

# Tannic Acid Selectively Extracting Titanium from Ilmenite: Experimental and Theoretical Investigation

Cho J<sup>1</sup>, Roy S<sup>2</sup>, Sathyapalan A<sup>2\*</sup>, Free LM<sup>2</sup> and Fang ZZ<sup>2</sup>

<sup>1</sup>School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA

<sup>2</sup>Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, USA

## Abstract

A novel route of extracting titanium using tannic acid from ilmenite was investigated. The strong affinity of tannic acid towards metal ions having high oxidation states was explored to extract titanium selectively from a multi-element solution prepared by dissolving ilmenite in sulphuric acid and ammonium sulphate. Titanium-tannic acid complex was selectively precipitated from the multi-element solution at pH 4.5. The precipitate was separated by vacuum filtration and the filter cake was washed with 2% hydrochloric acid solution, deionized water and isopropyl alcohol after filtration. The washed filter cake was dried at room temperature and ground into powder on drying. The titanium-tannic acid complex so obtained was composed of 98.6% of titanium, 0.2% of iron and 1.2% of other impurities. The density functional theory simulation at B3LYP method with a basis of 6-31G was also conducted to verify optimized structure and its stability. The result showed energy gap of 2.43 eV between two frontier orbitals (highest occupied molecular orbitals and lowest unoccupied molecular orbitals), which is large enough to indicate energetic feasibility of the complex formation.

**Keywords:** Tannic acid; Titanium; Ilmenite; Digallic acid; Density functional theory simulation

## Introduction

The merits of a metal production process have to be judged not only by the metallurgical quality of the product obtained but also by its impact on environmental and health. It has been reported that abnormalities in pulmonary function and pleural disease among people associated with titanium manufacturing can be correlated to exposure to titanium tetrachloride, titanium dioxide and duration of work in titanium production [1]. At the same time, titanium and its alloys have remarkable stability at high temperature, corrosion resistance and high strength to weight ratio [2]. This creates a demand for titanium and its alloys in a variety of applications including aerospace [3], biomedical [4] and nuclear waste storage [5].

In general, the extractions of titanium dioxide (TiO<sub>2</sub>) and titania pigment are performed using mainly two routes, sulfate and chloride processes. In the sulfate process, low grade ilmenite (FeTiO<sub>3</sub>) can be used as a feed stock which is treated by concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). In the next step, impurities are precipitated by cooling down the sulfuric acid solution and titanium dioxide can be obtained by performing hydrolysis on titanyl sulfate (TiOSO<sub>4</sub>) at 95-110°C and calcination at 1,000°C [6]. On the other hand, chloride process requires a high grade feed stock such as rutile (TiO<sub>2</sub>). The oxygen in the feed material rutile is removed by reducing agent, usually carbon, and titanium tetrachloride (TiCl<sub>4</sub>) is synthesized using chlorine gas. After that, pure titanium dioxide can be obtained by oxidizing titanium tetrachloride at 1200-1700°C [7]. However, greenhouse gases are generated in this process and an upgraded starting material is required, which increases the cost of production [8]. So alternate routes are still required to produce low cost environmentally friendly titanium from its naturally occurring ores such as ilmenite, by reducing prior treatments.

In this study, we investigate the ability of tannic acid to selectively chelate with titanium ions from a multi-element solution containing iron, vanadium, silicon, aluminium and other related ions, prepared by dissolving a complex ore such as ilmenite. It has been reported that hydroxyl-aromatic compounds can selectively complex with titanium

compounds at pH 4-5 [9-11]. Tannic acid, being a compound of such category and possess carboxylic acids expected to show a strong affinity towards metal ions having high oxidation states [9,12]. Also, tannic acid in water is hydrolysed to digallic acid and glucose [13]. Figure 1 shows the molecular structure of tannic and digallic acids. By adjusting a pH of the solution between 4 and 5 during precipitation, titanium-tannic acid complex can be precipitated selectively from a multi-element solution, containing impurities such as iron, magnesium, vanadium, and manganese as ions. The titanium-tannic acid complex so obtained has a strong potential to be used for titanium production following a scheme very similar to that developed by Fang et al. [14]. Metallic titanium can be produced by dehydrogenation of titanium hydride (TiH<sub>2</sub>), obtained by the reduction of titanium-tannic acid complex in the presence of hydrogen after the purification process of remaining impurities [15]. Moreover, tannic acid is commonly found in beverages and food stuffs and plant materials [16]. Using such an eco-friendly material to separate titanium can minimize the environmental and health concerns associated with current industrial titanium production process. To get a deeper scientific insight of the complication and selectivity for titanium chelation, density functional theory (DFT) simulations have been performed on the complex besides the exciting experimental result.

## Materials and Methods

### Preparation of titanium solution from ilmenite

16 M sulphuric acid was chosen as a lixiviant to prepare a titanium

\*Corresponding author: Sathyapalan A, Department of Metallurgical Engineering, University of Utah, Salt Lake City, UT 84112, USA, Tel: 801-581-7200; E-mail: [amarchand.sathyapalan@utah.edu](mailto:amarchand.sathyapalan@utah.edu)

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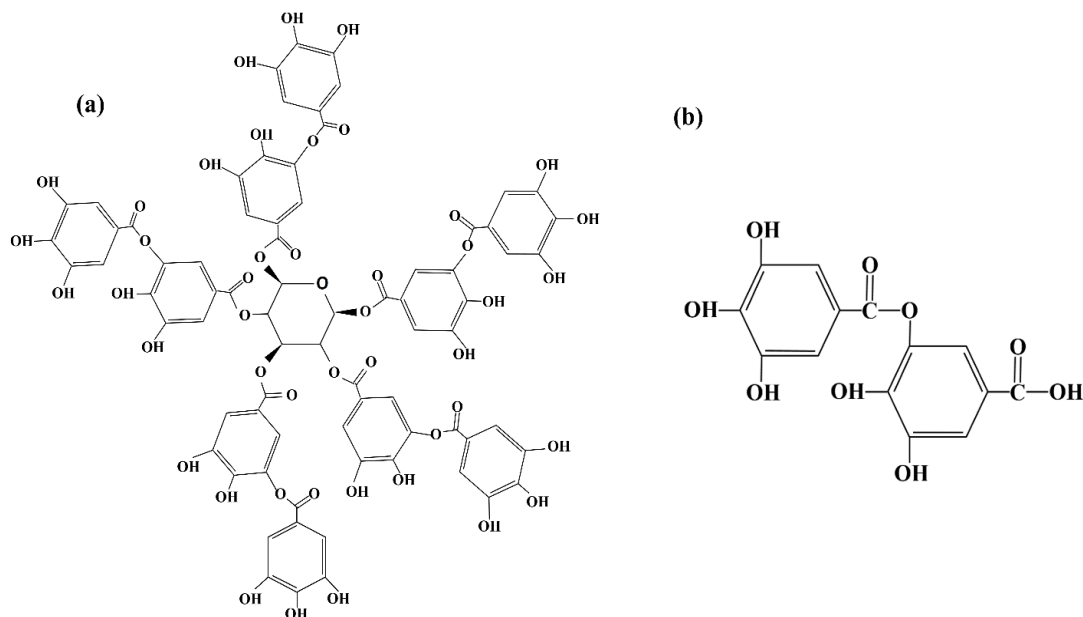


Figure 1: The structure of (a) tannic acid and (b) dissociation of tannic acid in aqueous solution as digallic acid.

containing multi-element solution from ilmenite. 10 g of ilmenite was added into 50 ml of sulphuric acid in a 500 ml round-bottom boiling flask. 20 g of ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) was also added to elevate the boiling point of the sulphuric acid solution during leaching. A 200 ml Graham condenser which has an inner coil for additional surface area was applied on the neck of the flask to maintain the volume. The solution was refluxed and the leaching was performed for 8 hours. A magnetic stirring bar at 1,000 RPM was used for homogenizing the solution. After the digestion process, the solution is allowed to settle. A dark brownish multi-element sulphate solution was obtained as supernatant liquid was collected for chelation.

### Synthesis of titanium-tannic acid complex

50 g of tannic acid in 200 ml water was taken in a 500 ml three neck flask, constantly stirred by a magnetic stirring bar at a rotational speed of 500 RPM. A 200 ml separator funnel fitted with a stopcock, containing titanium bearing solution, was installed on one of necks of the flask. A pH probe was also inserted through another neck and the third neck was sealed. A formate buffer solution was added from the separatory funnel so that the pH was maintained at 4.5 during the precipitation of the dark orange-colored precipitate. The experiment was carried out at room temperature. The precipitate was collected by a vacuum filtration, washed with 2% hydrochloric acid solution, followed by cold deionized water and isopropyl alcohol, dried at room temperature, and ground into powder. The filtrate was investigated by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The solid samples were characterized using Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDS) and Fourier Transform Infrared Spectroscopy (FTIR).

### Methodology of DFT simulation

DFT simulation using general ab initio quantum chemistry package, Gaussian 09, was carried out to determine optimized geometry of titanium-tannic acid complex and the stability based on highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). B3LYP [17,18] for the exchange-correlation

energy functional calculation was employed with a basis of 6-31G, which has been known as a most effective method for the simulation of organic molecules [19]. Also, the optimization was conducted without symmetry constraints.

## Results and Discussion

### Experiment result

The multi-element solution prepared by dissolving ilmenite in concentrated sulphuric acid was composed of 22.64% (w/w) of titanium, 71.28% (w/w) of iron, and 6.08% (w/w) of other impurities determined by ICP-OES. After precipitating out titanium-tannic acid complex with tannic acid containing ammonium hydroxide at a pH of 4.5, the yield of titanium was found to be 95.58% (w/w). Figure 2 shows the surface morphology and Table 1 exhibits the chemical composition of titanium-tannic acid as analysed by SEM and EDS, respectively. The particle shape looks irregular and it forms agglomerate. The sizes of individual particle are only few micron meters. The powder has 98.6% (w/w) of titanium, 0.2% (w/w) of iron, and 1.2% (w/w) of other impurities. When it is considered that iron is a difficult impurity to be removed in titanium production, Figure 2b shows a remarkable capability of tannic acid to extract titanium selectively.

Figure 3 shows IR spectra of titanium and titanium-tannic acid complex. The IR spectra present peaks at a broad range of 3500~3200  $\text{cm}^{-1}$  due to O-H stretching vibration in both tannic acid and titanium-tannic acid complex [20]. However, the positive shift and decreased intensity of the peak for O-H bond in titanium tannic acid complex were observed due primarily to coordination of phenolic -OH group with titanium ion by means of deprotonation [10,21]. This may suggest that tannic acid tends to form complexes with titanium using hydroxyl groups in benzene rings. Several peaks below 1800  $\text{cm}^{-1}$  are due to tannic acid ligands including benzene rings and carboxylic acids. C=O stretching vibration at 1685 and 1706  $\text{cm}^{-1}$  for tannic acid and titanium-tannic acid complex was observed [20]. The peaks 1500~1400  $\text{cm}^{-1}$  account for C-C stretching vibration in aromatic rings. Significant changes in spectra profile of titanium-tannic acid complex at a range of

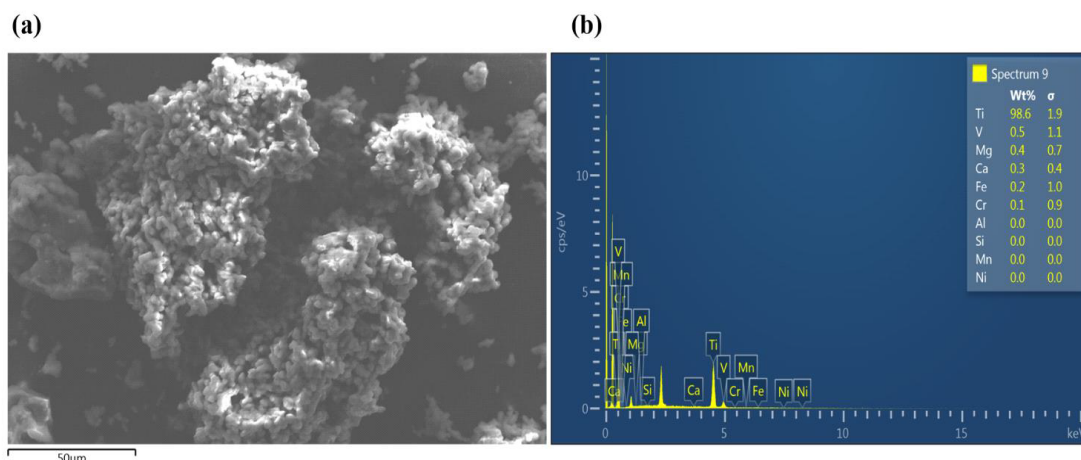


Figure 2: (a) SEM image of titanium-tannic acid complex (b) capability of tannic acid to extract titanium selectively.

| Elements | Ti   | V   | Mg  | Ca  | Fe  | Cr  |
|----------|------|-----|-----|-----|-----|-----|
| Wt (%)   | 98.6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 |

Table 1: The composition of titanium-tannic acid complex analyzed by EDS.

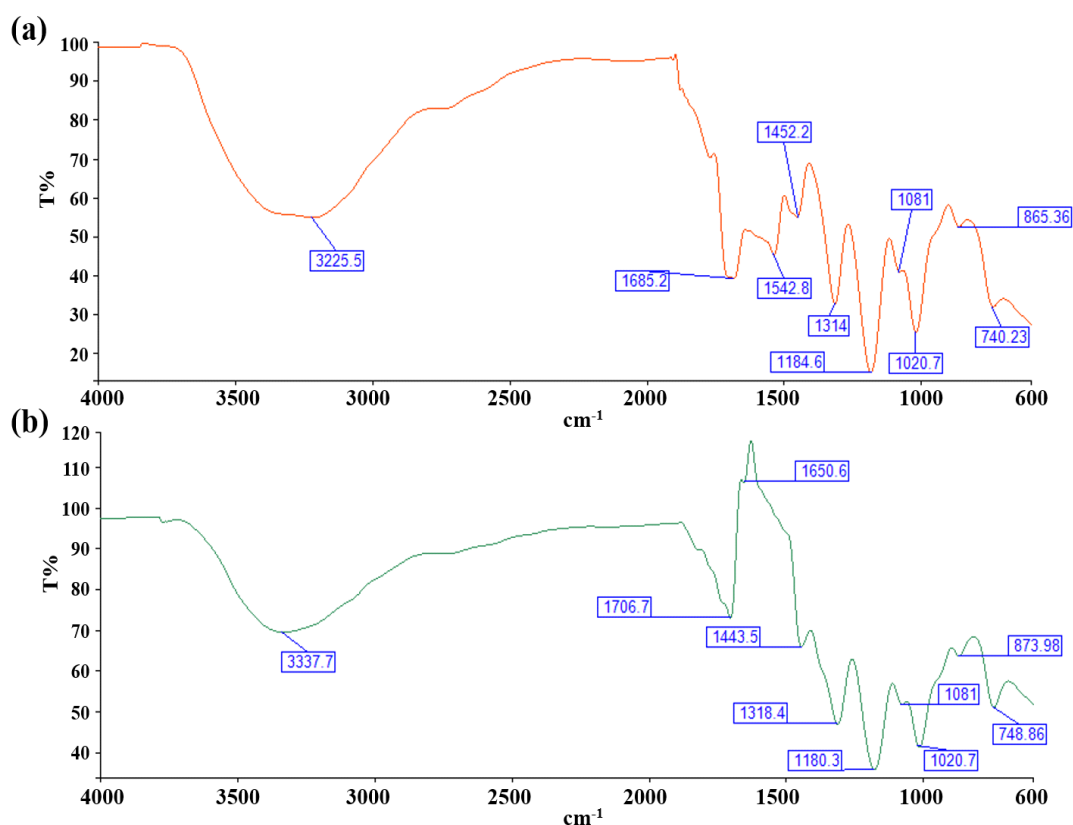


Figure 3: FT-IR spectra of (a) tannic acid (b) titanium-tannic acid complex.

1700~1450  $\text{cm}^{-1}$  are due to the chelation process for the formation of metal complex. The peaks due to C-O stretching vibration and O-H bending vibration in benzene rings and carboxylic acids appear at 1300~1000  $\text{cm}^{-1}$  in both Figure 3a and 3b [20]. The peaks below 900  $\text{cm}^{-1}$  can be explained

by C-H bonding in benzene rings. It is worthwhile to be noted that peaks below 1452  $\text{cm}^{-1}$  in tannic acid match with peaks in titanium-tannic acid complex, which may mean that there exists no significant participation of carboxylic group in coordination with titanium ion.

## Simulation

Based on the fact that titanium ion forms an ionic bonding with two -OH groups in a gallic acid [11], Figure 4 shows a probable schematic titanium-tannic acid complex and optimized geometry determined by DFT simulation. The geometry was fully stabilized.

A LUMO-HOMO gap is known as the important parameter that can describe the degree of stability of the complexes [22]. A molecule having a larger LUMO-MOMO gap is more stable than a molecule having a smaller LUMO-HOMO gap. Also, according to a concept of hard and soft Lewis acids and bases (HSAB), the global hardness of a molecule is the representative stability index of complexes [23]. A high value of the global harness implies a highly stable complex. In the DFT simulation, The LUMO-HOMO gap was calculated to be 0.08934 a.u (2.43 eV) as shown in Figure 5 and the global hardness (h) was found to be 0.04467 a.u based on the eqn. (1).

$$h = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (1)$$

Where h is the global hardness, the energy of the lowest unoccupied molecular orbitals and the energy of the highest occupied molecular orbitals. The LUMO-HOMO gap and the global hardness of titanium-tannic acid complex are large enough to indicate the energetic feasibility and stability for the formation of titanium-tannic acid complex.

Also, it is interesting to note that electron density mainly consists of carbon and oxygen from a conjugated gallic acid unit located at the end of the molecule in both HOMO and HOMO-1 levels in which there is no contribution from titanium atom. On the other hand, in LUMO level, molecular orbitals are uniformly distributed around titanium atom and adjacent gallic acid group, which has empty-orbitals of benzene rings. It is also observed in LUMO+1 level that the distribution of molecular orbitals is somewhat similar to that in LUMO level, but there are a more significant localization in titanium atom and

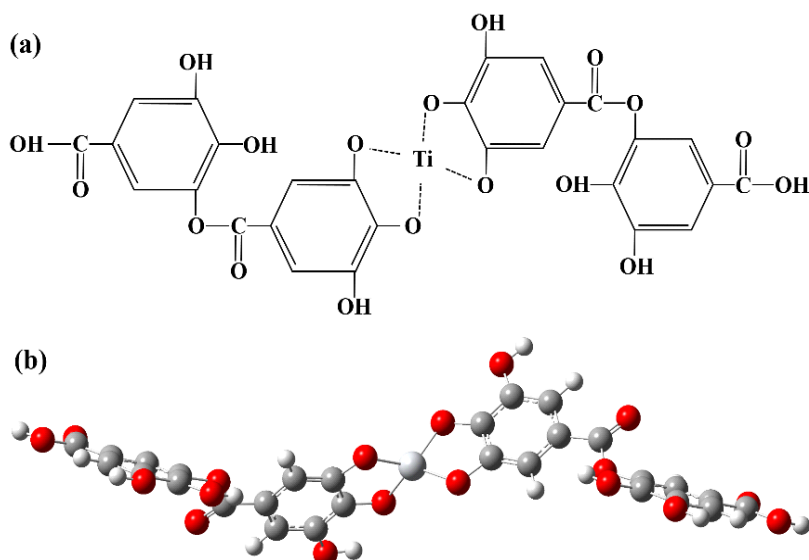


Figure 4: (a) The scheme of titanium and tannic acid and (b) optimized structure by DFT simulation at B3LYP with 6-31G: gray (carbon), red (oxygen), white and big atom (titanium), white and small atom (hydrogen).

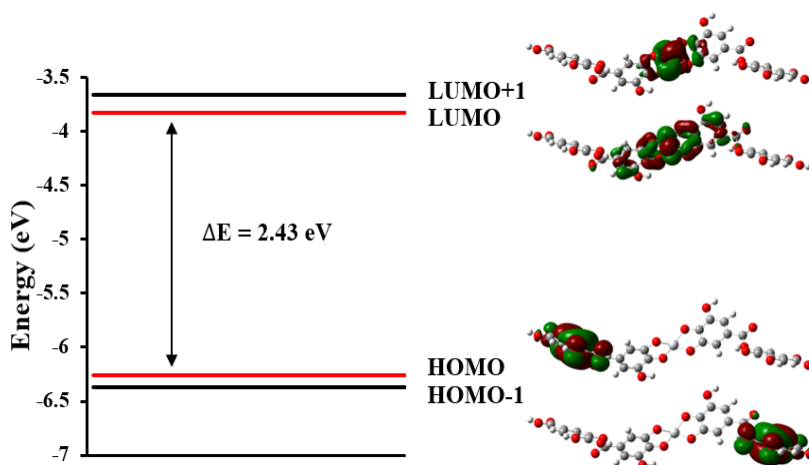


Figure 5: The molecular orbitals' energy levels of titanium-tannic acid complex at LUMO+1, LUMO, HOMO, and HOMO-1: green (positive isosurface of molecular orbitals), red (negative isosurface of molecular orbitals).

less contribution from digallic acid group. This can be explained by the relative energetic alignment between molecular orbitals of titanium and gallic acid group. Titanium atom in LUMO is lower in energy than digallic acid groups. Thus, titanium in titanium-tannic acid complex has a possibility of forming titanium hydride in a hydrogen atmosphere as titanium atom can easily accept excited electrons.

## Conclusion

The investigation of ability of tannic acid to extract titanium selectively from a multi-element bearing solution prepared by digesting ilmenite was performed through experiment and density functional theory simulation.

(1) Preparation of titanium-tannic acid complex coupled with careful control of pH of the solution was successfully performed and the complex showed a purity of 98.6%.

(2) A LUMO-HOMO gap of titanium-tannic acid complex was calculated to be 2.43 eV.

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