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# TİTANYUM DİOKSİT SENTEZİ (TİO$_2$)

## SYNTHESIS OF TITANIUM DIOXIDE (TİO$_2$)

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**ÖZET**

Titanyum dioksit ($TiO_2$), çevre dostu, sentezi kolay, stabil ve ucuz bir katalizör olarak, çoğunlukla su arıtımı gibi çevresel iyileştirme amaçlı hafif aktiviteye sahip bir katalizör olarak kabul edilmektedir. Bu çalışmada, $TiO_2$, kristal yapıları belirlemek için X-Ray difraksiyon cihazı (XRD), enerji dağıtıcı X-ışını spektroskopisi (EDX) ile donatılmış taramalı elektron mikroskobu (SEM), parçacık boyutunu belirlemek için BET analizi, ve bağları belirlemek için FT-IR analizi kullanılarak sentezlenmiş ve karakterize edilmiştir. Sonuçlar, 2θ piklerde 25º, 38º, 48º'de $TiO_2$ nanopartiküllerinin varlığı tespit edilirken, 65º ve 70º piklerde TiO tespit edildiğini göstermektedir. EDX analizi sonuçlarına göre; Ti, O, Au ve C elementleri belirlenmiştir. FT-IR analizine göre, 450 $cm^{-1}$'de oluşan pik $TiO_2$ varlığını gösterir. BET analizine göre; $TiO_2$'nin yüzey alanı 65 $m^2/g$ olarak belirlendi ve bu ticari $TiO_2$'den (40 $m^2/g$) önemli ölçüde yüksektir. Sonuçlar, literatürde kullanılanlara göre azalan sıcaklıklarda $TiO_2$ elde etmenin mümkün olduğunu göstermektedir. Ek olarak, oda sıcaklığında sentezlenen $TiO_2$ karakterizasyonu, yüksek sıcaklıklarda (>400Cº) gerçekleştirilen önceki çalışma sonuçlarından elde edilen sonuçlarla karşılaştırıldığında benzerdir.

**Anahtar Kelimeler:** Titanyum Dioksit, Nanopartiküller, Titanyum Dioksit Sentezi

**ABSTRACT**

Titanium dioxide ($TiO_2$) is regarded as an environmentally friendly, easy-to-synthesis, stable and inexpensive catalyst, often as a mildly active catalyst for environmental improvement purposes such as water treatment. In this study, $TiO_2$ was synthesized and characterized using an X-Ray diffraction instrument (XRD) to determine the crystal structures, scanning electron microscopy (SEM), equipped with energy-dispersive X-ray spectroscopy (EDX), BET analysis to determine particles size, and FT-IR analysis to determine bonds $TiO_2$. Results show that while the presence of $TiO_2$ nanoparticles at 25º, 38º, 48º at 2θ peaks was detected, TiO was detected at 65º and 70º peaks. According to the results of EDX analysis; Ti, O, Au, and C elements are detected. According to FT-IR analysis, the peak formed at 450 $cm^{-1}$ shows the presence of $TiO_2$. According to BET analysis; the surface region of $TiO_2$ was identified as 65 $m^2/g$ which was significantly higher than that of commercial $TiO_2$ (40 $m^2/g$). The results show that it is acceptable to achieve $TiO_2$ at decrease temperatures according to those used in the literature. Additionally, the characterization of synthesized $TiO_2$ at room temperature is similar compared to the results obtained from previous study results that have been conducted under high temperatures (>400ºC).

**Keywords:** Titanium Dioxide, Nanoparticles, Titanium Dioxide Synthesis

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## 1. INTRODUCTION

Titanium dioxide nanoparticles are among the most used nanomaterials due to their high stability, anti-corrosion properties, surface activities, and photocatalytic properties. These properties appear as stable for the extensive use of $TiO_2$ substances in diverse areas including light activity, hydrogen production, and such as wastewater treatment. (Burke, A., et al., 2008; Nakata, K., et al., 2013; G.L. Chiarello, et al., 2017; W. Zhou, et al., 2014; Z. Xing, et al., 2018). In recent years, optical and electronic characteristics of nanomaterials, which become severely size dependant have attracted attention to the preparation of nanoparticle semi-conductors (M. Tomkiiewicz, 2000). Titanium nanoparticles with very thin dimensions are encouraging in many practices such as wastewater treatment, adsorbents, and catalytic fields (G. Ramakrishna, 2003; M.M. Rahman, et al., 1999; E. Pelizzetti, et al., 1993). In almost all of these conditions, when the particle size is reduced greatly, due to the large surface area, some recent optical properties can be expected (S. Sahni, et al., 2007). The synthesis of titanium dioxide nanoparticles consists of four different methods; these, sol-gel process (Q. Zhang, L. Gao, 2003), hydrothermal methods (P.D. Cozzoli, et al., 2003), solvothermal methods (C.S. Kim, et al., 2003), and emulsion precipitation (G. Ramakrishna, H.N. Ghosh, et al., 2003). Many of them were succeeded by synthesizing high purity of (>99%) $TiO_2$. However, it is important to be easily reproducible at the industrial level by avoiding dangerous reagents (Zadeh, E.K, et al.,2017; Mezni, A., et al., 2017; Ojeda, M., et al., 2017; Lusvardi, G., et al., 2017). By using this approach, the purpose of this study was the synthesis and characterization of $TiO_2$ nanoparticles by avoiding harmful chemicals.

In this study, $TiO_2$ was synthesized in a procedure containing 50 mL titanium isopropoxide ($C_{12}H_{28}O_4Ti$), ≥99.8, 200 mL $H_2O$, and 1gr $CO(NH_2)_2$. The materials characterization was performed using an X-Ray diffraction instrument (XRD) to determine the crystal structures of $TiO_2$ particle, SEM, EDX, and BET analysis to determine particle size and crystal properties, FT-IR analysis to determine chemical bonds $TiO_2$.

## 2. MATERIAL AND METHODS

### *2.1. Preparations of Titanium Dioxide (TİO$_2$)*

The procedure reported in the literature have been tested and (Lusvardi, G., et al., 2017). $TiO_2$ synthesis was carried out with the best, simplest, and cheapest procedure. The used reagents are titanium isopropoxide ($C_{12}H_{28}O_4Ti$), ≥99.8, and urea ($CO(NH_2)_2$) (Lusvardi, G., et al., 2017). The reagents used for $TiO_2$ synthesizes are given in Table 1.

**Table 1. Reagents for $TiO_2$ Synthesis**

| Compounds | Amounts |
|---|---|
| $C_{12}H_{28}Ti$ | 50mL |
| $H_2O$ | 200mL |
| $CO(NH_2)_2$ | 1gr |

Distilled water ($H_2O$) and $CO(NH_2)_2$ were placed in a beaker and mixed for five minutes with the aid of a magnetic stirrer. Then, $C_{12}H_{28}Ti$ was added drop by drop to this solution, and stirring continued for thirty minutes. This solution was kept in a water bath at 90 C$^o$ for one hour. Finally, the product was separated by drying at 80 C$^o$ for 12 hours. (Lusvardi, G., et al., 2017).

### *2.2. Analyses of Nanoparticles*

#### *2.2.1. X-Ray diffraction (XRD)*

The diffraction patterns of synthesized $TiO_2$ nanoparticle substances were achieved with a high-resolution electron microscope (HRTEM, Tecnai G2, F30). X-ray diffraction (XRD) diffraction was made using a Miniflex II model (Malik S., et al. 2018).

### *2.2.2. Scanning electron microscopy-energy distribution spectrophotometer (SEM-EDX)*

The samples were coated with the gold plated mixture and given to the SEM (Carl Zeiss, EVO 50 model, Germany) and EDX (Bruker AXS Microanalysis GmbH, Germany) devices. Inorganic chemical composition was also determined using an EDX (EDX, analyzer to determine the inorganic composition.

### *2.2.3. Fourier transform infrared spectrophotometer-attenuated total reflection (FTIR-ATR) analysis*

Characterization of important functional groups of metabolites was measured using the FTIR-ATR device (Perkin Elmer Spectrum 400, Germany) located in the KSU ÜSKİM laboratory. The collected nanoparticle substances were dried at 50°C for 24 hours before FT-IR measurements. Characterization of functional groups were determined according to the procedures given by Şahinkaya et al. (2018) and Hu et al. (2013).

### *2.2.4. BET analysis*

The surface area and nanoparticle size of the synthesized titanium nanoparticles were analyzed by the BET surface area. The BET surface area was determined by $N_2$ gas using a Tristar 3000. Samples were dried under $N_2$ gas at 110 C$^o$ 15 hours before BET analysis (Martinson, C. A., et al. 2009).

## 3. RESULTS AND DISCUSSION

### *3.1. Characterization of Synthesized $TiO_2$ Particles*

$TiO_2$ is a strong, relatively cheap, easy to prepare, and non-toxic material (Mulmi et al., 2004). It consists of three different crystal structures, anatase, rutile, and brokite (Sekiya et al., 2004). The XRD plot of the prepared $TiO_2$ nanoparticle shows the presence of very large peaks. Large peaks either show particles with very small crystal size or show that the particles are semi-crystal in nature (C.L. Yeha, et al., 2004). XRD analysis of the synthesized $TiO_2$ nanoparticles was done in the range of 2θ 20-800. The XRD analysis of $TiO_2$ nanoparticles is shown in Figure 1. According to the XRD results of the synthesized titanium dioxide nanoparticles, the presence of peak points indicates that there is a crystal structure. Although the presence of the peaks symbolizing $TiO_2$ was detected, significant peaks could not be obtained. In addition, the dominant peaks observed at 45$^o$ and 65$^o$ indicate the presence of titanium oxide. While the presence of $TiO_2$ nanoparticle peaks was detected at 25$^o$, 38$^o$, 48$^o$ at 2θ, TiO nanoparticle substance was detected at 65$^o$ and 70$^o$ peaks (Figure 1). The obtained results are similar to the literature (Vijayalakshmi, R., et al. 2012, Abdulmajeed, B.A., et al. 2019). It is observed titanium dioxide nanoparticle substance has been successfully synthesized.

Figure 2 shows the SEM images of the synthesized $TiO_2$. The EDX analysis of $TiO_2$ is shown in Figure 3A. SEM and EDX were used to qualitatively determine the morphology, size, and composition of the synthesized titanium dioxide. At the selected area EDX spectrum shows a strong signal in the titanium area and confirms the formation of $TiO_2$. In this case, the nanoparticle substances are obtained to adhere to each other. Similar to our results, Srikanth et al. (2018) found that pure crystalline particles were in the form of spherical and rod-shaped clusters and pellets. At the same time, to obtain chemical compounds and surface atom distributions of the synthesized $TiO_2$, EDX spectra were performed in the selected areas on the surface of the nanoparticle substance. EDX elemental analysis was performed to identify the chemical components of nanoparticle substances. The presence and formation of titanium dioxide nanoparticle material were determined in the EDX spectrum region in the selected area. According to the results of EDX analysis; Ti, O, Au, and C elements are detected as shown in Figure 3B.

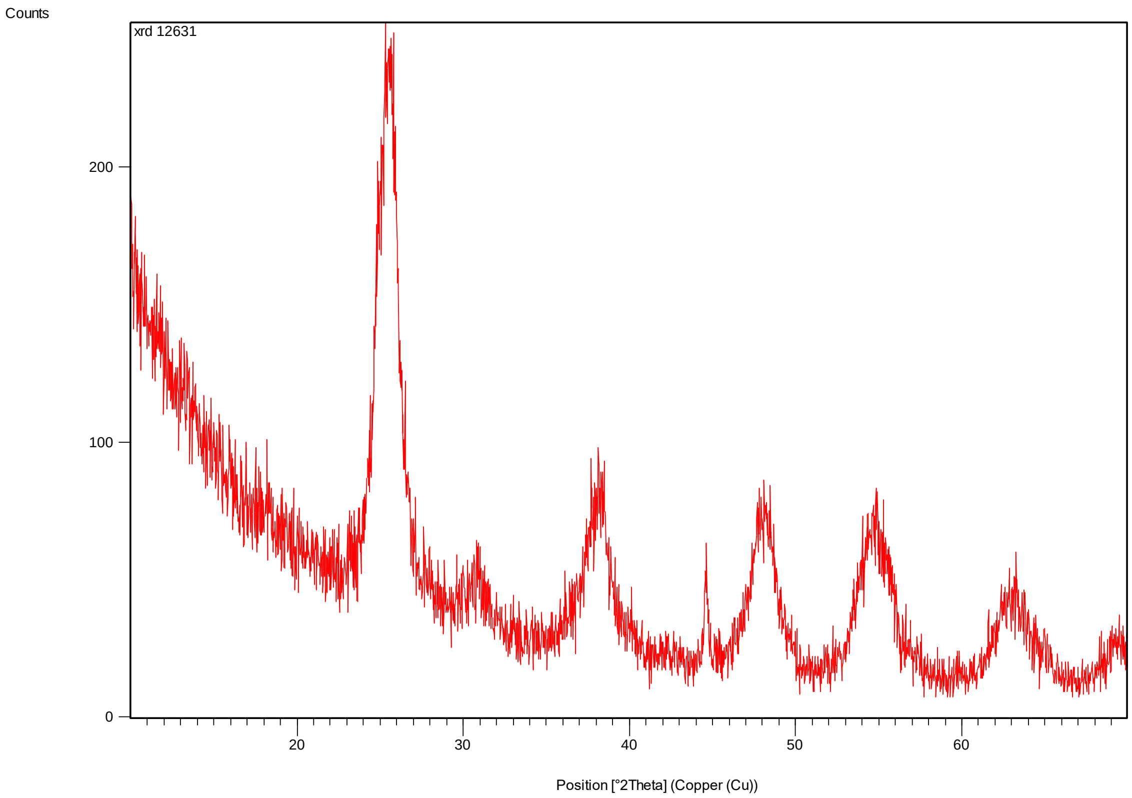
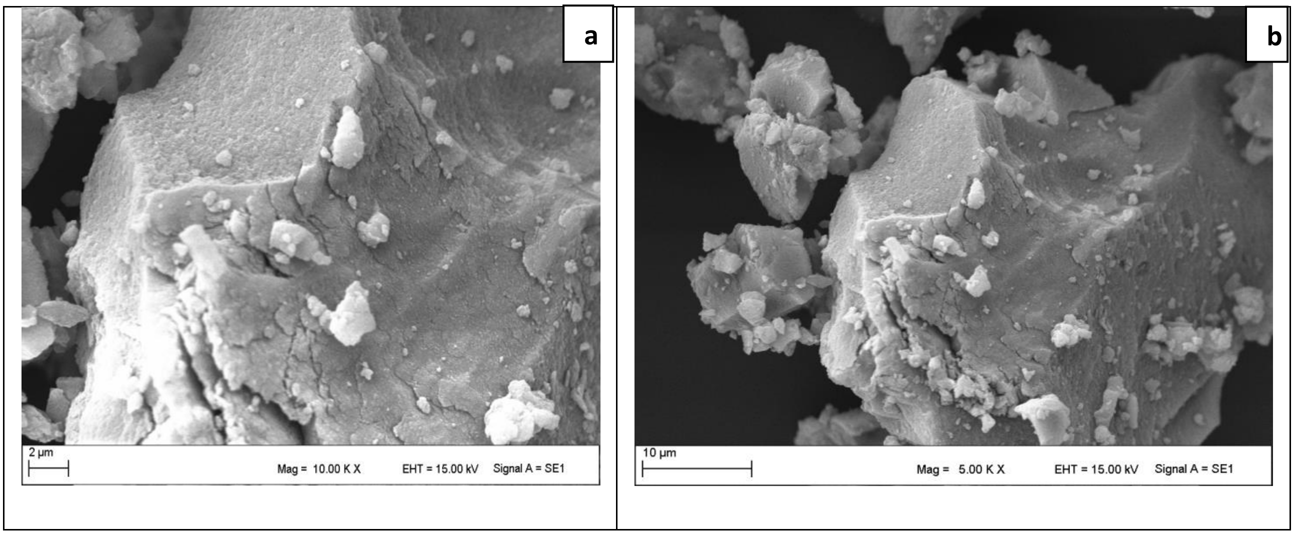



**Figure 1.** X-ray diffraction (XRD) of Titanium Dioxide ($TiO_2$) particles



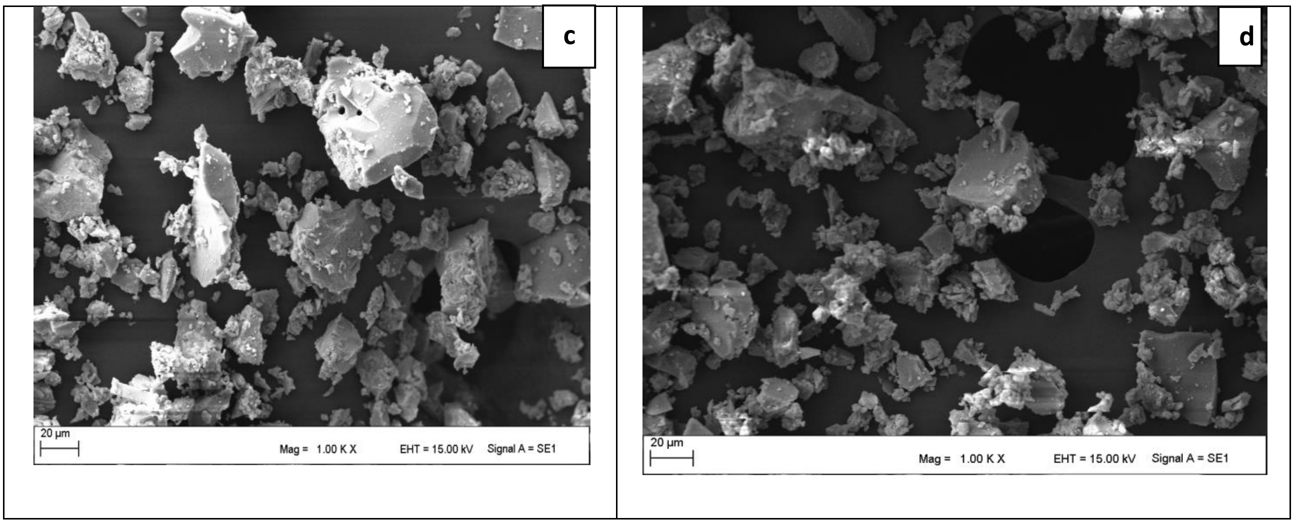
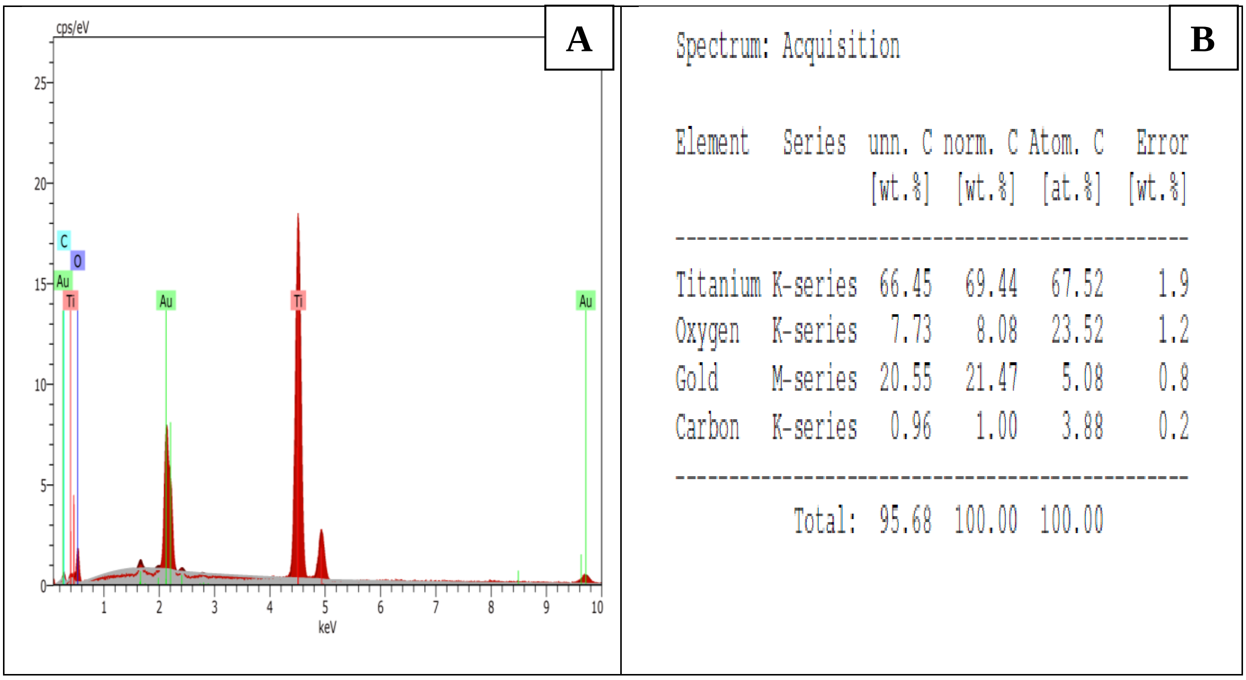



**Figure 2.** SEM images of different sizes of Titanium Dioxide ($TiO_2$) particles a) 10kx, b) 5kx, c) 1kx, d) 1kx




| Element | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [wt.%] |
|---|---|---|---|---|---|
| Titanium | K-series | 66.45 | 69.44 | 67.52 | 1.9 |
| Oxygen | K-series | 7.73 | 8.08 | 23.52 | 1.2 |
| Gold | M-series | 20.55 | 21.47 | 5.08 | 0.8 |
| Carbon | K-series | 0.96 | 1.00 | 3.88 | 0.2 |
| | Total: | 95.68 | 100.00 | 100.00 | |

**Figure 3. A:** EDX results of Titanium Dioxide ($TiO_2$) particles; **B:** EDX-Element content results of Titanium Dioxide ($TiO_2$) particles

Due to its nanoparticle structure, Ti and O are relatively higher than other elements. According to EDX results, the titanium content of the synthesized nanoparticle substance was relatively high (Figure 3B).

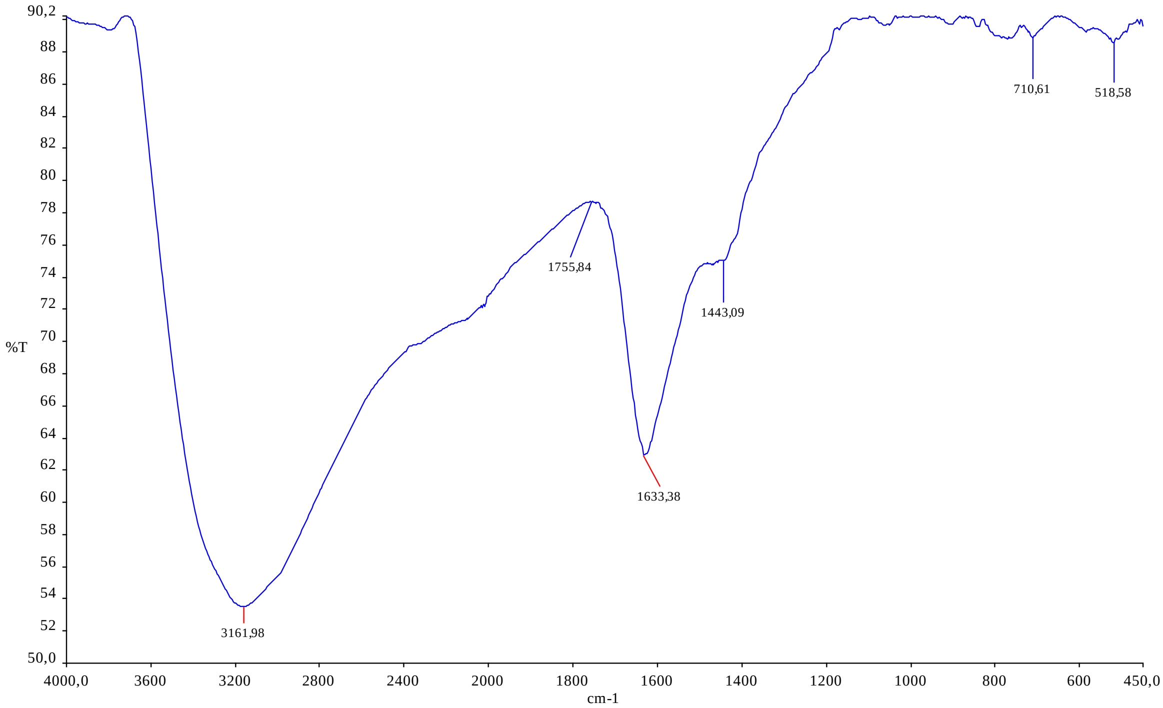



**Figure 4.** Titanium dioxide ($TiO_2$) FT-IR spectrum

FT-IR spectrum analysis was achieved to determine the characterization and chemical structure of the synthesized nanoparticle substances. The FT-IR spectrum of titanium dioxide is shown in Figure 4. The peak points obtained in the synthesized nanoparticle materials have been shown to be at 3200, 1800, 1600, 1400, 650, and 450 $cm^{-1}$. The band at 3421 $cm^{-1}$ corresponds to the weak stretching vibration of the surface hydroxyl groups. The peaks at 1415 and 1359 $cm^{-1}$ indicate the -COO- groups (Gao et al., 2016; Madhavi et al., 2013). Similar results were obtained in this study. Jose A.A et al. (1999) reported that the strong peak in the range of 880 and 450 $cm^{-1}$ confirmed the presence of $TiO_2$ nanoparticle material. They reported that the peak observed at 3391 $cm^{-1}$ revealed the presence of hydroxyl, possibly due to the lack of recording of the spectra in place and some reabsorption of water from the ambient atmosphere. In the same study, they reported that the peak water of 1638 $cm^{-1}$ was associated with hydroxyl groups of water. The peak formed at 450 $cm^{-1}$ indicates the presence of titanium dioxide.

The surface area of nanoparticle substances was identified by the classical BET method. BET analysis was performed to determine the pore sizes and surface area of nanoparticle materials obtained as a result of synthesis. According to the results obtained; The surface area of titanium dioxide nanoparticle material was determined as 65 $m^2/g$. Similar to study results performed by Hussain et al. (2010) surface area of $TiO_2$ nanoparticle material was 60-66 $m^2/g$. The results of this study support the findings obtained from other literature studies.

## 4. CONCLUSION

Synthesized $TiO_2$ characterization was carried out using XRD, SEM, and EDX, FT-IR, BET techniques. Results show that the presence of $TiO_2$ nanoparticles was detected at 25$^o$, 38$^o$, 48$^o$ at 2θ peaks, while TiO nanoparticle substance was detected at 65$^o$ and 70$^o$ peaks. According to the results of EDX analysis; Ti, O, Au, and C elements are mainly detected. According to FT-IR analysis, the peak formed at 450 $cm^{-1}$ shows the presence of titanium dioxide. According to BET analysis; the surface area of titanium dioxide nanoparticle substance was determined as 65 $m^2/g$ which was significantly higher than that of commercial $TiO_2$ (40 $m^2/g$, a non-porous material). The use, research, and development of titanium dioxide nanoparticle material in environmental applications will contribute to the literature.

## 5. ACKNOWLEDGE

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