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Preparation and Using of TiO_2 Nanoparticles for Treatment of Water Containing Formic Acid or Coliform Bacteria

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Abstract TiO_2 nanoparticles were prepared by the hydrolysis of titanium tetra chloride in water containing hydrogen peroxide. The yellow precipitate formed was dried, milled and then calcined at different temperatures. The produced TiO_2 nanoparticles were characterized by XRD, TEM, FTIR and UV-visible spectroscopy. TiO_2 prepared by calcination at 450°C contains pure anatase with an average particle size of 10.5 nm, calculated from XRD results using Sherrer equation. This sample showed high efficiency for formic acid removal from water as well as for the inactivation of the total coliform bacteria. TiO_2 samples calcined at 650°C and 750ºC contain a mixture of antase and rutile with an average particle size of 21.57 nm and 40.53 nm, respectively. The last two samples showed lower efficiency than the sample calcined at 450ºC for formic acid and bacteria removal from water.

Keywords TiO_2, Nanoparticles, Water Treatment

1. Introduction

Nanocrystalline materials have attracted a lot of attention due to their chemical, physical and optical properties which makes them suitable for applications in many fields[1–3]. Among the most important nanocrystalline materials is TiO_2, which exist as tetragonal (rutile, antase) and orthorhombic (brookite)[2-5]. TiO_2 can be synthesised by various methods as the sol-gel and the hydrothermal methods. There is a large number of researches concerning the synthesis, photocataly sis and applications of both anatase and rutile[3–6]. Rutile is used as a white pigment, a coating material for optical lenses and a dielectric material because of its high refractive index compared with other materials. Antase is used as a pure phase or mixed phase with rutile in many fields like air purification, water treatment and electrochemical applicatio ns[3-7].

An important purification branch is the photocatalytic degradation of organic compounds where a wide range of organic compounds can be oxidized to CO_2 and H_2O at room temperature on TiO_2 catalyst surface in the prescence of UV or near UV irradiation[8-11]. The energy of UV radiation should be sufficient to the electron transfer from the valence band to the conduction band[8-11]. This process of electron transfer creates an electron – hole pair which is responsible for the redox properties of TiO_2 photocatalyst surface. The energy separation between the conduction band and the valance band (band gap value) depend on many factors like the crystal size of the photocatalyst. By decreasing particle size the band gap of the semiconductor becomes larger and this is indicated by an absorption shift to shorter wavelengths (blue shift)[12-13].

Beside the well known photocatalytic properties of TiO_2 for the degradation of organic compounds, there are many studies concerning its potential application as a primary disinfection system of drinking water in terms of coliform bacteria inactivation[14-16].

In this work, TiO_2 nanoparticles were prepared by the calcinations of the yellow precipitate formed as a result of addition of $TiCl_4$ to water containing H_2O_2. The produced catalyst was characterized and used for the removal of formic acid and for the inactivation of bacteria as a pre -treatment step of natural surface water.

2. Experimental

2.1. Preparation of TiO_2

TiO_2 nanoparticles were prepared by the following procedures: 3 ml of H_2O_2 solution (a solution containing 30% wt/v) was added to 400 ml distilled water in a 500 ml Pyrex glass beaker. The solution was stirred using a magnetic stirrer with stirring velocity 100 rpm for five

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minutes. 5 ml of $TiCl_4$ was added to this solution at room temperature (25ºC) and then the solution was stirred again with the same previous stirring velocity for 15 minutes. The solution was left for two days for precipitation. The yellow precipitate was collected by decantation and the precipitate then was left for dryness in an oven for 6 hrs at 80℃ The dried precipitate was powdered in a mill and was calcined at different temperatures (450, 650 and 750℃) in a muffle furnace, in air, for two hours.

2.2. Characterization and Physical Measurements

X-ray diffraction spectra of the powders were recorded at room temperature using a powder diffractometer (Bruker axs D8 Advance, Germany with Cu Kα radiation source, λ=1.5406Å and 2Θ in the range (10-80°). The average crystallite size of the catalyst was determined using the Scherrer equation

$$D = 0.9\lambda / (\beta \cos \theta)$$

Where D is the average crystallite size (nm), λ is the X-ray wavelength used (λ = 1.54056 Å), θ is the angle of diffraction and ß is a full width at half the maximum of the diffraction line observed in radians.

Particle size determination was carried out with a transmission electron microscope (TEM), Jeol Jem-1230.

The Fourier transform infrared spectrum (FTIR) was recorded on a Jasco FT-IR-460 pluse Japan.

Ultraviolet-Visible spectra were performed with a JASCO Corp., V-570 UV-Vis spectrophotometer. Analysis was carried out between 200 and 800 nm.

2.3. Investigation of Photocatalytic Efficiency of the Prepared TiO_2

2.3.1. 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 TiO_2 was suspended in 400 ml of formic acid solution (5 X 10^{-4} M/L) in a 500 ml Pyrex glass beaker. The previous solution was held under a UV lamp (VILBER-LOURMAT, λ_{max} = 365 nm) at a fixed position inside the UV chamber and the solution was stirred for 7 hours using a magnetic stirrer at a constant speed. Samples were taken aftersuitable times and were analysed by Total Organic Carbon analyzer (TOC) (Phoenix 8000 Laboratory Analyzer using sodiumpersulfate in combination with UV light to oxidize organic material).

2.3.2. Photocatalytic Inactivation of Total Coliform Bacteria

Fresh water samples (each sample is 1L) were taken from the Nile River at the inlet of Salhia conventional plant (which serves Qena city citizens) and were treated simultaneously to test the inactivation percentage of total coliform. Bacterial count of the samples was performed before treatment and after 30 and 60 minutes of treatment. In this part, the possibility of bacteria inactivation due to using UV alone or as a result of adsorption on the catalyst surface was studied before the investigation of the effect of TiO_2 as a photocatalyt (TiO_2/UV) as follow.

Effect of UV alone on the inactivation of bacteria: one of the raw water samples in a 1000 ml Pyrex glass beaker was held under the UV lamp (λ_{max}=360 nm) at the same position inside the UV chamber and the solution was stirred using a magnetic stirrer (400 rpm).

The effect of TiO_2 alone (Adsorption effect) on the inactivation of bacteria: 0.25 mg of TiO_2 was suspended in the same volume of the raw water in a similar beaker and was kept in darkness with the same stirring speed.

To study the effect of TiO_2 as a photcatalyst on the inactivation of bacteria, the previous experiment was repeated but under UV irradiation.

Bacterial count

Membrane filter method was used to count bacteria according to the Standard Methods[17] using acetate cellulose type filter with 0.45mm pore size. Total coliform count was carried out using M-Endo agar media (Merk). The total coliform plates were incubated at 35±0.5℃ for 24 hrs. A fraction of the tested water sample was held at the same temperature and the total coliform bacteria were measured at the beginning and at the end of the experiment as a control sample. The results are expressed in colony-forming units (CFU) per 100 ml.

3. Results and Discussion

3.1. Characterizations

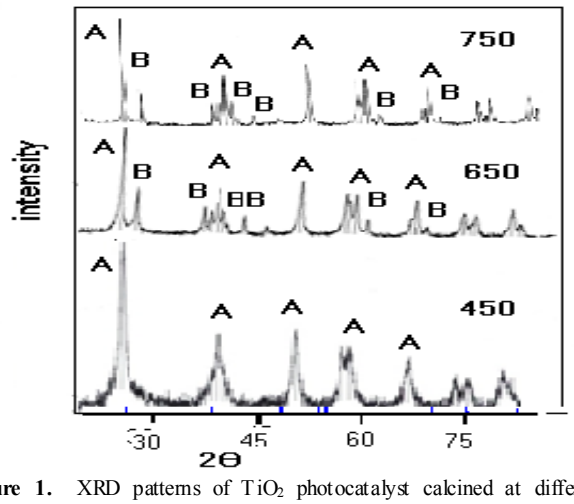


Figure 1. XRD patterns of TiO_2 photocatalyst calcined at different temperatures (450 ºC, 650 ºC, and 750 ºC). A: anatase, B: rutile

The XRD patterns of the catalysts calcined at different temperatures are shown in Fig. 1. This figure indicates that anatase was formed as the only phase at calcination temperature of 450℃. A mixture of anatase and rutile phases was formed at the higher calcination temperatures (650 and 750℃). The mean crystal size of TiO_2 calcined at 450, 650 and 750℃ was calculated from the XRD results using Sherrer equation to be 10.5, 21.57 and 40.53 nm, respectively.

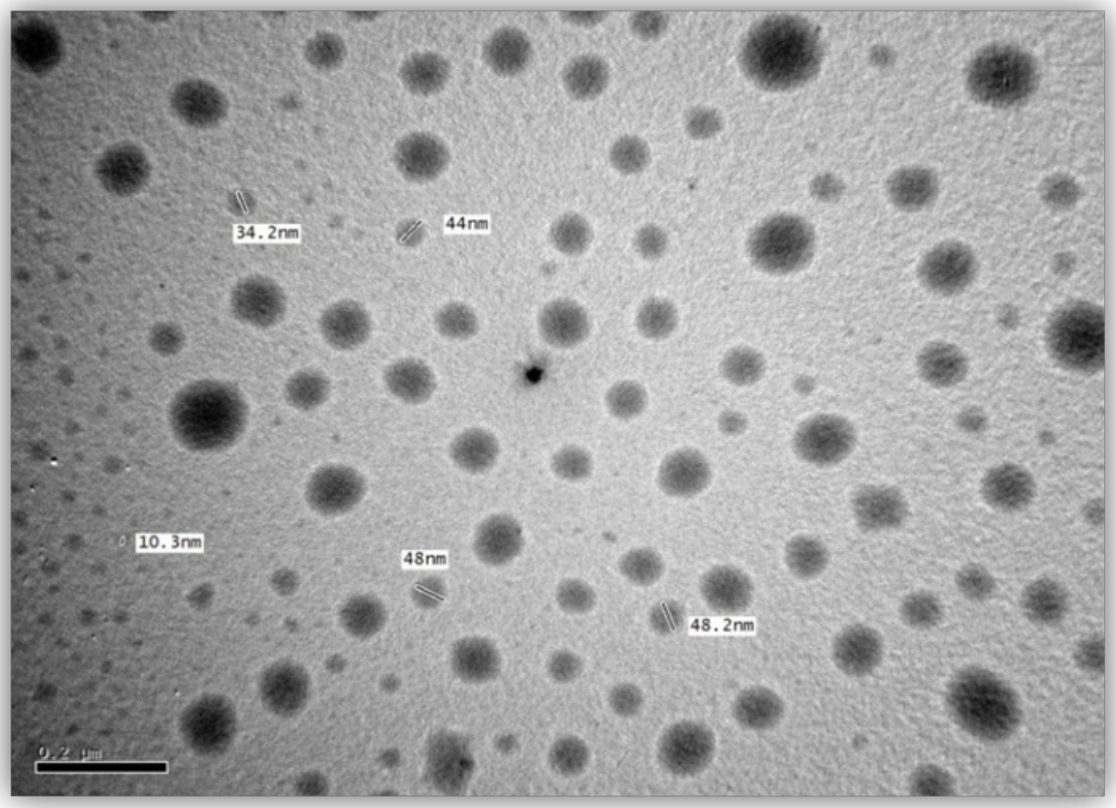


Figure 2. TEM image of TiO_2 calcined at 450℃

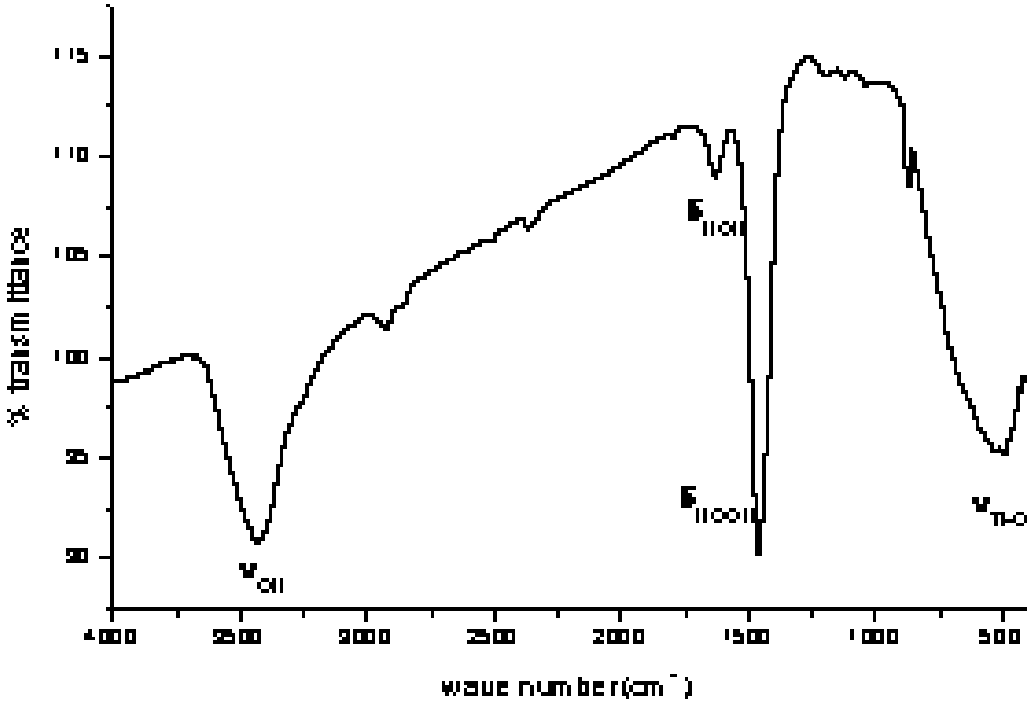


Figure 3. FTIR spectra for TiO_2 calcined at 450℃

The particle size and morphology of the sample calcined at 450℃ was further examined by its TEM image, Figure 2. This figure indicates spherical and uniform shape of the particles and it, also, confirms the nano size of the crystals of prepared catalyst in agreement with the Sherrer equation calculations.

The FT-IR spectrum of TiO_2, calcined at 450ºC, exhibits characteristic band at 3430.74 cm^{-1} corresponding to

structural OH^-. Presence of H_2O_2 on TiO_2 was confirmed by its bending vibration at 1454 cm^{-1} and presence of H_2O was confirmed by its bending vibration at 1629.55 cm^{-1} [18,19] as shown in figure 3. Also, the FT-IR spectrum of this sample exhibits a characteristic band at 517.11 cm^{-1} corresponding to Ti-O stretching band[18].

The UV-visible absorption spectrum of TiO_2 sample (calcined at 650), as an example, is shown in figure 4. The onset wavelength (λ) of absorption were determined by extrapolation of the base line and the absorption edge to calculate the optical band gap[13]. TiO_2 (650) sample has a band gap of 3.03 eV, which corresponds to an onset wave length of absorption of approximately 409.7 nm. This calculated band gap energy is consistent with data reported in the literature for titania materials[20, 21]. Table 1 includes the band gaps of samples calcined at different temp.

Table 1. summarize the particle size and band gap of samples at different calcinations temperatures

Calcinations temp (℃).	Average crystal size (nm)	Onset wave length of absorption(nm)	Band gap (e.v)
450	10.5	380	3.26
650	21.57	410	3.02
750	40.53	413	3

The onset wavelength of absorption of samples calcined at temperatures higher than 450℃ was red shifted to longer wave lengths and smaller band gap as shown in table 1. This can be attributed to increasing particle size with increasing calcination temperature which is confirmed by XRD analysis[22].

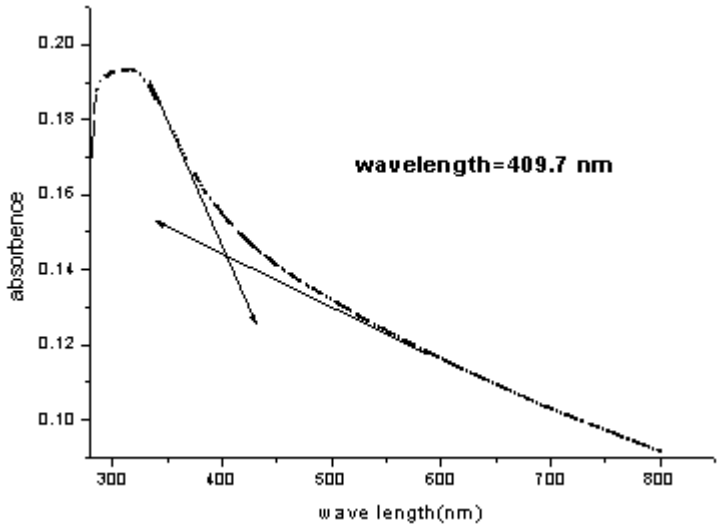


Figure 4. UV-V is absorption spectra of TiO_2 particles at 650°C

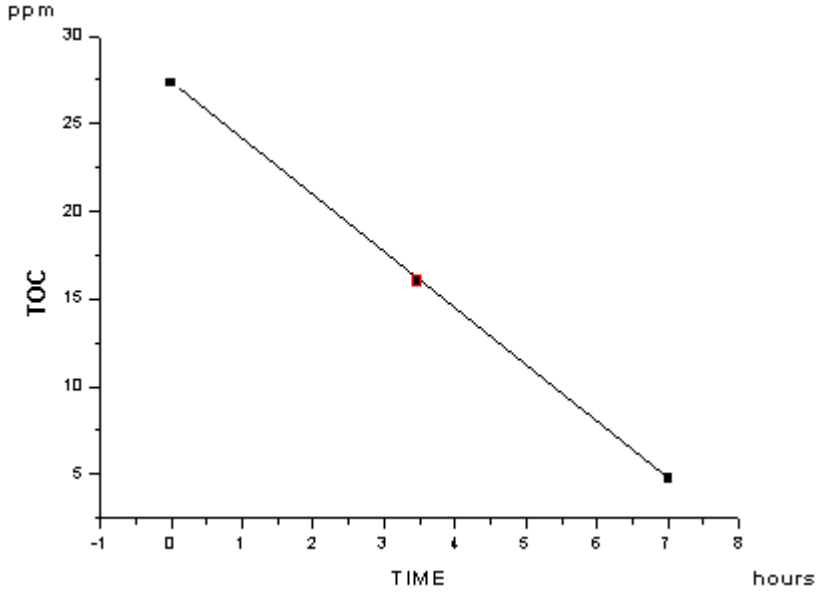


Figure 5. Removal of formic acid by TiO_2/UV (λ_{max} = 365 nm), TiO_2 wt. = 500 mg, formic acid conc. = $5x10^{-4}$ mol/l and formic acid volume = 500ml

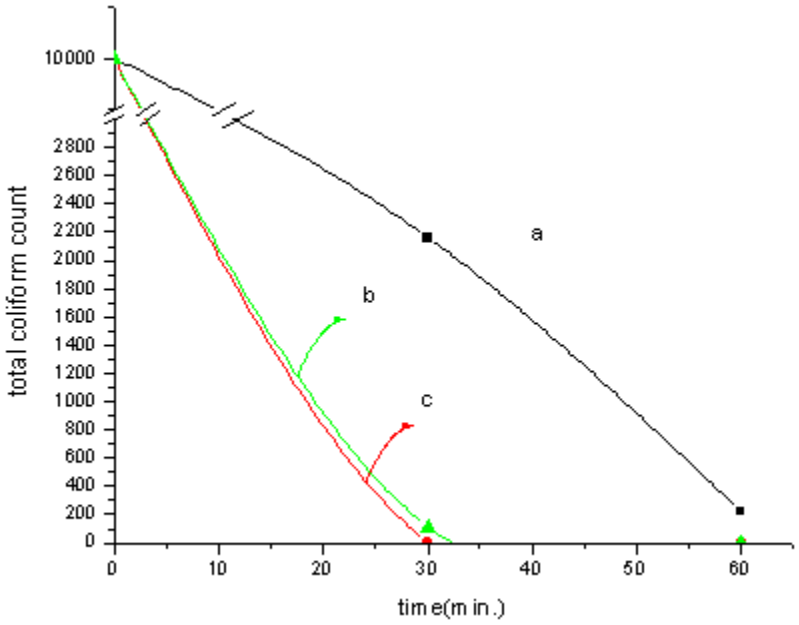


Figure 6. The total coliform inactivation after treatment of raw water by a)UV (λ_{max} = 365 nm) only , b)TiO_2 only(in the dark) and c) TiO_2/UV(λ_{max} = 365 nm)

3.2. Photocatalytic Efficiency of TiO_2

3.2.1. Formic Acid Photocatalytic Degradation

TOC analysis (Fig. 5) shows the phtocatalytic (TiO_2/UV) degradation of formic acid after 7 hours of reaction. TOC was changed from 27.32 ppm to 4.76 ppm which corresponds to about 83% of acid removal within the experiment time.

It is known that the mechanism of photocatalysis involves the formation of a hole -electron pairs. The removal of the simple molecule of formic acid may be initiated by the direct electron transfer to the positive hole. Also, hydroxyl radical 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[23, 24].

3.2.2. Disinfection of Total and Fecal Coliform by TiO_2 (Calcined at 450℃ in the Presence and Absence of UV Light)

A natural decay in absence of TiO_2 or UV of total coliform after 60 min (control test) showed that there is no significant change in the total coliform observed under the experimental conditions. It is clear from Fig. 6 that treatment of the raw water with UV irradiation (photolysis) or TiO_2 alone (adsorption) had a significant effect on the total coliform inactivation (78.4 and 98.9%, respectively, after 30 min). Photocatalysis using TiO_2/UV (λ_{max} = 365 nm) exhibited 99.97% and 100% after 30 and 60 min, respectively.

Removal of bacteria in the absence of UV may occur by adsorption of bacteria on the surface of TiO_2 particles[25, 26]. In the presence of UV (TiO_2/UV) hydroxyl radicals which can be formed are highly active for both the oxidation of organic substances and the inactivation of bacteria and viruses through the oxidation of the organic compound consisting the cell of bacteria. The adsorption effect also enhances this reaction[25, 26, 27]. Moreover, re-growth and reproduction of total coliform bacteria in water treated with UV alone is reported[28, 29] while the re-growth of bacteria in water samples treated with TiO_2/UV after storage in the dark isn't observed. This means that TiO_2/UV system has residual disinfecting efficiency. It is also reported that there is weak or no cell toxicity of TiO_2[15, 30, 31] and the adsorption of bacteria by TiO_2 (in dark) doesn't affect cell membrane or any cell component and accordingly desorption may occur after period of time freeing bacteria in water. However adsorption remains the rate limiting step in the photodisinfection reaction[24].

4. Conclusions

TiO_2 has been prepared by the hydrolysis method and characterized with many techniques. The particle sizes of the prepared catalyst are in the nanorange (10 - 40 nm) with spherical and uniform particles. This oxide is efficient for formic acid removal and for coliform bacteria inactivation in water.

REFERENCES

[1] Zheng, Y., Shi, E., Chen, Z., Li, W. and Hu, X., Influence of solution Concentration on the hydrothermal preparation of titania crystallites. J. Mater. Chem., 2001, 11, 1547–1551.

[2] Pottier, A., Chaneac, C., Tronc, E., Mazerolles, L. and Jolivet, J., Synthesis of brookite TiO_2 nanoparticles by thermolysis of $TiCl_4$ in strongly acidic aqueous media. J. Mater. Chem.,

2001, 11, 1116–1121.

[3] Kim, S. J., Park, S. D. and Jeong, Y. H., Homogeneous precipitation of TiO_2 ultrafine powders from aqueous $TiOCl_2$ solution. J. Am. Ceram. Soc., 1999, 82(4), 927–932.

[4] Gao, L. and Zhang, Q., The promoting effect of sulfate ions on the nucleation of TiO_2 (anatase) nanocrystals. Mater. Trans., 2001, 42(8), 1676–1680.

[5] Wang, C. C. and Ying, J. Y., Sol – gel synthesis and hydrothermal processing of anatase and rutile titania nanocrystals. Chem. Mater., 1999, 11(11), 3113–3120.

[6] Nam, H. D., Lee, B. H., Kim, S. J., Jung, C. H., Lee, J. H. and Park, S. D., Preparation of ultrafine crystalline TiO_2 powders from aqueous $TiCl_4$ solution by precipitation. Japn. J. Appl. Phys., 1998, 37, 4603–4608.

[7] Park, S. D., Cho, Y. H., Kim, W. W. and Kim, S. J., Understanding of homogeneous spontaneous precipitation for monodispersed TiO_2 ultrafine powders with rutile phase around room temperature. J. Solid State Chem., 1999, 146, 230–238.

[8] A.Henglein, Ber.Bunsenges.phys.chem.101(1997)1562.

[9] Y. Zhang, G. Xiong, Nan Yao,W. Yang, X. Fu" Preparation of titania-based catalysts for formaldehyde photocatalytic oxidation from $TiCl_4$by the sol–gel method" Catalysis Today 68 (2001) 89–95.

[10] S.J. Tsai, S. Cheng, Catal. Today 33 (1997) 227.

[11] D.S. Muggli, J.L. Falconer, J. Catal. 175 (1998) 213.

[12] Zhang, Q., Gao, L. and Guo, J., Effect of hydrolysis conditions on morphology and crystallizations of nanosized TiO_2 powder. J. Eur. Ceram. Soc., 2000, 20, 2153–2158.

[13] S. Kumar, N. K. Verma , M. L. Singla, Digest Journal of Nanomaterials and Biostructures, Vol. 7, No. 2(2012) p. 607 – 619.

[14] M. Bekblet, Photocatalytic bactericidal activity of TiO_2 in aqueous suspensions of E. coli,Water Sci. Technol. 35 (11–12) (1997) 95–100.

[15] A.G. Rincn, C. Pulgarin, N. Adler, P. Peringer, Interaction between E. coli inactivation and DBP-precursors dihydroxybenzene isomers in the photocatalytic process of drinking-water disinfection with TiO_2, J. Photochem. Photobiol. A 139 (2001) 233–241.

[16] P.S.M. Dunlop, J.A. Byrne, N. Manga, B.R. Eggins, The hotocatalytic removal of bacterial pollutants fromdrinkingwa ter, J. Photochem. Photobiol. A 148 (2002) 355–363.

[17] APHA, 2003. Standard Methods for the Examination of Water and Wastewater,21th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

[18] H. Wang, B. Li, Z. Yan, Z. Lu, R. Cheng, and D. Qian, "Fast synthesis of monodisperse TiO_2 submicrospheres via a modified sol-gel approach," Rare Metals, vol. 27, no. 1, (2008) pp. 1– 4.

[19] W. Zheng, D. Jewitt, and R. I. Kaiser "Formation of Hydrogen, Oxygen, and Hydrogen Peroxide in Electron Irradiated Crystalline Water Ice".

[20] S. J. Park, Y. C. Kang, J. Y. Park, Ed A. Evans et al., "Physical Characteristics of Titania Nanofibers Synthesized by Sol-Gel and Electrospinning Techniques," Journal of Engineered Fibers and Fabrics, Volume 5, Issue 1 (2010), 54.

[21] K. Nagaveni, M. S. Hegde, N. Ravishankar, G. N. Subbanna, and Giridhar Madras, "Synthesis and Structure of Nanocrystalline TiO_2 with Lower Band Gap Showing High Photocatalytic Activity", Langmuir 2004, 20, 2900-2907.

[22] H. Haug and S. W. Koch," Quantum Theory of the Optical and Electronic Properties of Semiconductors " world scientific publishing co.Ltd. 1990.

[23] V. Karpel, N. Leitner, M. Dore, Hydroxyl radical induced decomposition of aliphatic acids in oxygenated and deoxygenated aqueous solutions, J. Photochem. Photobiol. A 99 (1996) 137.

[24] M. N. Chong, B. Jin, C. W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, water research 44 : 2997-3027 , 2010.

[25] Luigi Rizzo, Inactivation and injury of total coliform bacteria after primary disinfection of drinking water by TiO2 photocatalysis, Journal of Hazardous Materials 165 (2009) 48–51.

[26] A. G. Rincón, C. Pulgarin, Effect of pH, inorganic ions, organic matter and H_2O_2 on E. coli K12 photocatalytic inactivation by TiO_2 Implications in solar water disinfection, Applied Catalysis B: Environmental 51 (2004) 283–302.

[27] D.M. Blake, P.C. Maness, Z. Huang, W.E.J.J. Huang, W.A. Jacoby, Sep. Purif. Methods 28 (1999) 1.

[28] S. Malato, P. Fernandez-Ibanez, M.I. Maldonado, J. Blanco and W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, J. Catalysis Today 147 (2009) 1–59.

[29] EPA, Ultraviolet disinfection guidance manual for the final long term 2 enhanced surface water treatment rule, 2006.

[30] N. Lydakis-Simantiris, D. Riga, E. Katsivela, D. Mantzavinos and N. P. Xekoukoulotakis, Disinfection of spring water and secondary treated municipal wastewater by TiO_2 photocatalysis, Desalination 250 (2010) 351–355.

[31] T. Matsunaga and M. Okochi, Environ. Sci. Technol. 29 (1995) 501.