

# Synthesis of TiO<sub>2</sub> nanopowders from red gypsum using EDTA as complexing agent

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**Abstract** TiO<sub>2</sub> white pigments were used in various applications due to their magnificent optical and electronic properties. In this paper TiO<sub>2</sub> was recovered from red gypsum which is a waste generated at TiO<sub>2</sub> production industry. The effect of time and temperature in sulphuric acid leaching processes was optimized. TiO<sub>2</sub> powders were synthesized through thermal precipitation process with the presence of ethylenediaminetetraacetic acid as a complexing and purification agent. The obtained powders were characterized by X-ray diffraction, transmission electron microscope, UV–Vis spectroscopy and inductively coupled plasma optical emission spectroscopy. Experimental results show that powders in anatase form have a 3.2 eV band gap with a crystallite size 30–50 nm.

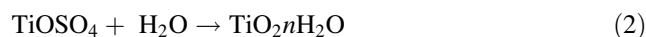
**Keywords** TiO<sub>2</sub> · Gypsum · Sulphate process · EDTA

## Introduction

Titanium dioxide, an important intermediate material, is widely used as a pigment in the manufacture of paints, paper, printing inks, rubber, floor covering, ceramics, pharmaceuticals and other areas of chemical industry paints, plastics, rubber, and paper industries. In recent application, TiO<sub>2</sub> has been used in photocatalytic application mainly in environmental purification such as reduction NO<sub>x</sub> gases [1] and water purification by treating various

chemicals [2]. TiO<sub>2</sub> has attracted to be used due to its chemical inertness, high reflectivity—brightness and brilliance, high refractive index, non-toxicity and thermal stability. There are three crystal forms of TiO<sub>2</sub> namely brookite, anatase and rutile. Among these three, anatase has shown higher photocatalytic activity due to its strong absorption capacity towards organic molecules and low recombination rate of photo-generated electron–hole pair in the anatase. Rutile is used in producing printing inks, cosmetics, plastics and paints.

There are two routes to produce titanium dioxide commercially which are through chlorination and sulphate process. Although the chlorination process is regarded as a clean process to yield titanium white, it is not suitable to be used for recovering titanium dioxide from titanium ores which contain low-titanium content. The chlorination process requires high-purity chlorine as a raw material. The processing of ore with a low-titanium content not only requires a large quantity of chlorine, but also produces chloride impurities that clog the transportation pipes [3]. The sulfuric acid process, which can digest many kinds of low-titanium-content resources, will continue to be used if its drawback of acid and iron disposal and environmental pollution is overcome.



Red gypsum is synthetic gypsum produced during titanium dioxide production to neutralize weak acid before release to the environment. Ilmenite as the source of titanium was exposed to high concentrated sulphuric acid to leach out titanium from ilmenite. After several clarification and purification steps, titanyl sulphate was hydrolyzed to

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produce titanium dioxide pigment which generated weak acid which will be further treated with lime generating red gypsum [4]. Red gypsum was composed of  $\text{SO}_3$  and  $\text{CaO}$  while  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  as the main crystalline phase. Gypsum also has higher  $\text{TiO}_2$  content around 5 % originated from weak acid. The reddish colour was explained by the presence of iron hydroxides, about 8 % [5].

In the hydrolysis process of  $\text{TiO}_2$ , the presence of  $\text{Fe}^{3+}$  in titanyl sulphate solution will commence to precipitate together with  $\text{TiO}^{2+}$  due to their small pH differences according to the different solubility product constants of  $\text{H}_2\text{TiO}_3$  ( $1 \times 10^{-29}$ ) and  $\text{Fe}(\text{OH})_3$  ( $4 \times 10^{-38}$ ). Thus, the removal of  $\text{Fe}^{3+}$  in the titanyl solution is a biggest challenge. It is also important to remove  $\text{Fe}_2\text{O}_3$  because at low content as low 100 ppm ( $10^{-6}$  wt%), it still gives  $\text{TiO}_2$  product yellow in colour which limited its photocatalytic application [3].

In the present work, we utilize gypsum as a source of titanium via sulphate process to leach out titanium to the solution by optimizing two parameters which are temperature and reaction time. Different ratio EDTA/Fe was also studied to determine the purity of  $\text{TiO}_2$  product.

## Methodology

### Material

Red gypsum (RG) used in the present study was supplied by the Tioxide (Malaysia) Sdn Bhd. RG was dried in 100 °C oven for 24 h and ground passed 500- $\mu\text{m}$  sieves. The chemical composition is listed in Table 1: hydrochloric acid (37 %), sulphuric acid (95–97 %) and ammonium hydroxide (30 %) EDTA.

### Experimental procedure

Summary of the production of  $\text{TiO}_2$  nanopowders was shown in flow chart in Fig. 1.

### HCl leaching

HCl leaching was carried out in 1-L flat bottom flask connected to a reflux condenser on a hot plate. Hydrochloric acid (20 wt%) was heated to 100 °C and definite amount of gypsum was added. The mixture was left under vigorous stirring for 2 h. After that the mixture was filtered and washed with 5 % HCl three times. The grey-colour

**Table 1** Titanium and iron content (wt%) in the gypsum after HCl leaching

Element	Before (wt%)	After (wt%)
Ti	0.16	0.13
Fe	16.85	1.16

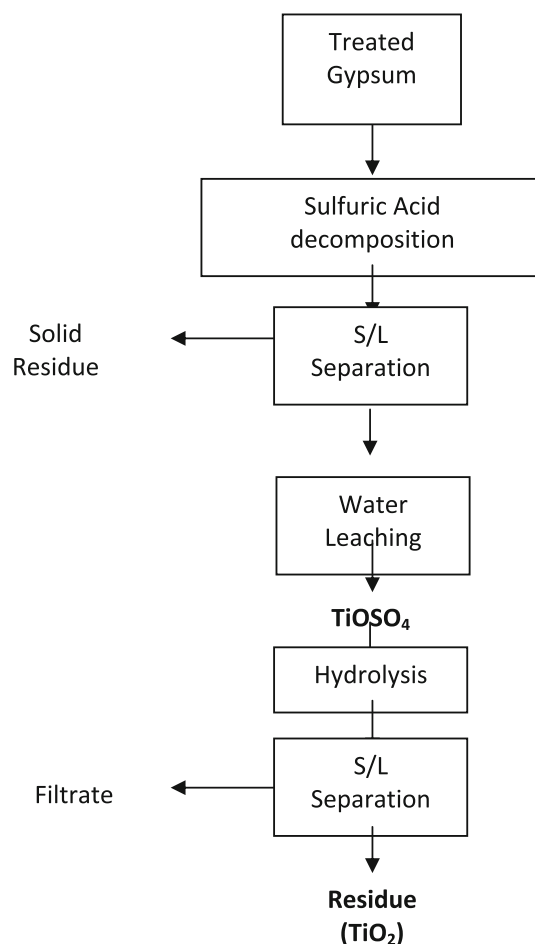
residue (high-titanium residue) was collected and dried in 100 °C overnight.

### $\text{H}_2\text{SO}_4$ decomposition

High-titanium residue (HTR) was decomposed on digital hotplate stirrer in 1-L flat bottom flask connected with condenser. Sulphuric acid was heated to definite temperature and an amount of HTR was added. Parameters that affected the titanium extraction were studied. Titanium extraction was calculated by the following formula

$$X \% = (V \times M_{\text{Ti}} / G_t \times C_{\text{Ti}} \%) \times 100$$

where  $X$  % is the titanium fractional conversion,  $M_{\text{Ti}}$  is the titanium concentration in the water solution measured by ICP after dissolution of the product ( $\text{g L}^{-1}$ ),  $G_t$  is the total mass of the titania slag (g),  $C_{\text{Ti}}$  % is the titanium mass fraction in the slag, and  $V$  is the volume of water solution. After digestion, water with a ratio 1:1 to a paste was added and stirred for 1.5 h at 90 °C for water leaching process.



**Fig. 1** Process flow of synthesization  $\text{TiO}_2$  nanoparticle from gypsum



### Hydrolysis and synthetic $TiO_2$

Titanyl sulphate solution (Ti: 2.54 g/L, Fe: 1.76 g/L) obtained from best leaching condition was used in hydrolysis process. Hydrolysis process was carried out in 1-L beaker complete with thermometer and stirrer. 100 ml of titanyl sulphate was mixed with 300 ml of distilled water (1:4) and left stir for 1 h. An EDTA solution was added into the mixture and subjected to the precipitation by slow addition of ammonium hydroxide (30 %) under constant stirring at 80 °C. The hydrolysis was controlled until mixture reached pH 8–9. White precipitate was separated by filtration and washed with distilled water for 3 times. The precipitate was collected and left for drying in room temperature for 24 h. The powder was calcined at 400 °C to obtain anatase crystal structure.

### Analysis

Elemental analysis of solution was analyzed using inductively coupled plasma–optical emission spectroscopy (ICP–OES). Crystal structure was analyzed using XRD (Phillips PW1729,  $CuK\alpha$ ); particles' size and surface morphology were analyzed using FESEM (FESEM: JEOL-JSM-7600F) and HRTEM (Technai G2 20S Twin TEM) and elemental mapping of the particles was observed with EDAX. The UV–Visible spectrum of the sample was recorded in the spectral range of 200–800 nm using a double-beam CARY 5000 UV–Vis–NIR spectrophotometer. The band gap calculation was based on method [6, 7].

### Results and discussions

#### Hydrochloric acid leaching

The gypsum was initially treated with hydrochloric acid leaching since it is advantageous in removing impurities such as MgO and CaO [8]. The slag produced by hydrochloric acid leaching was proven to contain reduced iron content from 16.85 to 1.16 %, with a little amount of titanium being leached during HCl leaching as shown in Table 2. This shows that HCl leaching is a good process to initially remove iron from gypsum.

**Table 2** Impurity in  $TiO_2$  product (EDTA/Fe = 3)

Elements	Content (%)
Fe	0.17
Al	0.08
Si	0.38

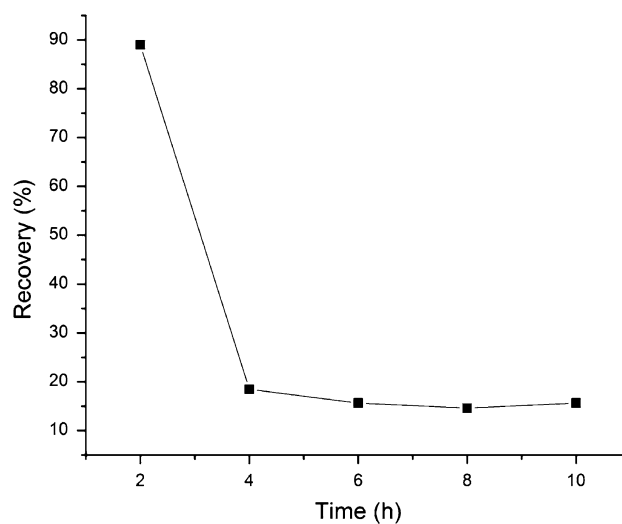
### Factors affecting decomposition with sulphuric acid

#### Effect of time

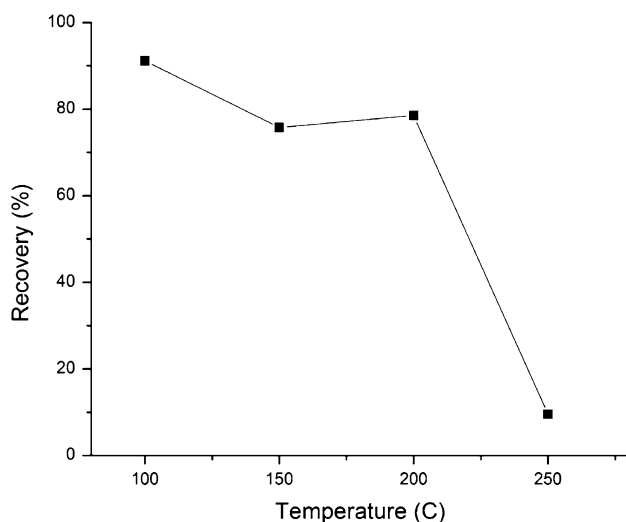
To study effect of leaching time on red gypsum by 80 %  $H_2SO_4$  several experiments were performed at different reaction times ranging from 2 to 10 h. The other parameters were fixed at  $L/S$  mass ratio of 3/1 and temperature 110 °C. The results tabulated in Fig. 2 show that the dissolution of Ti decreases as reaction time increases. The higher recovery of Ti was at 2 h of reaction time with 90 % recovery while recovery values decrease tremendously after 4 h and are constant at 6, 8 and 10 h of reaction. This trend was matched with previous works that reported the decreases of recovery value as time increases [9–11]. During long exposure to temperature near boiling point, some of the polymeric species (including  $TiOSO_4$ ,  $[TiO(SO_4)_2]^{2-}$ ) were destroyed which encourages the formation of multinuclear complexes of types  $[Ti_2O_2(OH)_3]^+$  and  $[Ti_4O_6(OH)_3]^+$  [12]. This will lead to reduction of Ti at longer leaching time, therefore 2 h represents an optimum leaching time of Ti by sulfuric acid [9].

#### Effect of temperature

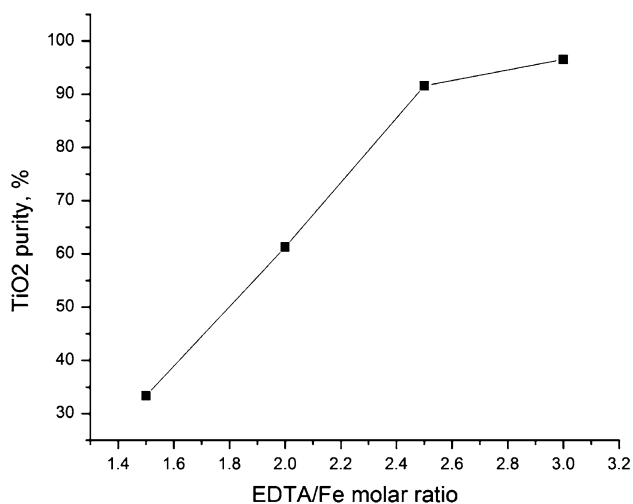
The effect of temperature on leaching of titanium was studied in the range 100–250 °C under constants of others parameters:  $S/L = 1:3$ , time = 2 h, acid concentration = 80 %. The results obtained are shown in Fig. 3. Amount of titanium recovered is highest at 100 °C and starts to decrease at 150 °C. This result is same as reported by other researchers where at near 100 °C the recovery of titanium is above 90 % and starts to decrease extremely at higher temperature [12]. This is due to instability of



**Fig. 2** Effect of leaching time on Ti recovery



**Fig. 3** Effect of temperature on Ti recovery



**Fig. 4** Effect of EDTA/Fe on purity of TiO<sub>2</sub>

titanium-contained solution, therefore it greatly enhanced polymerization and hydrolysis which led to decrease in the amount of titanium extracted [13]. Thus, temperature

100 °C was chosen as optimized temperature for Titanium extraction in this study.

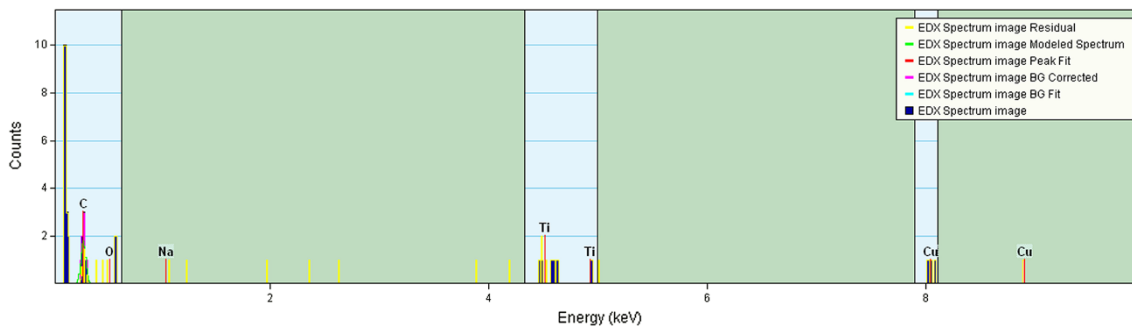
### Hydrolysis and synthetic TiO<sub>2</sub>

#### Purity

The relationship between TiO<sub>2</sub> product purity and EDTA/Fe<sup>3+</sup> molar ratio is shown in Fig. 4. The purity of TiO<sub>2</sub> rose from 90.1 to 96.9 % as the EDTA/Fe<sup>3+</sup> molar ratio increased from 1.5 to 3.0. High purity of TiO<sub>2</sub> was obtained when EDTA/Fe molar ratio is 3. High amount of EDTA is needed to chelate out Fe since EDTA has six forms in solution, which are H<sub>6</sub>Y<sup>2+</sup>, H<sub>5</sub>Y<sup>+</sup>, H<sub>4</sub>Y, H<sub>3</sub>Y<sup>-</sup>, H<sub>2</sub>Y<sup>2-</sup>, HY<sup>3-</sup> and Y<sup>4-</sup>. Among six forms, only HY<sup>3-</sup> anion was capable to chelate Fe<sup>3+</sup> since it carries same amount of charge as that of Fe<sup>3+</sup>. Chelating effect of EDTA decreased Fe<sup>3+</sup> free ions and prevents Fe<sup>3+</sup> from precipitating together with TiO<sup>2+</sup> therefore helping improve the purity of TiO<sub>2</sub> [3]. From EDAX analysis at Fig. 5 and Table 3 only titanium, carbon and copper appeared in the result. Carbon element comes from the reaction of laser and sample while copper element appeared since analysis used copper grid as a holder. From this result, it shows that EDAX analysis was correlated with ICP–OES analysis since there are no foreign elements existing in the powder.

#### Morphology

Figure 6 shows the FESEM micrographs of calcined TiO<sub>2</sub>. The secondary particles comprised agglomerated irregular primary particles (Fig. 6a). The size of secondary particles is varied from 100 to 200 nm where the primary particles varied from 30 to 50 nm (Fig. 6b). This evolution of primary size to secondary size was caused by the agglomeration of primary particles during drying process. Removal of water will reduce the distance between individual particles and lead to the agglomeration due to the van der Waals force [14]. In this analysis we also found that

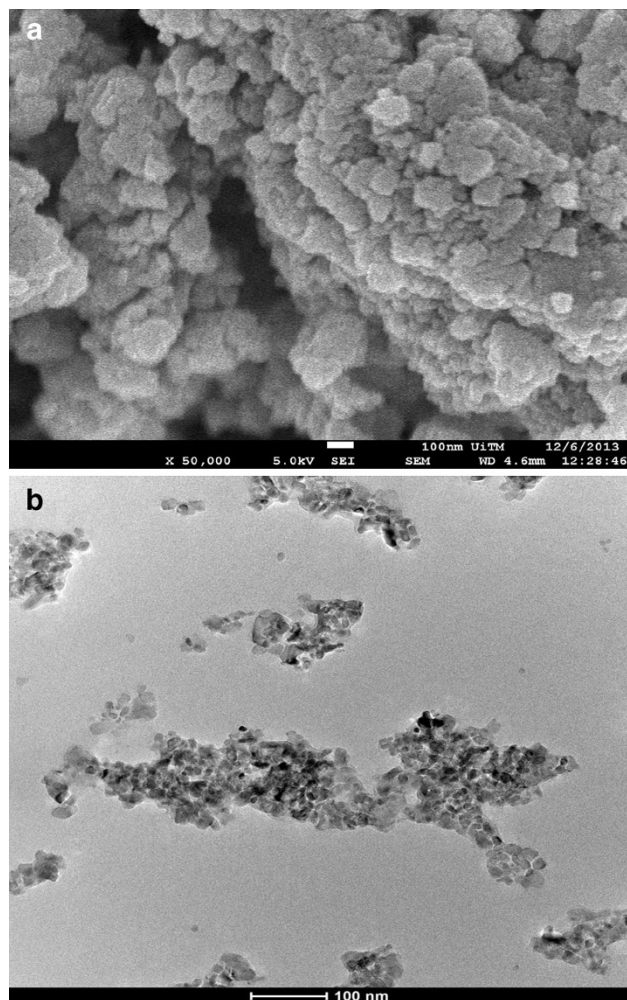


**Fig. 5** Elemental analysis of TiO<sub>2</sub>

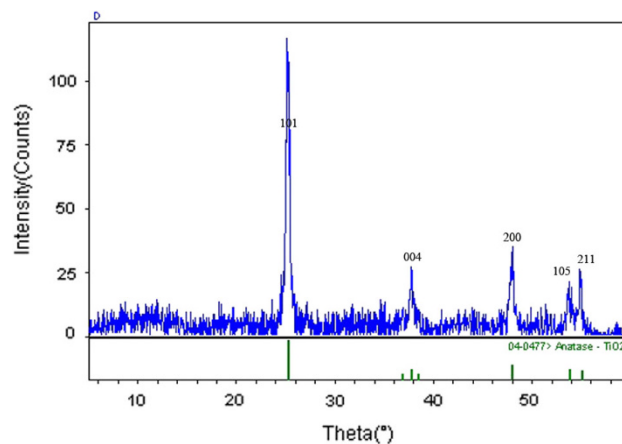
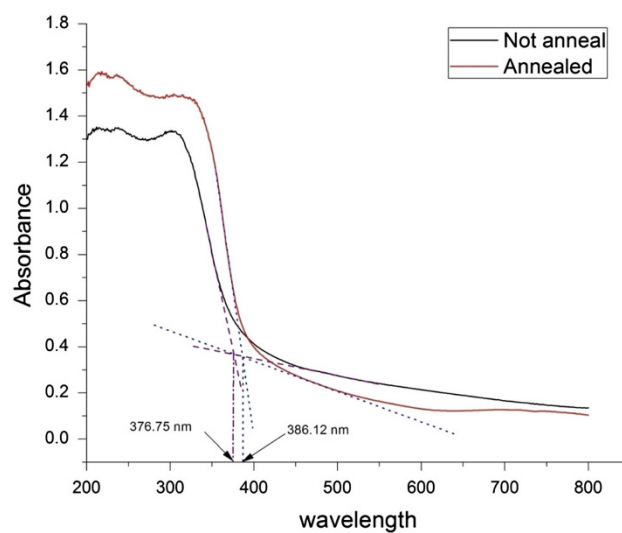


**Table 3** Quantification results of EDX

Element	Weight %
O	60.29
Ti	39.70

**Fig. 6** Morphology of TiO<sub>2</sub> nanoparticles **a** FESEM **b** TEM

primary particles are in nanosize due to the presence of EDTA which controls the precipitation rate by adsorbing the primary particles and preventing them from growing. It is well known that in preparing TiO<sub>2</sub> nanopowder, bidentate ligands are always used to control the reactivity of metal alkoxides [15]. Ligand functionality served as a versatile tool to control the assembly behaviour of titania nanocrystals [16]. Ligand functioned as assemblers that usually are adsorbed on the surface of particles resulting nanostructure particles. In this study, EDTA acts as a control for the agglomeration and also improves the purity of TiO<sub>2</sub> nanoparticles [16, 17].

**Fig. 7** XRD pattern of TiO<sub>2</sub> calcined at 600 °C**Fig. 8** UV–Vis absorbance of TiO<sub>2</sub>

### XRD

Figure 7 presents the powder XRD pattern of TiO<sub>2</sub> synthesized via Ti-EDTA chelated complex. The diffraction peaks (101), (004), (200), (105) and (211) are analogous to anatase crystal structure and the peaks of other polymorphs; rutile or brookite is not detected.

### UV–Vis diffuse reflectance spectra of TiO<sub>2</sub>

According to Fig. 8, the uncalcined and calcined TiO<sub>2</sub> had the absorption edges at 376 and 386 nm, respectively. The band gap values of uncalcined and calcined TiO<sub>2</sub> are 3.30 and 3.22 eV, respectively. These values are normal for anatase phase and support the XRD analysis for uncalcined TiO<sub>2</sub> having an anatase phase. Even though there is no significant value of band gap energies, the absorption

values between these two samples are different whereas calcined TiO<sub>2</sub> shows higher absorption values of UV light which is useful to improve the photocatalytic performance.

## Conclusion

Titanium ions were extracted from gypsum using sulphate method by studying effect of reaction temperature and leaching time which gave a 90 % extraction recovery at mild condition compared to the extraction at low and extreme condition. TiO<sub>2</sub> nanoparticles were produced from control precipitation of extracted titanyl sulphate with the presence of EDTA as a complexing agent. The presence of EDTA will help to inhibit Fe(OH)<sub>3</sub> from precipitate and subsequently help improve purity of TiO<sub>2</sub> as a final product. Effect of EDTA/Fe ratio has been studied and as results 96 % of purity level was achieved at EDTA/Fe ratio 3. Using EDTA as complexing agent also produces a TiO<sub>2</sub> nanoparticle with size ranging from 30 to 50 nm.

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