

Synthesis, Characterization and Using of Nanosize Anatase Phase TiO₂ for Water Treatment

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Abstract— Nanosize anatase phase TiO₂ was prepared by the precipitation method through calcination of the resulting precipitate at 3 temperatures 450, 650 and 750 °C. The resulting TiO₂ samples characterized and used for the inactivation of fecal coliform bacteria and the removal of formic acid from water. UV-visible spectroscopy, XRD, EDX, TEM and FTIR analyses are used for the characterization of TiO₂ samples. Anatase phase was produced at all calcination temperatures. The band gap was calculated to be 3.3 eV for TiO₂ calcined 450°C and the average particle size was calculated to be 6 and 22 nm for TiO₂ calcined at 450°C and 750 °C, respectively. The prepared TiO₂ showed high efficiency for the inactivation of fecal coliform bacteria and the removal of formic acid from water.

Index Terms— Nanosize TiO₂, water treatment, fecal coliform bacteria, formic acid.

1 INTRODUCTION

Nanosized TiO₂ attracts attention of many researchers due to its distinct electronic and optical properties originating from the quantum confinement (1, 2). This leads to excellent features as a semiconductor and as a photocatalyst (3, 4) and hence qualifies it to a wide range of applications (5-7). Controlling of crystallite structure during preparation takes a lot of attention. Anatase phase TiO₂ is thermodynamically metastable and can be easily transformed into the stable rutile phase when heated to 500-600 °C resulting in the growing of crystals, decreasing of band gap, decreasing of photocatalytic activity (8) and shifting the absorption edge to longer wave lengths (red shift) (9). Band gap increase, as a result of decreasing crystallite size, may favor redox processes because this phenomenon slows the recombination of the generated holes and electrons (8, 10). It is practically important to explore methods to prepare thermally stable anatase TiO₂ avoiding phase transformation by thermal treatment. Phase transformation may be governed by some factors as the particle size and shape and many methods were reported to avoid phase transformation as a result of the thermal treatment by doping TiO₂ with cationic and/or anionic dopants (11, 12). However, the presence of significant amounts of doping impurities in TiO₂ may result in some changes in its properties and affecting its final applications. In this study, thermally

stable nanosized anatase TiO₂ was prepared and used for treatment of water containing formic acid or coliform bacteria.

2 EXPERIMENTAL

TiO₂ nano particles were prepared by the following procedures: 2 ml of H₂O₂ solution (a solution containing 30% wt/v) was added to 400 ml distilled water in a 500 ml Pyrex glass beaker. 5 ml of TiCl₄ was added to this solution to form a yellow color (HOO-Ti(OH)₃) and then the solution was stirred. Mercaptoethanol was added to about 300 ml of the clear solution till the disappearance of the yellow color. Ammonium hydroxide was added to this solution dropwisely for complete precipitation. The precipitate was collected by centrifugation and then was dried in an oven at 80 °C for 6 hrs. The dried precipitate was powdered in an agate mill and then was calcined at three different temperatures (450, 650 and 750 °C) in a muffle furnace, in air, for two hours.

Characterization

X-ray diffraction patterns were recorded at room temperature using a powder diffractometer (Bruker axs D8 Advance, Germany with Cu-K α radiation source $\lambda=1.5406\text{\AA}$ and 2θ in rang (10-80°). The average crystallite size of the particles was determined using the Scherrer equation. EDX analysis was carried out with JSX-3222 element analyzer (include EDS detector with 149 eV) manufactured by JEOL LTD., Japan. Particle size determination was carried out with a transmission electron microscope (TEM), Jeol Jem-1230. The Fourier Transform Infrared (FT-IR) was recorded on a Jasco FT-IR-460 plus, Japan.

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Ultraviolet-Visible spectra were performed with a JASCO Corp., V-570 UV-Vis spectrophotometer.

Investigation of the photocatalytic efficiency of the prepared TiO₂ catalyst

i- Formic acid removal

The efficiency of the prepared catalysts was investigated through the removal of formic acid as a model organic pollutant from water. 0.4 mg of TiO₂ was suspended in 400 ml of formic acid solution (~ 5 X 10⁻³ M) in a 500 ml Pyrex glass beaker. The previous solution was held under a UV lamp (VILBER-LOURMAT, λ= 360 nm) at a fixed position inside the UV chamber and the solution was stirred using a magnetic stirrer at a constant speed.

Samples were taken after 5 hrs and were analysed by Total Organic Carbon analyzer (TOC) (Phoenix 8000 Laboratory analyzer using sodium persulfate in combination with UV light to oxidize organic material) and then formic acid removal percentage (degradation rate) was calculated from the following equation:

Formic acid removal percentage

$$= \frac{\text{Initial TOC} - \text{Final TOC}}{\text{Initial TOC}} \times 100$$

ii- Bacteriological inactivation

Fresh water samples were taken from the Nile River at the inlet of Salhia conventional plant (which serves Qena city citizens). All samples (1000 ml) were treated simultaneously. Bacterial count of the samples was performed before treatment and after 30 and 60 minutes of treatment as follows:

Effect of UV alone on the inactivation of bacteria: one of the Nile water samples was taken in a 1000 ml Pyrex glass beaker. The solution was held under the UV lamp at the same position inside the UV chamber and the solution was stirred using a magnetic stirrer (400 rpm).

Effect of TiO₂ /UV on the inactivation of bacteria: 0.25 mg of TiO₂ was suspended in 1000 ml of the Nile water sample in a similar beaker. The solution was held under the UV lamp inside the UV chamber and was stirred with the same stirring speed.

Effect of TiO₂ alone (adsorption effect) on the inactivation of bacteria: 0.25 mg of TiO₂ was suspended in 1000 ml of the Nile water in a similar beaker and was held in dark under the same conditions.

Bacterial count

Membrane filter method was used to count bacteria according to the APHA Standard Methods (13) using acetate cellulose type filter with 0.45 mm pore size. Fecal coliform count was carried out using M-Fc agar media (Merk). Fecal coliform plats were incubated at 44.5±0.2 °C for 24 hrs. For

each one set of tests, a fraction of the test water sample was held at room temperature and the coliform bacteria were counted at the beginning and at the end of the experiment as a control test. This control test confirmed that at room temperature, there is no significant change in bacterial count occurs. The results are expressed in colony-forming units (CFU) per 100 ml.

The bacteria removal percentage (disinfection or inactivation percentage) was calculated from the following equation:
The bacteria removal percentage

$$= \frac{\text{Initial bact. Count} - \text{Final bact. count}}{\text{Initial bact. count}} \times 100$$

3 RESULTS AND DISCUSSION

Characterization of the prepared TiO₂

(XRD) analysis

The XRD patterns of dried precipitate before calcinations showed amorphous product. The XRD patterns of the samples calcined at different temperatures are shown in figure 1. It is clear that all samples are composed of anatase phase only. This result indicates the high thermal stability of the anatase phase prepared by this method.

It is worth mentioning that calcination of the dried precipitate, resulting from the basic hydrolysis of TiCl₄ in the presence of ammonium hydroxide at 750°C or calcination of the yellow precipitate (resulting from aging the Ti⁴⁺-H₂O₂) at 650°C (4) result in the formation of a mixture of anatase and rutile.

The crystal size of TiO₂ calcined at 450, 650 and 750°C was calculated from XRD results using Scherrer equation to be 6, 13 and 22 nm, respectively. This indicates that the crystal size increases with increasing calcination temperatures.

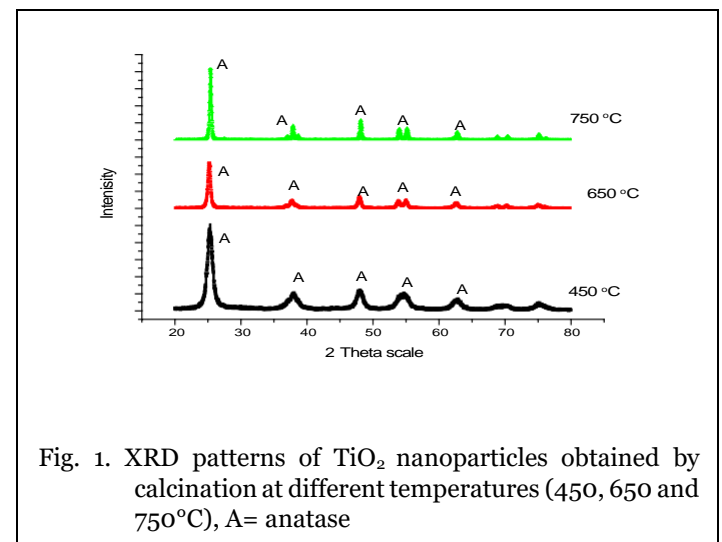


Fig. 1. XRD patterns of TiO₂ nanoparticles obtained by calcination at different temperatures (450, 650 and 750°C), A= anatase

EDX analysis

EDX analysis was carried out for the dried powder used for TiO₂ before calcination and TiO₂ samples calcined at 450 and 650 °C. Sulfur was detected in the dried powder and, also, in TiO₂ (450) sample, figure 2. However, it was not detected in the sample calcined at 650°C, figure 3.

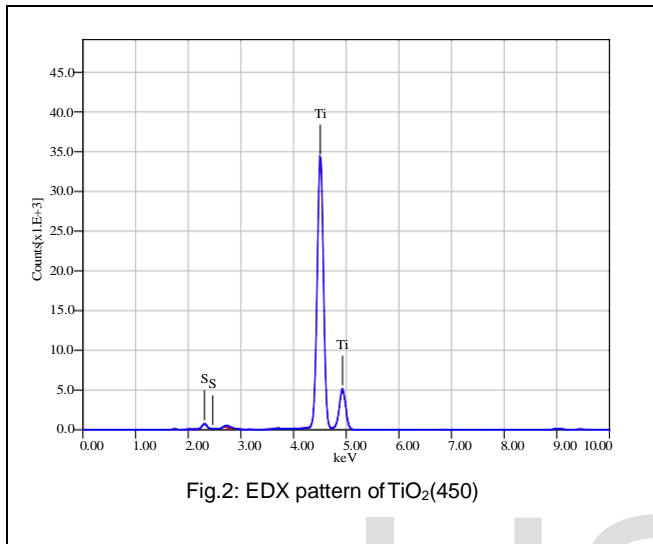


Fig.2: EDX pattern of TiO₂(450)

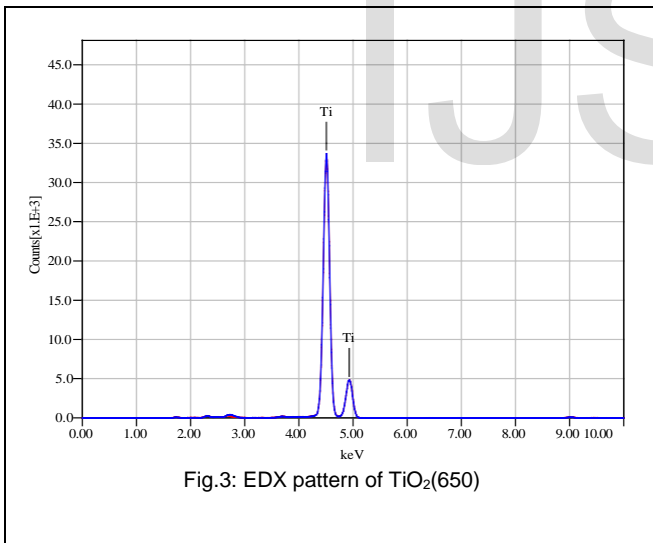


Fig.3: EDX pattern of TiO₂(650)

Transmission electron microscopy

TEM was used to further examine the particle size and morphology of the sample calcined at 450 °C. Figure 4 shows the TEM images of that sample. This figure indicates nearly spherical and uniform shape of particles with a very narrow distribution range and it also confirms the nano size of the prepared catalyst.

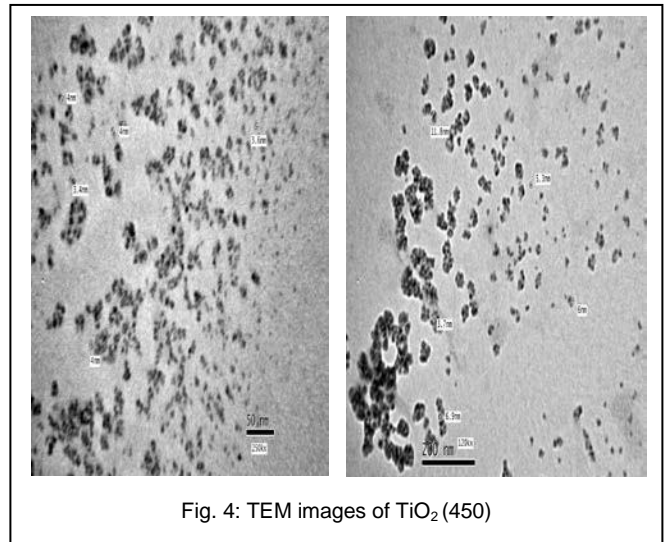


Fig. 4: TEM images of TiO₂ (450)

Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectrum of the TiO₂ (450) sample exhibited

characteristic band at 3430 cm⁻¹ corresponding to structural OH. The spectrum also exhibits a band at 1629 cm⁻¹ corresponding to the bending vibration of H₂ O while presence of H₂ O₂ was confirmed by its bending vibration at 1462 cm⁻¹ as shown in figure 5. The FT-IR spectrum of TiO₂ sample also exhibits characteristic band at 534 cm⁻¹ corresponding to Ti-O stretching band (14, 15).

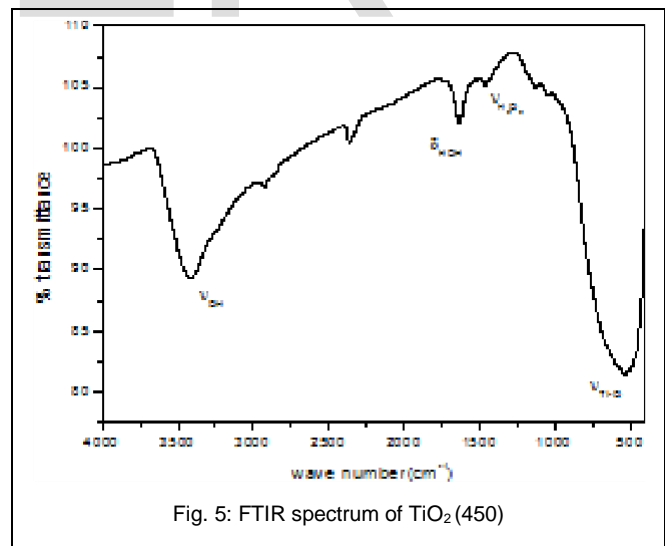


Fig. 5: FTIR spectrum of TiO₂ (450)

The UV-visible absorption

The band gap value determines the optimum wavelength of photocatalytic reaction. The UV-visible absorption spectrum of TiO₂ (450) sample is shown in figure 6. The onset wavelength (λ) of absorption was determined by extrapolation of the base line and the absorption edge to calculate the optical

band gap (16). The band gap was calculated by the following equation: $E_g \text{ (eV)} = 1239.8/\lambda$.

TiO₂ (450) sample has a band gap of 3.24 eV corresponding to an onset wavelength of 382.7 nm. The calculated band gap energy is consistent with data reported in the literature (17, 18).

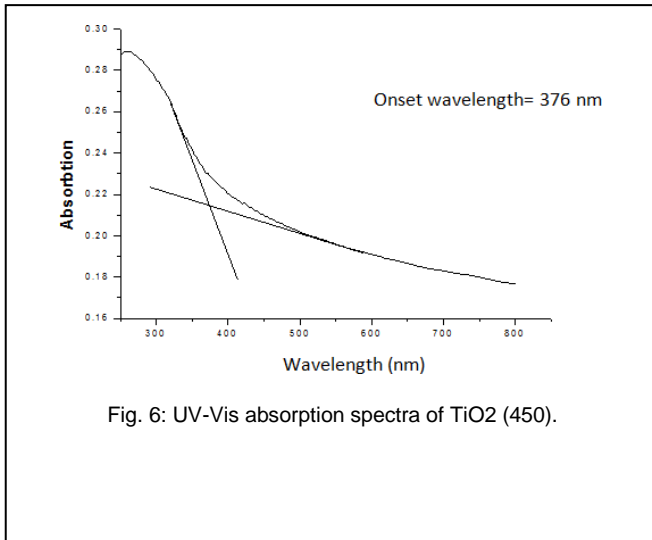


Fig. 6: UV-Vis absorption spectra of TiO₂ (450).

Table 1 lists the values of the onset wave length of absorption and the corresponding band gap values for different samples. It is observed that there is a red shift in the onset wave length of absorption from 376 nm for the TiO₂ (450) to 393 for the TiO₂ (750)

TABLE 1

THE PARTICLE SIZES, THE ONSET WAVELENGTHS AND BAND GAPS OF TiO₂ SAMPLES AT DIFFERENT CALCINATION TEMPERATURES.

sample	Average crystallite size (nm)	Onset wavelength of absorption (nm)	Band gap (eV)
TiO ₂ (450)	6	376	3.3
TiO ₂ (650)	13	384	3.23
TiO ₂ (750)	22	393	3.15

sample. This red shift can be attributed to the increasing of particle size with increasing calcination temperature (19).

The photocatalytic efficiency of the prepared catalysts

Formic acid degradation

Figure 7 shows the removal of formic acid using TiO₂ /UV. It can be concluded that the photocatalytic efficiency increases

with increasing calcination temperatures. About 34.1, 50 and 58.8 % of the acid was removed after 5 hours of treatment using the samples calcined at 450, 650 and 750°C, respectively.

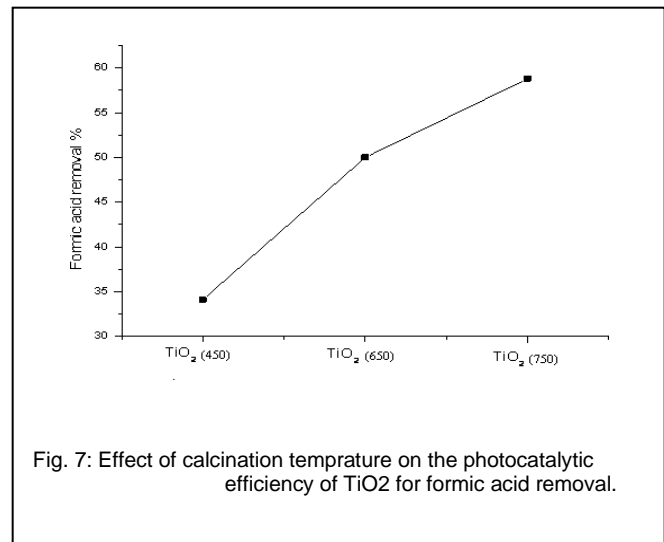


Fig. 7: Effect of calcination temperature on the photocatalytic efficiency of TiO₂ for formic acid removal.

It is known that the mechanism of photocatalysis involves the formation of a hole and electron pairs where the removal of formic acid can be achieved through the direct electron transfer to the positive hole. Also, under the experimental conditions, hydroxyl radicals can be formed under the UV irradiation in the presence of oxygen. The removal of formic acid may be achieved through the hydroxyl radical pathway (16, 20).

Disinfection of fecal coliform bacteria by TiO₂/UV light

Natural decay of fecal coliform bacteria after 60 min (control test) showed that there is no significant change in the fecal coliform bacteria observed under the applied experimental conditions. Figure 8 shows the efficiency of the TiO₂, calcined at different temperature, for the removal of fecal coliform bacteria by only adsorption. The sample calcined at 450°C exhibited the highest efficiency for the adsorption of bacteria where the removal percentage exceeds 73% by this sample. However, it is clear that bacterial count during treatment with the sample calcined at 450 °C increases from 23 CFU/100 ml (after 30 min.) to 48 CFU/100 (after 60 min.). This may be attributed desorption of bacteria and their survival under the adsorption conditions (21). This behaviour was not observed with other samples.

It is well known that UV alone can inactivate bacteria (21). The effect of UV only and TiO₂ /UV is given in Figure 9. It is clear from this figure that inactivation of fecal coliform by UV alone (photolysis) is significant. About 65 % of bacteria were inactivated after 30 minutes of treatment. However, the bacteria removal percentage is about the same after 60 min of treatment. The efficiency of TiO₂ (calcined at different temperatures) /UV for the disinfection of fecal coliform bacteria is presented in Figure 9. From this figure it is clear that the pho-

tocatalytic disinfection percentage slightly increases with increasing calcinations temperature.

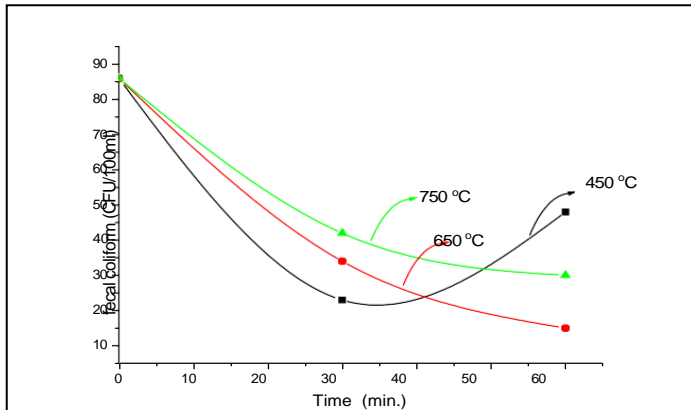


Fig. 8: The fecal coliform count after treatment of the Nile water samples by TiO₂ only calcined at different temperatures.

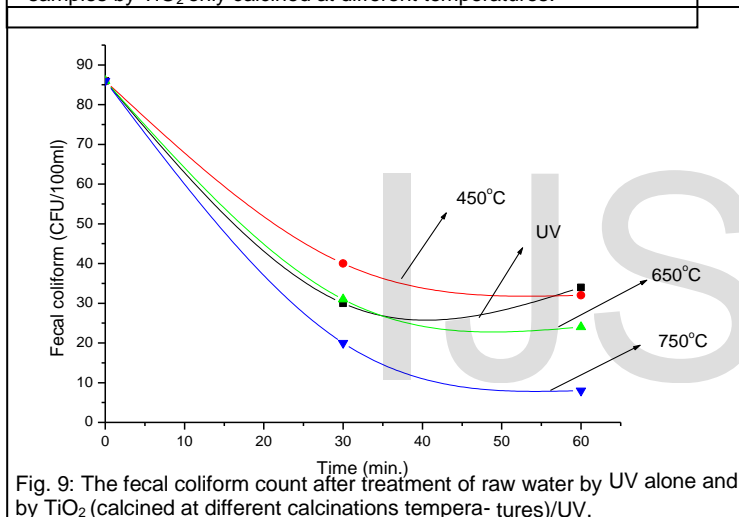


Fig. 9: The fecal coliform count after treatment of raw water by UV alone and by TiO₂ (calcined at different calcinations temperatures)/UV.

In the absence of UV radiation the inactivation of bacteria occurs by adsorption of bacteria on the surface of TiO₂ particles (21, 22). In the presence of UV (TiO₂ /UV) •OH can be formed under the experimental conditions. These •OH are highly active for both the oxidation of organic substances and the inactivation of bacteria and viruses through oxidation of the organic compound consisting the cell of bacteria, where the adsorption effect can enhance this reaction (21-23).

4 CONCLUSIONS

Nanosize anatase phase TiO₂ was prepared by the precipitation method through calcinations at different temperatures. Mercapto ethanol was added to (HOO-Ti(OH)₃), resulting from the addition of TiCl₄ to H₂O₂ in water, till the disappearance of the yellow colour. The pH of the resulting solution was raised using NH₄OH. The precipitate formed

was dried and then calcined at different temperatures (450, 650 and 750°C). Anatase phase TiO₂ was formed as the only product. The prepared TiO₂ oxide exhibited high efficiency for the inactivation of fecal coliform bacteria and the removal of formic acid from water.

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