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The Separation and Concentration of Titanium(IV) from Sulfuric Acid Solution with Trioctylamine

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ABSTRACT: This paper presents research on separating and concentrating titanium(IV) from aqueous sulfuric acid solution, using trioctylamine (TOA) as extractant and kerosene as a diluent. We investigated the effects of reaction time, temperature, sulfuric acid concentration, organic/aqueous phase ratio, TOA concentration, and titanium concentration on the removal efficiency of titanium(IV). The results show that it is possible to recover over 99% of titanium(IV) after 15 min reaction time by TOA from the sulfuric acid solution under the optimum operation conditions and the loading capacity of TOA for titanium(IV) is 30 g Ti(IV)/100 g TOA. We expect that results studied would be applicable to separate and concentrate titanium from secondary sources such as red mud produced in the aluminum/alumina industry.

1. INTRODUCTION

It is well-known that titanium and its alloys are widely used in the aerospace industry because of their excellent characteristics, such as thermal and corrosion resistance, and titanium dioxide finds application as pigment in the paint industry. However, the reserves of some primary sources cannot meet the heavy demand for this element. Thus it is of considerable significance to find secondary sources and develop an approach to recover titanium from low-grade ores. Red mud, a solid waste residue formed after the caustic digestion of bauxite ores during the production of aluminum, contains quantities of titanium and may be considered as their secondary raw material. Generally, the process proposed for the recovery of titanium dioxide from red mud required the leaching of red mud by H_2SO_4[1−4] or HCl[5] followed by hydrolysis or extraction of sulfate/hydrochloride. Many extractants were tested for the extraction of titanium(IV) from aqueous acid solutions. It has been recognized that neutral organo-phosphorus compounds are effective extractants for titanium(IV), such as tri-n-butyl phosphate (TBP),[6,7] bis-(2-ethyl-hexyl) phosphoric acid (D2EHPA),[8−11] 2-ethylhexyl phosphonic acid mono-2-ethyl-hexyl ester (EHEHPA)[12,13] and Cyanex 923 (TRPO).[14] However, the use of TBP leads to third phase formation and D2EHPA is found to have a relatively slower reaction rate and is less selective during the extraction. Moreover, due to chemical stability and higher loading capacity of titanium, Cyanex 301 and Cyanex 302[15,16] are also found to be able to separate titanium(IV) from red mud.

In recent years, a basic extractant, such as TOA, has been widely used in the metallurgical industry to extract and separate a number of precious and rare metals,[17,18] including cobalt, nickel, actinide, lanthanide, and so on, because of its chemical stability, good extraction kinetics, and low solubility in aqueous phase.[19,20] However, little research has been devoted to extraction and separation of titanium(IV) from its H_2SO_4 solutions in TOA.

The present work is aimed at studying a separating process from its H_2SO_4 solutions and a concentrating process for titanium(IV). In this paper, separation data of titanium(IV) in TOA are presented, and the effects of different variables on the separation are investigated. The loading and recycling capacities of the reagent are determined.

2. EXPERIMENTAL SECTION

2.1. Reagents. The extractant TOA (99%) was provided from Fluka, Sweden. Sulfonated kerosene (technical grade, density, 0.82 g/m^3, and viscosity of 1.6 mPa·s at 20 °C) was purchased from the Chinese Suzhou Wenyi Petrochemical Co. Ltd. The kerosene, with a initial distillated boiling point greater than 185 °C, was used as a diluent due to its high extraction efficiency previously observed.[21] All other chemicals were of analytical grade.

Titanium(IV) stock solution was prepared by dissolving their sulfates in double distilled water containing a minimum amount of the corresponding acid, and the insoluble residue was filtered off.

2.2. Procedure. Concentration experiments were carried out by shaking equal volumes of aqueous and organic phases for 15 min in conical flasks in a temperature-controlled air oscillator; the mixture was vibrated with a constant vibrating rate. After a 15 min shaking, the organic phase was separated from the aqueous phase. Phase separation was conducted using a centrifuge for 20 min at 5000 rpm, and then the phases were allowed to stand for 5 min. After phase disengagement, the equilibrium pH in the aqueous phase was measured with a pH meter (Radiometer PHM250 ion analyzer). TOA concentration varied from 20% to 100% throughout the experiments.

The titanium concentration varied from 12 g/L to 120 g/L, and sulfuric acid concentration varied from 0.04 to 0.08 M. The concentrations of the titanium(IV) in the aqueous phase were measured by inductively coupled plasma optical emission spectrometer (ICP–OES).The concentration in the organic phase was calculated from the difference between the organic concentrations in the aqueous phase before and after separation. The IR spectra of titanium(IV) loaded organic phase were obtained with a Nicolet Nexus670 spectrometer.
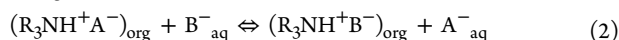
2.3. Separation of Ti(IV) from Acidic Solution by TOA. TOA is nonmiscible with water and can form oil soluble salts of anionic species at low pH. Since TOA contains a basic nitrogen atom, it typically can react with variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions with a lot of other anions. The general reactions can be described as follows:[22]
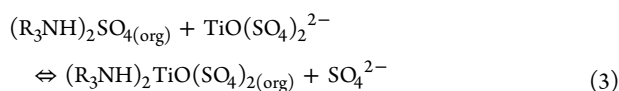
protonation:

$$(R_3N)_{org} + H^+ + A^- \Leftrightarrow (R_3NH^+A^-)_{org} \tag{1}$$

exchange:

$$(R_3NH^+A^-)_{org} + B^-_{aq} \Leftrightarrow (R_3NH^+B^-)_{org} + A^-_{aq} \tag{2}$$

The extent to which B will exchange for A was a function of the relative affinity of the two anions for the organic cation and the relative salvation energy of the anions by the aqueous solution.

The Ti(IV) ions may exist in acidic solution in different forms,[23] such as TiO^{2+}, $TiO(OH)^+$, $Ti(OH)_2^{2+}$, and $Ti(OH)_3^+$. However, TiO^{2+} cation dominated in the acidic aqueous solution when the pH was lower than 1.3. In sulfate solutions, titanium formed electrically neutral and anionic complexes, since the SO_4^{2-} and HSO_4^- ions took part in complex formation. In sulfuric acid, species such as $TiOSO_4$, $TiO(SO_4)_2^{2-}$ and $Ti(SO_4)_3^{2-}$ formed with increasing sulfate concentration and $TiO(SO_4)_2^{2-}$ would predominate when the concentration of SO_4^{2-} rangeed from 0.5 to 10 mol/L. Thus, in this study, we believed that titanium(IV) ions would exist as $TiO(SO_4)_2^{2-}$.

The chemical reactions in the experiment were given below:

$$(R_3NH)_2SO_{4(org)} + TiO(SO_4)_2^{2-}$$
$$\Leftrightarrow (R_3NH)_2TiO(SO_4)_{2(org)} + SO_4^{2-} \tag{3}$$

In addition, the hydrolysis behaviors of titanium(IV) occur in the solutions, which were expressed as follows:

$$Ti^{4+} + H_2O \rightarrow TiO^{2+} + 2H^+ \tag{4}$$

$$TiO^{2+} + 2H_2O \rightarrow H_2TiO_3\downarrow + 2H^+ \tag{5}$$
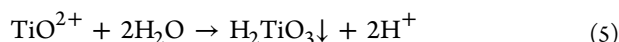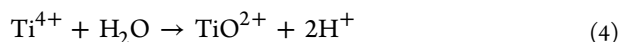
The hydrolysis rate of titanium(IV) was accelerated in the protonation process of TOA and the precipitate H_2TiO_3 was generated. This precipitates could attach with the oil phase, due to smaller particles size and larger specific surface area, and could be separated from sulfuric acid solutions well. Hence, in this work, separation and concentration process for titanium-(IV) from its H_2SO_4 solutions by TOA was a complex process in which chemical precipitation and extraction happen together.

3. RESULTS AND DISCUSSION

3.1. Effect of Reaction Time. The effect of equilibration time on the separation of titanium(IV) using TOA was investigated, and it is observed that 15 min was sufficient for the separation and concentration of titanium(IV) from its

H_2SO_4 solutions (0.08 M) with an organic phase containing 60% TOA. It can be seen from Figure 1 that the reaction rate
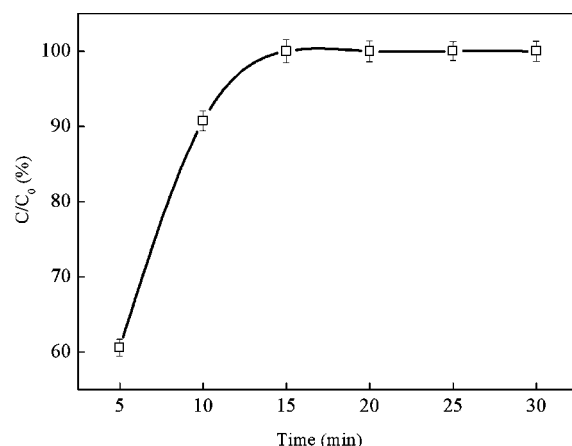

Figure 1. Effect of reaction time on the removal efficiency of Ti (reaction temperature, 308 K; sulfuric acid concentration, 0.08 M; Ti concentration of feed solution, 30 g/L; organic/aqueous phase ratio, 1; TOA, 60%; kerosene, 40%; equilibrium pH, 6.8).

was relatively fast, since only 15 min were required to reach equilibrium and removal efficiency approximately reached 100%.

The removal efficiency is defined as

$$R = \frac{C}{C_0}$$

where C is the mass of metal ions in the organic phase and C_0 is the initial metal ions mass.

3.2. Effect of Reaction Temperature. The separation of titanium(IV) was studied at different temperatures (293–323 K) with 60% TOA in kerosene as the reagent. It is observed from Figure 2 that the removal efficiency of titanium(IV)
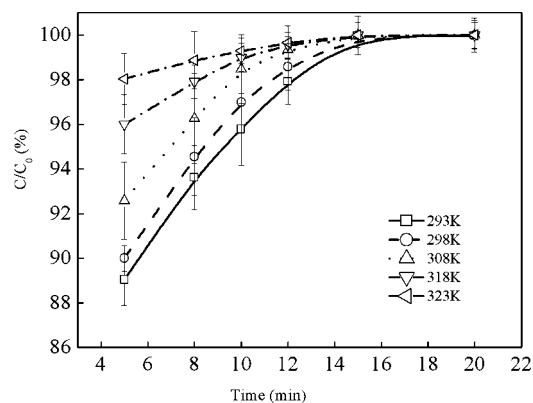

Figure 2. Effect of reaction temperature on the removal efficiency of Ti (reaction time, 15 min; sulfuric acid concentration, 0.08 M; Ti concentration of feed solution, 30 g/L; organic/aqueous phase ratio, 1; TOA, 60%; kerosene, 40%; equilibrium pH, 6.8).

increased with increasing temperature. Especially, the removal efficiency of titanium(IV) increased sharply within a temperature range of 293–308 K and then became steadily when the temperature was greater than 308 K. Moreover, it is also observed that the equilibrium time varied with the temperature and decreased with increasing temperature. But, even so, the

removal efficiency of titanium(IV) became nearly constant at the final equilibrium state within a temperature range of 293–308 K. So, the change of temperature does not influence extraction equilibrium.

3.3. Effect of Sulfuric Acid Concentration. In a general way, sulfuric acid is mainly used for the leaching of titanium oxide and its ores.[24] It is of importance to study thoroughly the effect of sulfuric acid concentrations on the removal efficiency of titanium. So, the effect of sulfuric acid concentration on the separation of titanium(IV) was investigated within the range of 0.04–0.08 M, with the titanium concentration being constant at 30 g/L in the aqueous phase and 60% TOA in kerosene as reagent. It can be seen from the Figure 3 that the removal
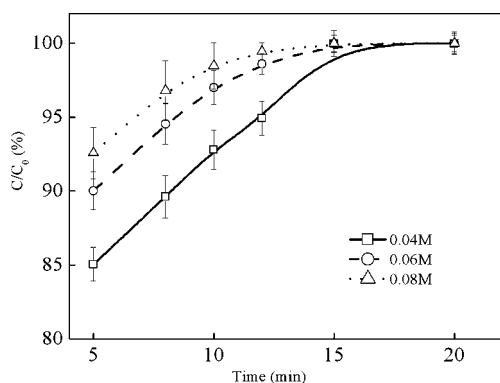

Figure 3. Effect of sulfuric acid concentration on the removal efficiency of Ti (reaction time, 15 min; reaction temperature, 308 K; Ti concentration of feed solution, 30 g/L; organic/aqueous phase ratio, 1; TOA, 60%; kerosene, 40%; equilibrium pH, 6.8).

efficiency of titanium(IV) increased with increasing of sulfuric acid concentration within the first 15 min reaction time. This phenomenon can be explained by the fact that the concentration of cationic species of R_3NH^+ decreases due to the less availability of protons for the reaction at low concentration of H^+.[25] Similar results are previously observed by Kumbasar et al.[22] When the reaction time was beyond 15 min, the removal efficiency of titanium was approximately 100% at different acidity and it indicated the reaction reached equilibrium. Moreover, the effect of sulfuric acid concentration on the extraction equilibrium was investigated, too. It is observed that the equilibrium time varied with the sulfuric acid concentration and decreased with increasing sulfuric acid concentration. But, different acidity does not affect the final equilibrium state, because of nearly identical removal efficiency.

3.4. Effect of Organic/Aqueous Phase Ratio. The organic/aqueous phase ratio, defined as the ratio of the oil phase volume to the aqueous phase volume, has a profound influence on separation of titanium(IV). The effect of the phase ratio is depicted in Figure.4. It is observed that the removal efficiency of titanium(IV) increased remarkably with the increasing of the ratios from 0.2 to 1, and the system was in equilibrium state when the organic/aqueous phase ratio was 1. This may be due to the increase of concentration of cationic species of R_3NH^+ with increasing the phase ratios or the saturation of TOA at low organic/aqueous phase ratios. Above this phase ratio, the removal efficiency decreased. This is because that the acidity and SO_4^{2-} concentration decreases with the increase of TOA and a species-like TiOSO$_4$ in the feed solutions will form, which may not be ionized completely at
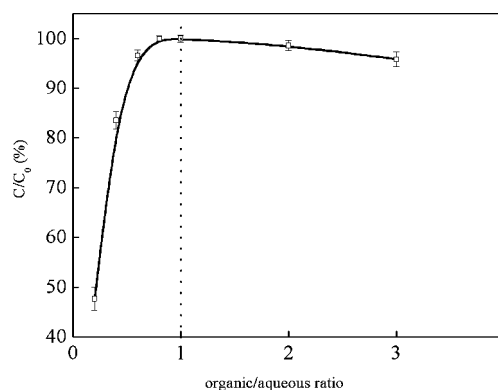

Figure 4. Effect of organic/aqueous phase ratio on the removal efficiency of Ti (reaction time, 15 min; reaction temperature, 308 K; sulfuric acid concentration, 0.08M; Ti concentration of feed solution, 30 g/L; TOA, 60%; kerosene, 40%).

lower acid concentrations to form a complex with R_3NH^+ cation.

3.5. Effect of TOA Concentration. TOA concentration plays a significant role in separation of titanium(IV) in terms of effective and reasonable utilization of materials. So it is necessary to investigate the effect of TOA concentration on the separation of titanium(IV). The effect of TOA concentration (20%–100%) on the separation of titanium(IV) is shown in Figure 5. It is observed that the removal efficiency of
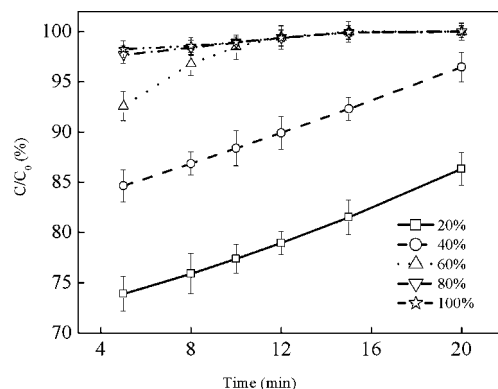

Figure 5. Effect of TOA concentration on the removal efficiency of Ti (reaction time, 15 min; reaction temperature, 308 K; sulfuric acid concentration, 0.08 M; Ti concentration of feed solution, 30 g/L; organic/aqueous phase ratio, 1; equilibrium pH, 6.8).

titanium(IV) increased with increase of the TOA concentration ranging from 20% to 100% in the first 15 min. However, after the fifteenth minute, the removal efficiency remained the identical and constant when the TOA concentration ranged from 60% to 100%, which indicated that extraction equilibrium was reached and the change in concentration of TOA did not affect the equilibrium. Thus, a TOA concentration of 60% is considered to be enough for the separation of titanium(IV) and is accepted as the best reagent concentration.

3.6. Effect of Titanium Concentration and Metal Loading Capacity of TOA. The 0.08 M H$_2$SO$_4$ solutions, with different amounts of titanium (12–120 g/L), were equilibrated separately with 60% TOA in kerosene, and the organic/aqueous ratio was 1. Figure 6 is a plot of the removal efficiency of titanium(IV) and the loading amount of Ti(IV) on the reagent versus the titanium concentration. The results
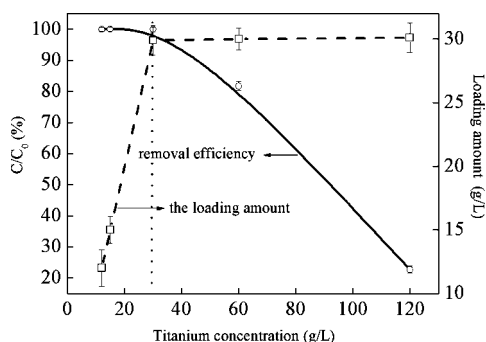
Figure 6. Effect of titanium concentration on the removal efficiency of Ti and loading capacity of TOA (reaction time, 15 min; reaction temperature, 308 K; sulfuric acid concentration, 0.08 M; organic/aqueous phase ratio, 1; TOA, 60%; kerosene, 40%).

showed that the removal efficiency was influenced by the initial titanium concentration and the removal efficiency decreased with the increasing of the initial concentration of titanium.

The loading capacity defined as the amount of metal ions in grams that is separated from 1 L of pure reagent, is a very important factor for its commercial applicability. High value of loading capacity is desirable for a particular extractant–metal ion system. In addition, the species extracted at high loading may be easily converted to pure (usually solid) complexes for its structure determination by chemical and instrumental methods.

It can be seen from Figure 6 that when the initial titanium concentration was below 30 g/L, the loading amount of titanium(IV) on the reagent increased with increasing of initial titanium concentration and then it became independent when the initial titanium concentration was above 30 g/L. This indicates that the loading amount of titanium(IV) on the reagent does not reach the maximum value of 30 g Ti/L reagent until the titanium concentration is up to 30 g/L (the system is in equilibrium state in this condition), and this also accounts for the decreasing removal efficiency of titanium(IV) with the increase of the initial titanium concentration.

3.7. IR Spectra of Titanium(IV) Loaded Organic Phase. The IR spectra of titanium(IV) loaded organic phase is shown in Figure 7. The spectra of trace "a" and trace "b" represent the organic phase before and after extraction, respectively. In trace

b, the peaks at about 2927, 2856, and 1466 cm^{-1} are the typical asymmetrical stretching vibration peaks of −CH$_2$, the peaks at about 2955 and 1376 cm^{-1} are the typical asymmetrical stretching vibration peaks of −CH$_3$, and the peak at about 2792 cm^{-1} is the stretching vibration peak of NH$^+$. The absorption peaks observed at about 1040 and 966 cm^{-1} indicate that the peaks are attributed to S−O, and the absorption peak observed at about 649 cm^{-1} is attributed to O−S−O possibly. It is inferred that the peak at about 1095 cm^{-1} is the absorption spectral band of Ti−O.

The results suggested that a certain amount of titanium(IV) is extracted by organic phase; separation and concentration process for titanium(IV) from its H$_2$SO$_4$ solutions by TOA is a complex process which chemical precipitation and extraction happen together.

3.8. Stripping and Recovery of Titanium(IV) from the Organic Phase. In general, metallic ions extracted by amines can be stripped from the protonated amine by removal of a proton using neutral alkaline solutions. The stripping reaction for the Ti(IV)−TOA complex with an alkaline solution is expressed by

$$(R_3NH)_2TiO(SO_4)_{2(org)} + 4OH^-_{(aq)}$$
$$\rightarrow 2R_3N_{(org)} + H_2TiO_3\downarrow + 2SO_4^{2-} + 2H_2O \qquad (6)$$
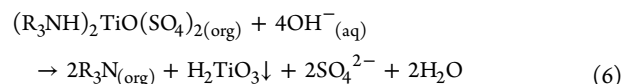
In this work, 10% sodium bicarbonate was used as a stripping agent. The stripping of titanium was very fast, and the time required for the complete stripping was only 5 min. Moreover, almost 100% of titanium(IV) was stripped, and the XRD data of the roasted solid (at 973 K, 5 h) showed (Figure 8) the presence of TiO$_2$ with anatase structure.

3.9. The Recycling Capacities of the Extractant. To investigate the recycling capacities of the extractant, the stripped organic phase was recycled back to separate and concentrate titanium(IV) under the optimum conditions (reaction temperature, 308 K; sulfuric acid concentration, 0.08 M; Ti concentration of feed solution, 30 g/L; organic/aqueous phase ratio, 1; 60% TOA; 40% kerosene). The experiment results are shown in Figure 9. It is observed that the removal efficiency of titanium(IV) showed a small decrease of 1−2% within the range of 5−20 min, comparing the recycled extractant with the original extractant, and the removal efficiency of titanium(IV) was approximately 100%. Therefore,
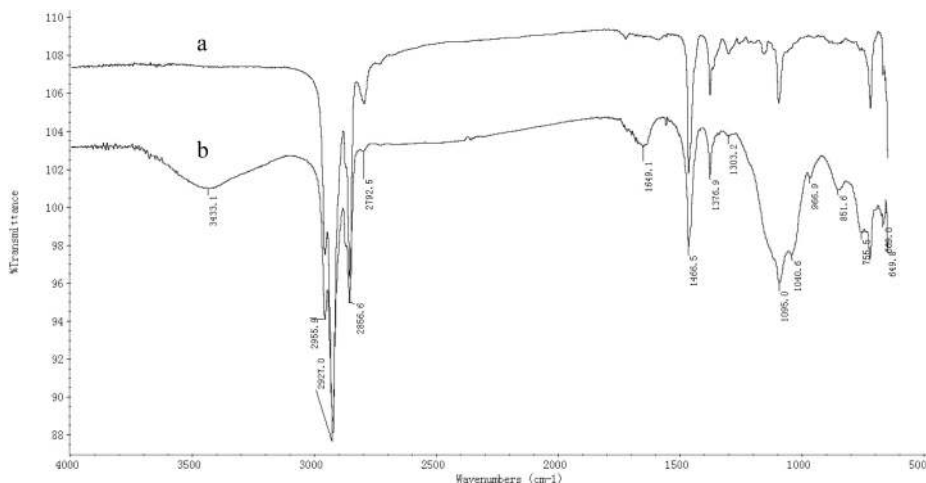

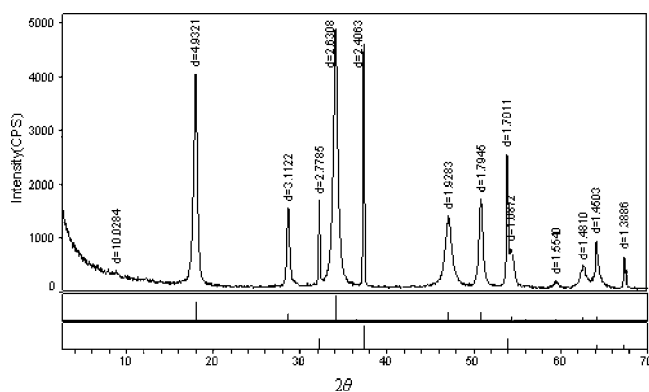**Figure 7.** IR spectra of organic phase before and after extraction.

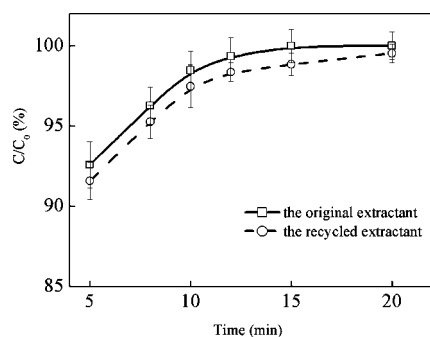**Figure 8.** XRD of TiO$_2$ obtained after calcination at 973 K.

Figure 9. Recycling capacities of the extractant.

the reagent TOA is available for recycle and has the potential for significant economic benefits.

4. CONCLUSIONS

A liquid−liquid separation and concentration processes of titanium(IV) from its H$_2$SO$_4$ solutions using TOA as reagent has been investigated. From this study the following conclusions can be drawn: (1) The experimental results obtained show that TOA is a very effective reagent for the separation of titanium(IV) from acidic medium and the kinetics of the reaction is very fast; the time required is only 15 min. (2) The separation of titanium(IV) has been achieved with an efficiency of about 100% from the sulfuric acid solutions with 30 g/L Ti(IV) in it. (3) The titanium(IV) separation is influenced by a number of variables such as reaction time, reaction temperature, sulfuric acid concentration, organic/aqueous phase ratio, and TOA concentration.

From the practical point of view, the results of this study suggest that the separation and concentration of titanium can be performed using a TOA with sulfuric acid solution. In particular a concentration scheme can be designed for titanium recovery from a sulfuric acid leaching solution which is prepared by leaching red mud.

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