Production of Nanosized Synthetic Rutile
from Ilmenite Concentrate
by Sonochemical HCl and H₂SO₄ Leaching

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ABSTRACT: *Titanium dioxide is widely used in the manufacturing of paints, varnishes, lacquer, paper, paperboard, printing inks, rubber, floor covering, and ceramics and so on. White titanium dioxide pigment has been produced by two main processes. The sulfate and the chloride processes. Each of these two routes requires different feedstocks. However, economic and environmental pressures are shifting the world balance of titanium dioxide production away from sulphate based manufacture towards the more cost effective and cleaner chloride route. According to usage of titanium dioxide, the nano sized TiO_2 was produced by the sulfuric acid and hydrocholoric acid leaching by using Sonochemical technique during the leaching process. No adding extra materials and no milling after precipitate, no vaporization during the leaching are advantages of this work which reduced the processes of leaching. All of determination techniques of particle size (Zeta Sizer, XRD, SEM, and TEM) prove this matter. The particles sizes of nano TiO_2 which was leached by HCl and H_2SO_4 are 83 and 85 nm respectively.*

KEY WORDS: *Sonochemical, Acid leaching, Nanosize, TiO_2, Ilmenite.*

INTRODUCTION

The main titanium-containing minerals are rutile, ilmenite and leucoxene. Ilmenite (FeO·TiO₂ or TiFeO₃) contains 40-65% TiO₂, depending on its geological history. Leucoxene (Fe₂O₃·nTiO₂) is a natural alterationproduct of ilmenite, typically containing more than 65% TiO₂. Rutilecontains about 95% TiO₂ and is the most titanium-rich mineral. Itsdeposits are often found In coastal areas such as beach sands, and are thesimplest to mine and concentrate in a form adaptable for metal production. Titanium dioxide, an important intermediate in the manufactureof paints, paper, printing inks, rubber, floor covering, ceramics, pharmaceuticals and other areas of chemical industry [1], is commercially manufactured by two main processes, namely the sulfate process and

the dry chlorination process [2, 3]. The sulfate process is lengthy and also brings with it tons of unmarketable copperas, spent sulfuric acid and acid-containing waste water for each ton of TiO_2 production [4], which leads to severe environmental problems. Nowadays, about 60% of titanium dioxide is produced by the dry chlorination process in the world [5], in which naturalor synthetic rutile is used as the raw material. The shortage of natural rutile has encouraged research efforts to convert ilmenite into synthetic rutile for the dry chlorination process, which can be summarized into two categories, pyrometallurgy and hydrometallurgy methods. Pyrometallurgical production of synthetic rutile includes smelting process [6], Becher process [7], MURSO process [8], and ERMS process [9] which are all extensive energy consuming processes. So in recent years, several researchers have published the direct hydrometallurgical treatment of ilmenite to produce synthetic rutile using hydrochloric acid [10–12].

In Iran, at least 90 wt. % of titanium resources is located in Kahnooj. The high impurity content makes them unsuitable for the chlorination process and can only be processed by the sulfate process, which is suitable for many kinds of low-titanium-content resources.

The sulphate process was the first commercialised technology to convert ilmenite to titanium pigment. In the sulphate process, ilmenite(40–60% TiO_2) and/or titanium slag (72–87% TiO_2) is digested with sulphuric acid to form water soluble sulphates (Titanylsulphate $TiOSO_4$ and iron sulphates). Metallic iron scrap is used to reduce the ferric iron toferrous iron which otherwise will co-precipitate with TiO_2 and contaminate the product. The solution is then cooled down to crystallize the iron as ferrous sulphateheptahydrate ($FeSO_4 \cdot 7H_2O$). To this point, the process is in the "black stage". The solution is then subjected to hydrolysis and the resultant solids are subjected to calcination to produce anhydrous TiO_2. This is so-called the "white stage". It uses simple technology and lower grade and cheaper raw materials to produce a form of pigment called anatase (tetragonal, near octahedral), which is preferred over the pigment from the chloride process for use in papers, ceramics and inks industries. However, the traditional sulphate processes produce lower quality products for most applications and large quantities of waste iron sulphate. Therefore, it generally has higher production costs for expensive acid

treatment than the chloride process. A typical conventional sulphate process involves the following reactions:

A direct leaching process with concentrated HCl was developed by *Berkovich* [13] to dissolve at least 80% of the titanium and iron in the ilmenite ore. Ferric ions were reduced to ferrous ions by SO_2 and the resultant $FeCl_2$ was crystallised and separated. The titanium chloride in the solution was hydrolysed, precipitated, further purified and calcined as pigment grade TiO_2 (at least 99.5%). The conversion of Fe (III) to Fe (II) is essential in view of the affinity of TiO_2 for Fe (III) and the difficulty in separating Fe (III) from TiO_2. A small excess of a reductant is also useful to reduce some Ti^{4+} to Ti^{3+}. Due to the greater affinity of Ti^{3+} for oxidation, as compared to Fe^{2+}, the presence of a small quantity of Ti^{3+}in the solution decreases the tendency for Fe^{2+} ions to later oxidise to Fe^{3+} and possibly contaminate the later-formed TiO_2[13]. Leaching and reduction proceed according to following equations for the subsequent separation of iron by conventional hydrolysis or solvent extraction. Pyrohydrolysis is a distinct feature of the chloride leaching process to recover TiO_2 and MgO reagents.

A hydrometallurgical process was developed for producing ultrafine titanium dioxide from aqueous titanium chloride solutions [15, 16, 18]. It features hydrolysing the solution via complete evaporation under well controlled temperature to form amorphous titanium oxide followed by further evaporation. The biggest consumer of TiO_2 is the pigment industry. Unusual optical properties appear when the average particle size of TiO_2 is reduced to 100 nm, including high transparency to visible light and high UV absorption [22]. Nano-particles of TiO_2 also cause some components of visible light to be reflected and refracted differentially, leading to the phenomenon of iride scence. Nano-particles of TiO_2 have found wide applications in cosmetics, porcelains and ceramics industries as coating material and additives. Nano-particles of titanium oxide have received great attention recently for their potential applications in catalysis and as photo-electrochemical material. Nano-sized particles of TiO_2 could be obtained in a process by adding a chemical control agent including various inorganic salts and organic acids and organic salts, e.g. oxalic acid to the titanium chloride solution [16]. After hydrolysing, the titanium hydroxide is calcined to the desired form of titanium dioxide, being either anatase

Table 1: Chemical composition of the ilmenite(wt%).

constitute	Before thermal treatment	After thermal treatment
Fe_2O_3	1.60	0.07
Na_2O	0.23	0.24
MgO	2.01	2.04
Al_2O_3	1.94	1.90
SiO_2	7.28	7.29
P_2O_5	0.17	0.15
K_2O	0.02	0.04
CaO	1.90	2.00
TiO_2	43.61	46.53
MnO	1.05	1.90
FeO	39.16	36.96

or rutile. The titanium dioxide ismilled to provide the desired particle size distribution. The advantages of the process include a high quality titanium pigment, readily controlled physical and chemical characteristics of the product, and low costs, since dilution of the solution is avoided and the acid can be recycled. Nano-technology for producing particles of less than 100 nm has developed rapidly in recent years due to their special usage as catalysts. A process has been developed, which comprises the steps of(i) reacting a titanium compound with ammonia in an amount exceeding the stoichiometric amount necessary to convert the titanium compound to a titanium hydroxide or reacting a titanium compound with a base in a pH range of 2–7, to obtain a reaction product, and (ii) calcining the obtained product [19, 20]. The process easily produces titaniumoxide, which exhibits high photocatalytic activity under irradiation by visible light, and having an average particle size of 20nm. Solvothermal techniques (especially the hydrothermal method) are widely used in the synthesis of the nanoparticles [21]. Unlike most other synthetic processes, the solvothermal synthesis is performed under much milder chemical conditions under relatively low temperatures. Compared to those methods involving calcination and milling, which tend to result in agglomerate formation and degradation of the surface, hydrothermal processing maintains the particles in solution throughout the process so thatnon-aggregated nanomaterials may be obtained readily. The solvothermal synthesis route is very similar to the hydrothermal route, the only difference is the precursor solution is usually non-aqueousand allows for the precise control over shape, size distribution, crystallinity of titanium dioxide nanoparticles or nanostructure. Some of these experimental parameters may include reaction temperature, reaction time, solvent type, surfactant type and precursor type.

Therefore the use of Solvothermal synthesis to produce a tailored TiO_2 shape is very advantageous to maximize the TiO_2 applications in industries.

Therefore in this study, according to usage of dioxide titanium, the nano size of TiO_2 was produced by the H_2SO_4 acid and Hydrocholoric acidleaching by using sonochemical technique during the leaching process. No adding extra materials and no milling after precipitate, no vaporization during the leaching are advantages of this work which reduced the processes of leaching.

EXPERIMENTAL SECTION

The ilmenite concentrate was received from Kahnooj/Iran processing plant (Iran) mine. The chemical composition of the representative sample is presented in Table 1. XRF results (detected by an ARLX[+]) show $FeTiO_3$ as the major composition.

Leaching experiments were carried out under sulfuric acid leaching process.0.5g $TiFeO_3$ was added to 20mL pure H_2SO_4(Merck,Germany) by 120°C heat. After 30 min the mixture was filtered, and then H_2O was added to precipitate in ultra sounding bath(BANDELIN-SONOREX DIGITEC) at 50°C for 15 min. Leaching
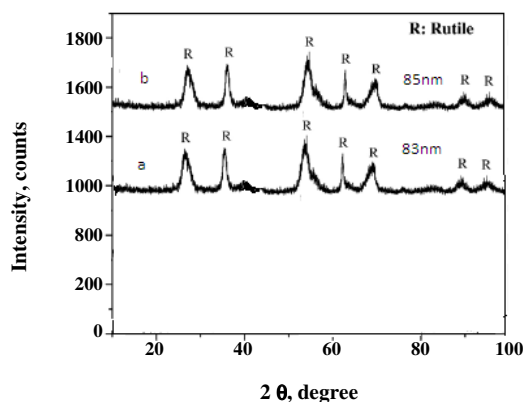
Fig. 1: XRD patterns of rutile synthesized with HCl(a) and H₂SO₄(b).

Fig. 2: FT-IR spectra of the TiO₂ products obtained by HCl(a) and H₂SO₄(b).

experiments were carried out under Hydrochloric acid leaching process. 1g of thermal treatment TiFeO₃ was added to 100 mL HCl 6M (Merck,Germany) with 100°C heat. After 8 hours the mixture was filtered, and then HCl was added to wash the precipitate. This process repeated for three times to attain pure rutile. The precipitate has calcinated for 1 hour at 950°C.

Before using an ilmenite concentrate (Kahnooj/ Iran), the ilmenite concentrate was given athermal pre-leach treatment (oxidation at 800°C, for 30 min and reduction in argon at 950°C, for 1h and 1/0.75 ratio ofilmenite to active coal and finally cooling in nitrogen. The pre-leach thermal treatment converts most of the contained iron back to the ferrous state, and transforms the pseudorutile phase.

Particle size of the produced nano particles (rutile) was determined using ZEN 3600 Zeta Sizer(Malvern), XRD (PANanalytical X'PERT), SEM (CAMSCAN-MV2300) and TEM (TEM.LEO912-AB), FT_IR (Bruker-Tensor27).

RESULTS AND DISSCOTION
Analysis and characterization

The crystalline TiO₂ materials produced were analyzed and characterized with a variety of techniques. The titanium concentrations in solutions were determined by atomic absorbtion (VARIAN-specter AA220) was used to determine the impurity content of the powders. The analysis annealed the purity of TiO₂ that leached by HCl and H₂SO₄ were 93% and 91% respectively.The identification of crystalline phases was achieved by X-raydiffraction analysis Fig. 1 using Cu-Kα radiation. The intensities of the strongest peaks
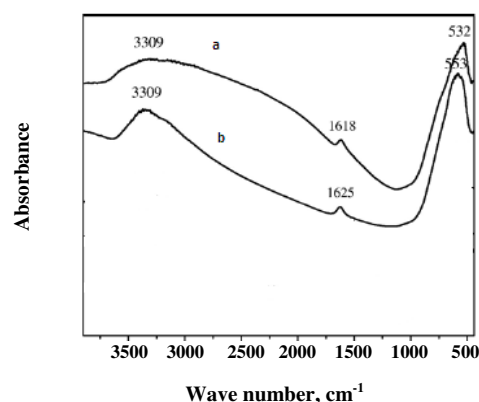
of anatase (101) (2θ=25.4°) and rutile (110) (2θ=27.4°) were used to make a relative comparison of phase content between the different types of TiO₂ powders. A quantitative estimation of the weight fraction of the rutile phase in the sample was made by the following equation [23]:

$$W_R = 1/(1 + 0.81_A/I_R)$$

Where W_R is the weight fraction of the rutile present, I_A and I_R are the X-ray integrated intensities of anatase and rutile reflection, respectively. The primary crystallite size of the obtained powders was estimated using the Scherrer equation [24]:

$$D_c = K\lambda/(B\cos\theta)$$

Where D_c is the average crystallite size; K (=0.89) is the Scherrer constant; λ (=15.406 nm) is the X-ray wave length; B is the full-width at half-maximum (FWHM); and θ is thediffraction angle.

The FT-IR spectra of the TiO₂ products obtained by neutralization (shown in Fig. 2) exhibited three peaks. The very broad band centered around 3300 cm⁻¹ indicates the presence of –OH groups, which can be attributed to the water of hydration or residual –OH in the crystal structure of titanium dioxide: $Ti(OH)_2zO_2- z$. The δ-H₂O band around 1618–1635 cm⁻¹ demonstrates the presence of molecularly adsorbed water. The band in the range between 530–610 cm⁻¹has been attributed to Ti–O–Ti bonds in titanium dioxide [25-27].

The nanostructured character of the produced titania powders was verified by employing the Scherrer method, TEM and SEM examination. Thus estimation of the crystallite size of the rutile phase precipitates Fig. 1
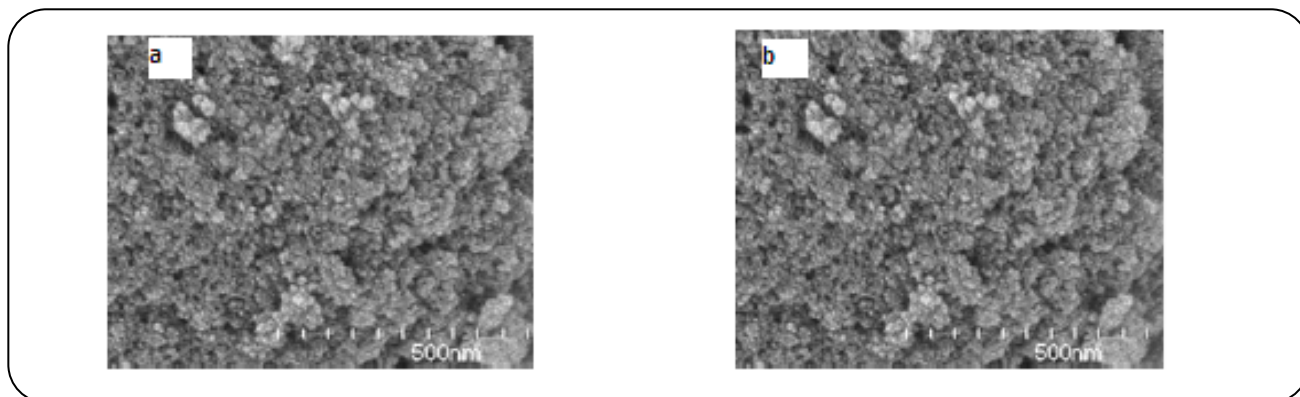
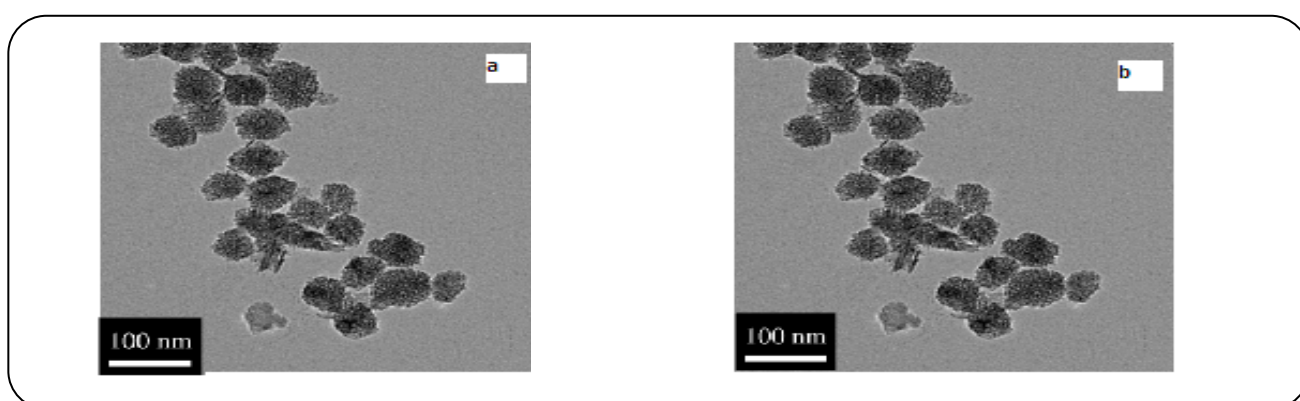*Fig. 3: SEM images of TiO₂ products obtained by HCl(a) and H₂SO₄(b).*

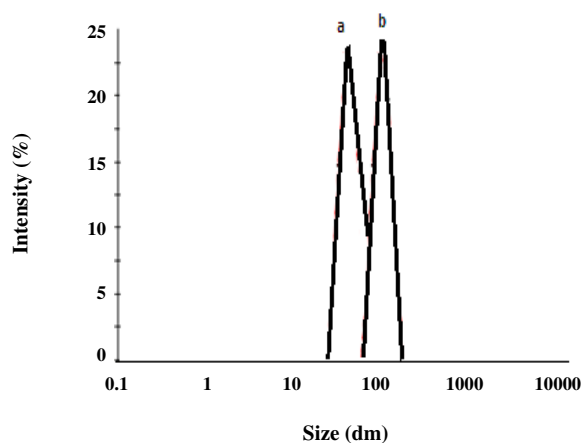*Fig. 4: TEM images of the product obtained by HCl(a) and H₂SO₄(b).*

Fig. 5: Size distribution of nanoparticle in solution for TiO₂ synthesized by HCl(a) and H₂SO₄(b).

by the Scherrer equation showed the size to vary from 83 to 85 nm. SEM images of the produced powders are illustrated in Fig. 3. It is clearly evident that the produced powders consisted of heavily aggregated particles.

The morphologies of all powders were similar but their aggregate particle sizes were different from each other: the particle size of the powders obtained by HCl was much finer than the others. From the TEM examination it was further revealed the primary aggregated particles to consist of secondary honeycomb-shaped aggregated nanoparticles with aggregate size of 84 nm. The nanoparticle aggregates consisted of many fine acircular (needleshaped) nanocrystallites, as can be evidenced at the edge of the nanoparticle image in Fig. 4.

The size distribution also shows that the size of nano particle of TiO₂ is in agreement with the others examination Fig. 5.

An importance of produced, nano size of TiO₂ is using ultra sonic bath during the synthesis process. Sonofication of solution caused that particles did not contact to each other and dispersed on solution. In the other hand when the precipitate was produced, ultra sonic wave did not allow each molecule aggregates to the other molecules and the nano size of particles prepared.
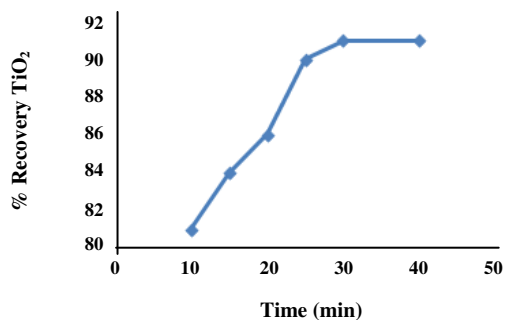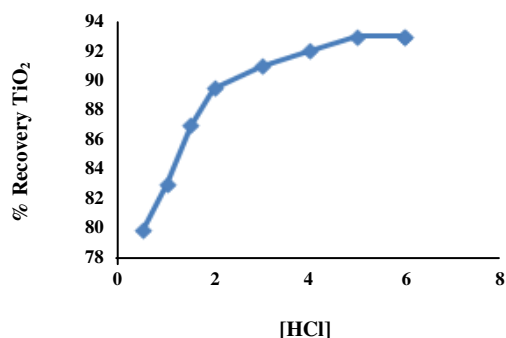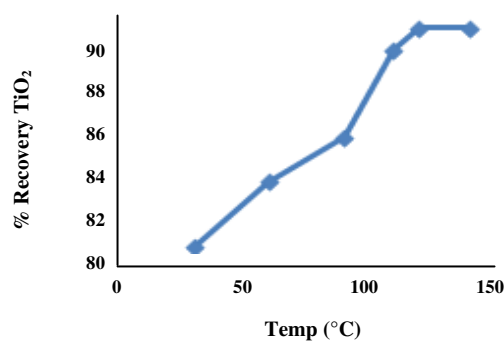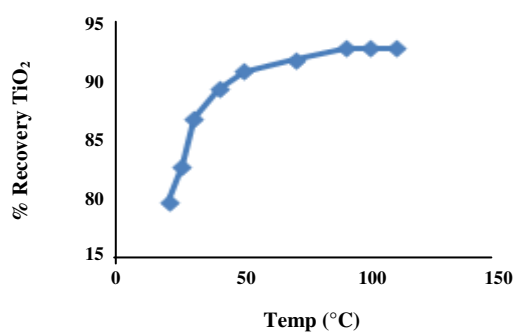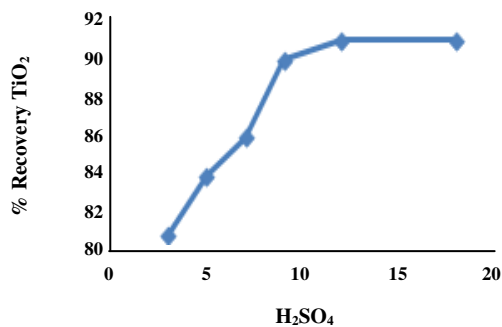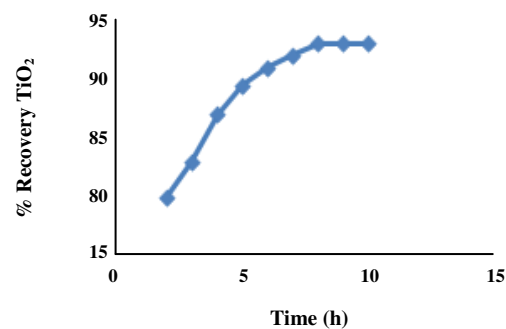
Fig. 6: Optimum conditions of HCl leaching.

Fig. 7: Optimum conditions of H2SO4 leaching.

For preparing TiO_2 by acid leaching, some parameters should be optimized. In Figs. 6 and 7 the optimum parameters were obtaind. Optimum HCl leaching dissolution conditions were Fig. 6: hydrochloric acid 6M, at 100 °C, ilmenite/acid ratio 1 g:100ml, and reaction time 8h. The optimum H_2SO_4 leaching dissolution conditions were Fig. 7: Pure sulfuric acid, reaction temperature 120 °C, ilmenite/ acid ratio 0.5 g:20ml, and reaction time 0.5 h.

CONCLUSIONS

The nano TiO_2 particles were synthesized by acid leaching. The process is composed of the ultra sounding

Of ilmenite, hydrochloric acid leaching atambient pressure, solid/liquid separation, calcination, grain agglomeration, and HCl recycle. The optimum HCl leaching dissolution conditions were Fig 6:

hydrochloric acid 6M, at 100 °C, ilmenite/ acid ratio 1g:100mL, and reaction time 8h. The synthetic rutile was prepared under the optimal conditions contains over 93% TiO_2. The ultra sounding treatment can take place instead of the traditional high temperature pretreatment of ilmenite and avoid the dissolution being conducted under pressurized condition.

The optimum H_2SO_4 leaching dissolution conditions were Fig 7.

Pure sulfuric acid, reaction temperature 120 °C, ilmenite/ acid ratio 0.5 g:20mL, and reaction time 0.5 h. The synthetic rutile prepared under the optimal conditions contains over 91% TiO_2.

According to ultra sounding and leaching process, HCl leaching produced the nanosized TiO_2 less than the H_2SO_4 leaching. All of determinations particle size techniques show this matter. The particle size of nano TiO_2 was leached by HCl and H_2SO_4 are 83 and 85 nm respectively.

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