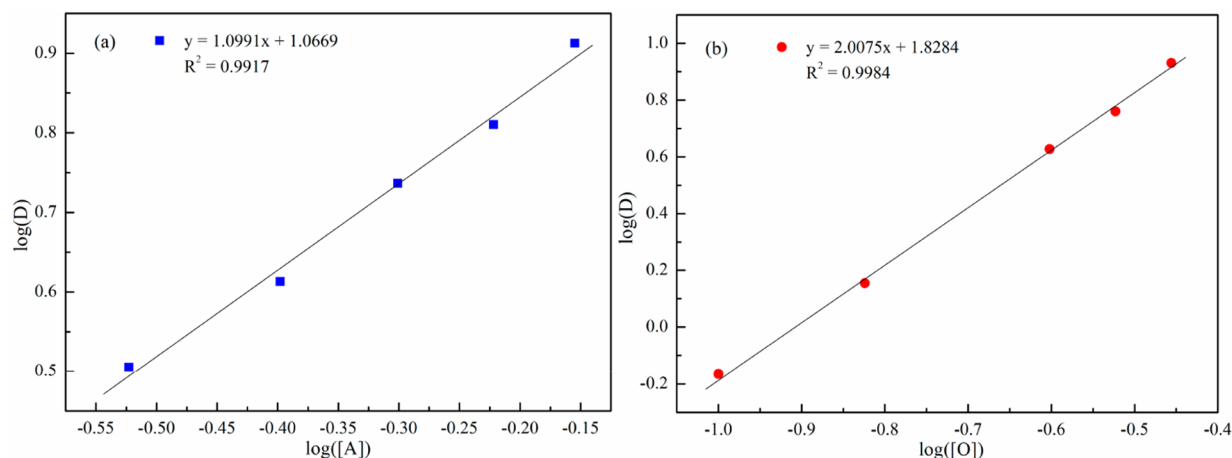
Figure 5. Relationship of $\log(D)$ with $\log[A]$ (a) and $\log[O]$ (b).

respectively. this could provide a certain reference for further analysis of the extraction mechanism.

The extracted complex of P507 extractant and vanadium was analyzed by using the saturation capacity method, in which the organic phase included 20% P507 and 80% sulfonated kerosene (P507 concentration of 0.664 mol/L). An aqueous phase with a concentration of vanadium of 2 g/L with a pH value of 2 was prepared. The organic phase (30 mL) and aqueous phase (30 mL) were mixed in an oscillator and shaken for 4 min. Subsequently, the new aqueous phase and loaded organic phase with the same volume of 30 mL would be taken to continue to mix and shake for many times until the content of V(IV) was unchanged. At this moment, the extraction process reached the equilibrium state. The composition ratio of the extracted compound was calculated and obtained. The results are shown in Table 1.

Table 1. Saturated Extraction Method of Vanadium Extraction with P507

Extraction times	$C(V)_0$ $(mol \cdot L^{-1})$	Extraction times	$C(V)_0$ $(mol \cdot L^{-1})$	$n(HA)/$ $n(V)$
1	0.037	11	0.266	2.006
2	0.071	12	0.274	
3	0.108	13	0.278	
4	0.141	14	0.289	
5	0.168	15	0.295	
6	0.189	16	0.308	
7	0.208	17	0.316	
8	0.229	18	0.324	
9	0.242	19	0.331	
10	0.255	20	0.331	

Table 1 shows that P507 could extract vanadium from the acid solution with a ratio of 2:1. The abbreviation of P507 was usually HA, but the existing forms of vanadium in the sulfuric acid medium were various.[33,34] The existing forms and ranges of V(IV) in the sulfuric acid medium were investigated and are indicated in Figure 6.

Figure 6 shows that V(IV) existed in a variety of forms in the sulfuric acid solution system. Vanadium mostly existed in the form of VO^{2+} at pH < 2. Under the weakly acidic conditions (pH value of 2−5), vanadium mainly existed as $VOSO_4$ at a low concentration of vanadium. Vanadium mainly existed as polymeric anions at pH > 7. This is consistent with the
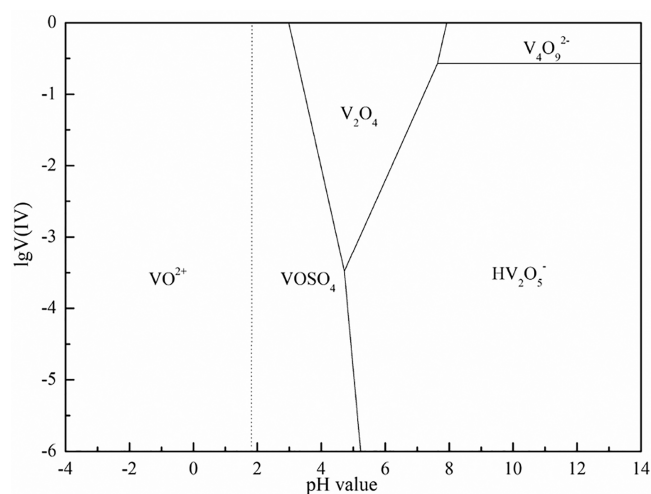
Figure 6. Relationship between concentration of V(IV) and pH value in H_2SO_4 medium.

experimental results in Figure 2(e), in which the extraction efficiency of vanadium by P507 increased first and then decreased with the increase of pH value.

In this investigation, the pH value of raffinate was 1.0−1.5 after the extraction of acid from the strongly acidic solution, in which vanadium mainly existed as VO^{2+}. Therefore, the extraction process of vanadium by using P507 (HA) could be expressed by the following formula:

$$VO^{2+} + 2HA = VOA_2 + 2H^+ \tag{7}$$

3.5. FT-IR Analysis of Organic Phase and Extraction Mechanism. Through the above research, it is shown that the two extractants could effectively extract and separate sulfuric acid and vanadium. Therefore, The FT-IR was applied for detecting the functional group of the organic phases with a simulated solution containing only sulfuric acid and vanadium in order to explore the interaction mechanism between acid, vanadium and organic phases in this process. The introductions of metal ions such as iron, aluminum and titanium were avoided due to the increasing difficulty of analyzing the infrared spectroscopy results. The results are indicated in Figure 7.

The characteristic peak of $-SO_4^{2-}$ appeared at 661 cm^{-1} in the extracted complex of TEHA and N-pentanol. Furthermore,
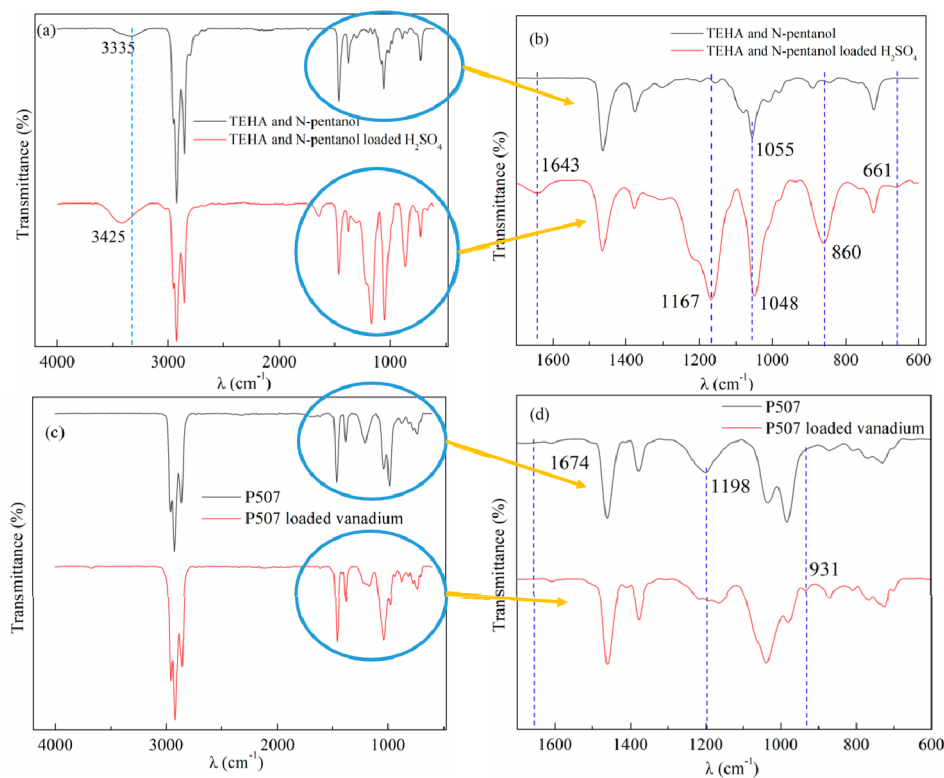
Figure 7. Analysis of FT-IR with initial and loaded organic phase: (a, b) TEHA and *N*-pentanol; (c, d) P507.

the bending vibration peak of N−H at 860 and 1643 cm⁻¹ and the stretching vibration peak of C−O at 1167 cm⁻¹ also appeared in the extracted complex after the recovery of H₂SO₄ with TEHA and *N*-pentanol. It indicates that the spatial structure of the organic compounds was changed, in which the red shift of the N−H bond from 1055 to 1048 cm⁻¹ and the blue shift of −OH from 3335 to 3425 cm⁻¹ were obtained.[20] The *N*-pentanol combined with sulfuric acid and TEHA in the extraction process, which played a certain synergistic role. The bending vibration peak of P−OH at 1674 cm⁻¹ disappeared after extracting vanadium with P507, where the stretching vibration peak of V=O appeared at 931 cm⁻¹. It indicates that H⁺ in the P−OH group was replaced by VO²⁺ during the extraction reaction to form a new group.[35] Furthermore, the bond stretching vibration peak of P=O at 1198 cm⁻¹ was weakened to some extent, which indicates that the formation of the new coordination bond of P=OV weakened the electron cloud of the group.

Based on the above research, the extracting mechanism of sulfuric acid with TEHA and *N*-pentanol, and the extracting characteristics of vanadium with P507, can be shown and are illustrated in Figure 8.

The recovery of H₂SO₄ by using TEHA and *N*-pentanol was the collaborative extraction process. The extracted complex contained both TEHA and *N*-pentanol, in which the proportion of the extraction complex was H₂SO₄·TEHA·2-*N*-pentanol. It was worth noting that the molecule of sulfuric acid (not hydrogen ion) was extracted. The cation exchange of vanadium(IV) from acid solution by using P507 occurred, in which the extraction ratio of P507 and VO²⁺ was 2:1.

3.6. Stripping and Reuse of Extractants. The saturated organic phase of TEHA with sulfuric acid and the saturated organic phase of P507 with vanadium were stripped according

to the experimental process. The recycling and reuse of the extractant were studied and are indicated in Figure 9.

Figure 9(a) indicates that the stripping efficiency of H₂SO₄ showed an obvious growth trend with increasing A/O, in which the stripping efficiency of sulfuric acid increased from 24% to 82% with increasing A/O from 0.2 to 2.0. The McCabe−Thiele diagram of sulfuric acid stripping was obtained by multistage countercurrent extraction with a sulfuric acid concentration of 78.6 g/L at an A/O ratio of 1:1 as the operating line. This indicates that the theoretical stripping order of sulfuric acid was four stages, in which the residual concentration of sulfuric acid in the organic phase was lower than 1 g/L. The TEHA and *N*-pentanol were reused for 10 times, as shown in Figure 9(b), which indicates that the organic phase had a good reuse effect, where the extraction efficiency of the acid remained about 85% during the reuse process of the organic phase for 10 times. The recovery of H₂SO₄ was slightly lower than 85% in the fourth time, which was within the controllable range. The influence of A/O on the stripping recovery of vanadium was mainly studied by using 2 mol/L H₂SO₄ as the stripping agent of P507 loaded vanadium (see Figure 9(c)). It indicates that the stripping recovery of vanadium showed an obvious growth trend with increasing A/O. The stripping recovery of vanadium increased from 48% to 87% with increasing A/O from 0.2 to 2.0. The McCabe−Thiele diagram of vanadium stripping was obtained by multistage countercurrent stripping with an initial vanadium concentration of 9.4 g/L at an A/O ratio of 2:1 as the operating line. It shows that the theoretical stripping order of vanadium was three stages. The residual vanadium concentration in the organic phase was less than 0.1 g/L after stripping. P507 was reused for 10 times after stripping, as shown in Figure 9(d), in which the recovery of vanadium was
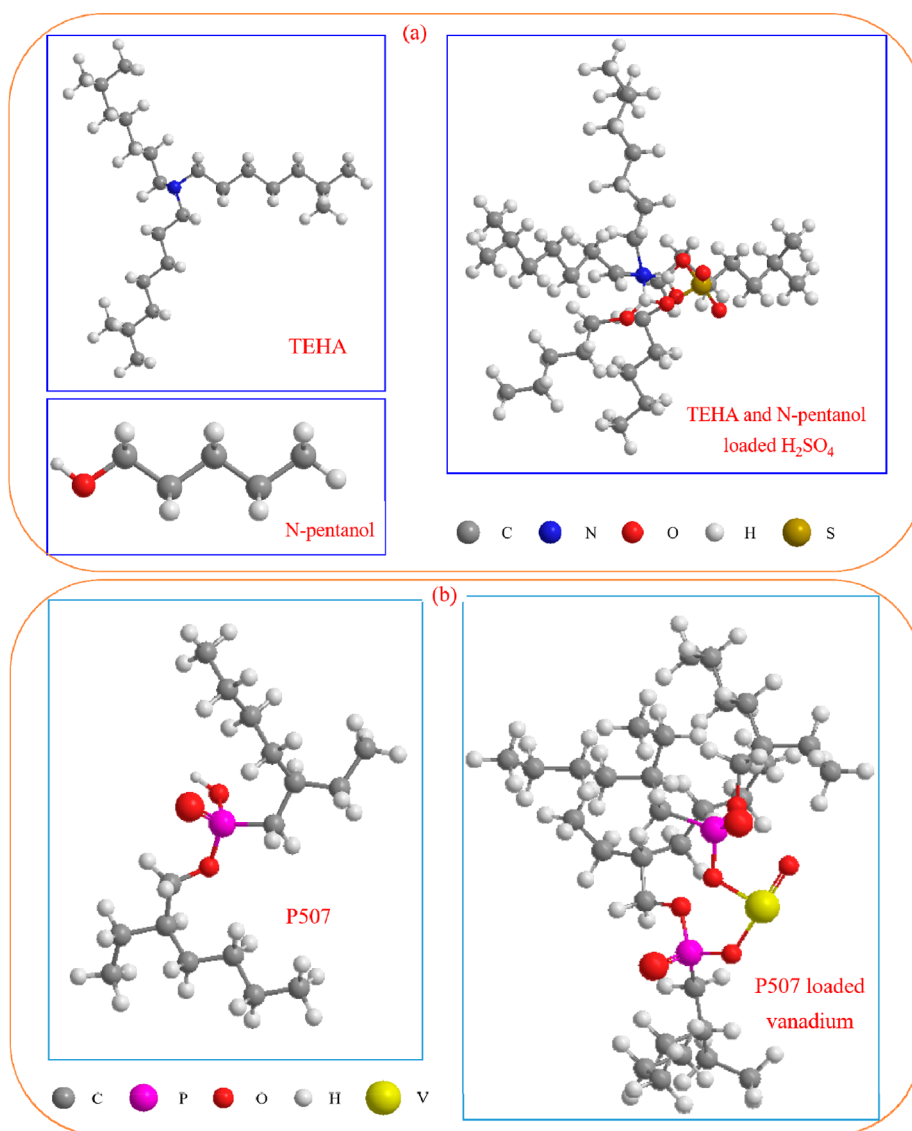
Figure 8. Schematic diagram of the extraction mechanism of sulfuric acid with TEHA + *N*-pentanol (a) and vanadium with P507 (b).

still more than 92% during the reuse process. The organic phase of P507 could be reused for many times without being affected.

3.7. Continuous Solvent Extraction of TDWA. The sulfuric acid and vanadium could be effectively separated and recovered by two-stage continuous extraction with TEHA and P507 from the strongly acidic aqueous solution according to the above extraction experiments and theoretical studies. In addition, the extraction equilibrium time is crucial for the correct execution of the process. Therefore, the TDWA was selected as the real acid wastewater for the extraction research, in which the separation effects of TEHA on sulfuric acid and P507 on vanadium at different extraction times were studied, respectively (see Figure 10).

Figure 10(a) shows that H_2SO_4 in TDWA could be extracted and separated with TEHA and *N*-pentanol, where the extraction effect of H_2SO_4 was obvious. The extraction efficiency of H_2SO_4 reached 72% at 2 min, while the recovery efficiencies of vanadium, iron, iron, titanium and other metal ions were less than 5%. The recovery of H_2SO_4 reached the maximum value of 91% at 4 min, in which the recovery of

vanadium was less than 10% and the recovery of other metal ions was still less than 5%. The extraction efficiency of sulfuric acid decreased slightly with the prolonged duration, while the recovery of vanadium was significantly increased by nearly 20%. At this time, the organic phase was turbid and unclear, which may be caused by a lot of metal ions in the organic phase.[28] Furthermore, P507 extractant was used to extract the residual liquid obtained from the TDWA. Figure 10(b) indicates that P507 had a good selective extraction effect on vanadium. The recovery of vanadium increased from 67% to 86% with increasing time from 1 to 3 min, where the recovery of iron increased from 5% to 8% and the extraction efficiencies of aluminum and titanium were always lower than 5%. The recovery of vanadium was 92% at 5 min, while the recoveries of iron, aluminum and titanium were less than 10%. The recovery of vanadium did not significantly increase with further prolonging the time, in which the recovery of iron increased to 15% and the recoveries of aluminum and titanium were also close to 10%. The optimum extraction time of sulfuric acid was 4 min, and the optimum extraction time of vanadium was 5 min. Finally, the main process and related mechanism of
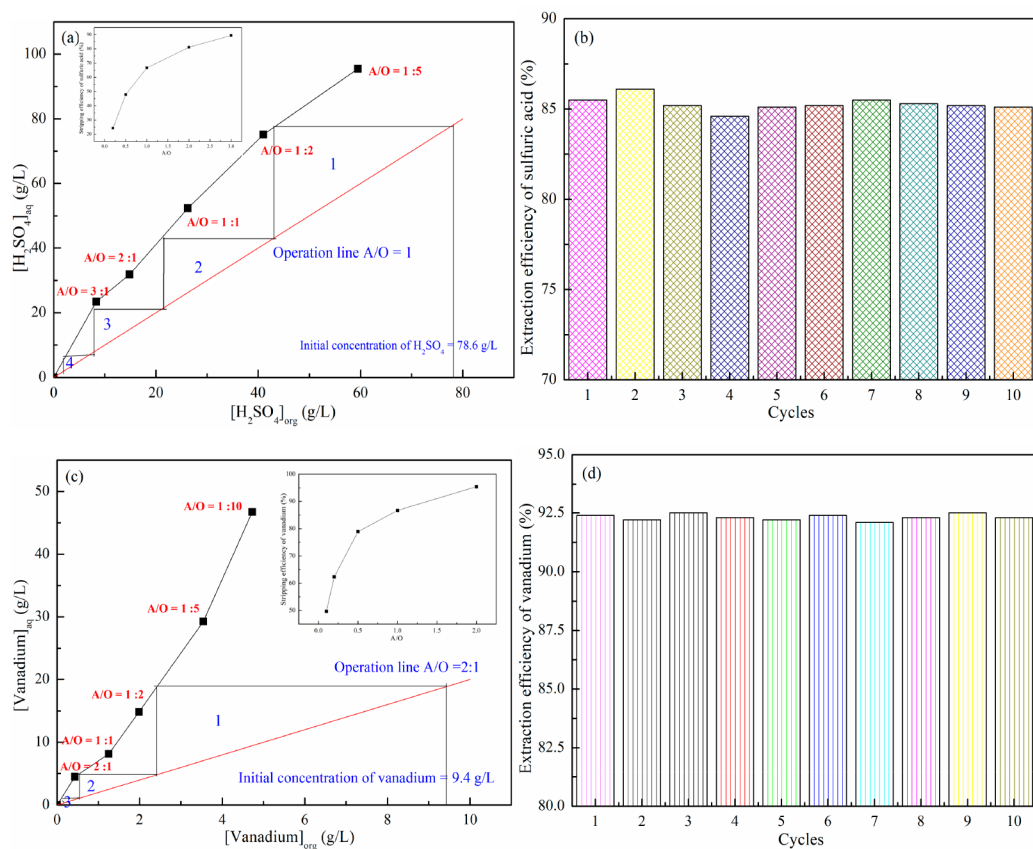
Figure 9. Stripping of sulfuric acid (a) and vanadium (c) and extractant recycling of TEHA (b) and P507 (d).
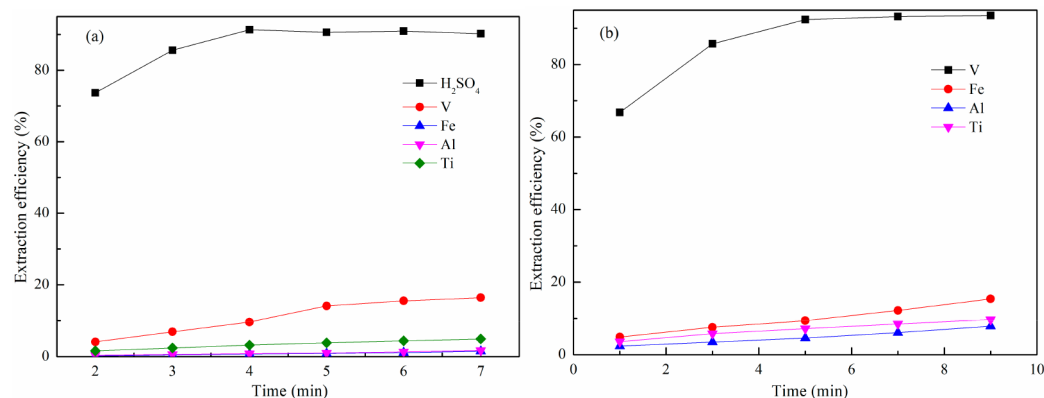
**Figure 10.** Separation of sulfuric acid (a) and vanadium (b) from TDWA.

separation and recovery of H_2SO_4 and vanadium in this study are listed and shown in Figure 11.

The sulfuric acid and vanadium in the solution were obviously separated and recovered with two-stage extraction of TDWA. H_2SO_4 was extracted by using TEHA and *N*-pentanol with the ratios of 1:1 and 1:2, respectively. VO^{2+} was extracted in the form of exchange by using P507 with the ratio of 1:2. At this time, the two-stage raffinate mainly contained the metal ions of iron and aluminum. The flocculant was prepared and applied from the solution containing aluminum, iron and other metal ions through our previous research, in which good experimental results were achieved.[36,37] Therefore, it was feasible to prepare an inorganic flocculant of aluminum and iron by the flocculation precipitation method. TDWA was an

acidic waste liquid with a large discharge amount, which contained a large amount of sulfuric acid, aluminum, iron and a certain amount of vanadium. The extractants of TEHA, *N*-pentanol, and P507 are commonly applied in solvent extraction in this investigation. Therefore, the technology had broad application prospects for the separation and recovery of valuable components from TDWA.

4. CONCLUSIONS

The organic phase combination of TEHA and *N*-pentanol was a suitable extraction solvent for the separation and recovery of H_2SO_4. The extraction efficiency of H_2SO_4 was more than 99% after three-stage countercurrent extraction with an A/O ratio of 3:1 by using 60% TEHA and 35% *N*-pentanol from a 196 g/
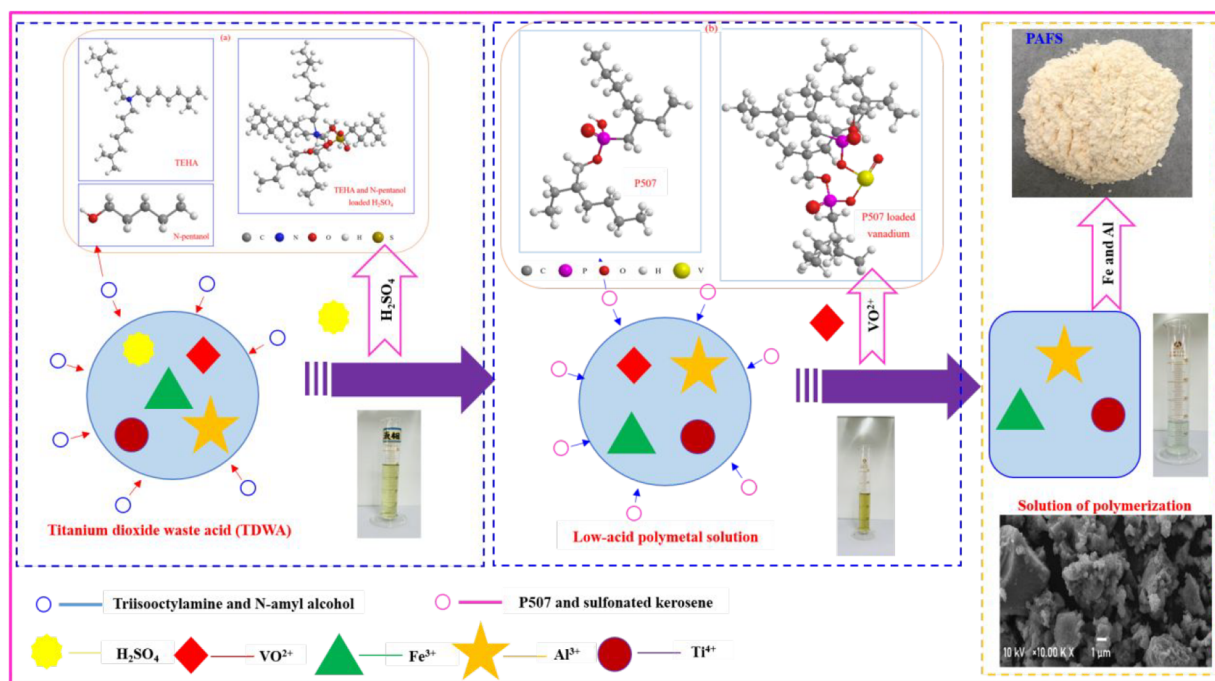
Figure 11. Extraction and separation of valuable components from TDWA.

L H_2SO_4 solution. However, the extraction efficiencies of V, Fe, Al and other metals were less than 10%. The ΔH of -61.31 kJ/mol was obtained in the extraction reaction, where the extraction complex was $H_2SO_4 \cdot TEHA \cdot 2\text{-}N\text{-pentanol}$. The pH value of the raffinate was $1.0-1.5$, which was directly used to extract and separate vanadium by using P507. The extraction efficiency of V was more than 98% after three-stage extraction with an A/O of 4:1 by using 20% P507, in which the extraction efficiencies of Fe, Al, Ti and other metals were lower than 10%. The extraction reaction was endothermic reaction with a ΔH of 14.69 kJ/mol, in which the extracted complex with P507 was $VO \cdot 2A$. The distilled water and 2 mol/L H_2SO_4 were applied for the stripping process for the recovery of H_2SO_4 and V, in which the stripping efficiencies of H_2SO_4 and V were more than 90% and 98%, respectively. The extraction effect of H_2SO_4 and V by using the two organic phases after regeneration was equivalent to that of the new organic phases with cycle numbers of less than 10. TDWA was operated by two-stage extraction, where the extraction efficiencies of H_2SO_4 and V were more than 91% and 92%, respectively, but less than 10% of impurity ions were extracted.

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