

The nano-TiO₂ synthesis using ultrasonic assisted sol-gel method and its photocatalytic degradation of methylene blue

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The application of ultrasonic assisted sol-gel method at various % amplitude ultrasonic energy (AS) and reaction time of 40-80% and 1-4 hrs, respectively for preparation of nano-TiO₂ crystals was carried out. Synthesized nano-TiO₂ was characterized for its structure, particle size, morphology, adsorption energy, and functional groups using X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), ultraviolet-visible (UV-VIS) and Fourier transform infrared (FTIR) spectrophotometries. A best nano-TiO₂ crystal (6.8 nm), was observed at 40% AS for 1 hr showed the highest methylene blue degradation yield of 80%.

Key words: The ultrasonic assisted sol-gel method, the nano-TiO₂ photocatalysts, Photocatalytic degradation.

Introduction

Nano-TiO₂ material has been widespread attended due to its high potential of photocatalytic environmental applications, such as CO₂ conversion, water treatment, and air quality control [1]. It is also considered to be a non-toxic material and therefore used in several bio-applications as well [2]. For many of these applications, the particle size, crystal structure and phase, porosity, and surface area influence the activity of TiO₂ dramatically [1]. Synthesis of nano-TiO₂ serves as a fundamental requisite to realize the potential applications and therefore various synthetic approaches have been explored. Conventionally majority of the TiO₂ photocatalysts have been synthesized via sol-gel route. Titanium alkoxide and titanium tetrachloride are the most common choices of starting materials for sol-gel based TiO₂ synthesis. Typically these precursors upon hydrolysis produce titanium hydroxide that upon further calcinations at above 400 °C generate crystalline phases of TiO₂ such as anatase, rutile and brookite [2]. In the sol-gel synthesis process, ultrasound (US) effected the preparation of amorphous mesoporous titania, anatase and rutile titania, depending upon reaction temperature and time [3], in addition to, several ceramists for the atomization of a precursor containing solution into fine and uniform droplets, which are subsequently dried and pyrolyzed in a furnace to produce chemically uniform and highly sinterable powders [4]. Formation and behavior of a cavitation bubble is closely linked to the applied sound

pressure field, which in turn depends on the type of the reactor and the ultrasonic source (frequency, area of emitting surface, intensity and energy). To optimize any given chemical reaction, the primary objective is in making the cavitation process as efficient as possible. This would encapsulate minimal loss of energy and optimum frequency of bubble oscillation and collapse, since the topology of the acoustic pressure field depends on the type of reactor as well as on the source of the ultrasound. Thus, before applying ultrasound in pilot scale reactors, it becomes imperative to find out and optimize all the factors in the energy transformation cascade to achieve maximum useful cavitation [4]. For all sonochemically aided reactions there exists an optimum power at which a given reaction can be performed optimally in order to avoid unnecessary loss of energy. Particularly, this power optimization strategy becomes so important, that in many industrial applications, the primary objective is to reduce the power cost. In case of reactions such as hydrolysis, increase in sonic power density, initially increases reaction rates which ultimately reach a maximum/optimum value but thereafter the reaction rates decrease with further increase in power density [4].

Here, nano-TiO₂ was synthesized by an ultrasonic assisted sol-gel method. The effect of amplitudes of sonication (AS) are varied from 40% to 80% and sonicated reaction times for 1-4 hrs, respectively, on the properties of synthesized-TiO₂. Selected methylene blue is a model for organic dyes in water pollutant.

Materials and Methods

Materials

Titanium tetraisopropoxide (TTIP) precursor was

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obtained from Sigma-Aldrich, Co. Ltd. Ethanol (95% pure) and Glacial acetic acid solution was ordered from Flinn Scientific Ltd. Methylene blue (MB) was purchased from May & Baker Ltd. All chemical reagents were used without any purification.

Synthesis of nano-TiO₂ by an ultrasonic assisted sol-gel method

The mixture solution of 100 mL ethanol and 0.2 mL acetic acid in 250 mL glass beaker was stirred for 5 min and then the glass beaker containing the solution was putted to ultrasonic bath and sonicated under ultrasonic irradiation (40 kHz, 210 W, Elma Transsonic Digital (T 760 DH)) for 5 min. After that 9 mL TTIP was dropped to the solution and continuously sonicated with variation of amplitudes are 40% (84 W), 60% (126 W) and 80% (164 W) and sonicated reaction times for 1, 2, 3, and 4 hrs, respectively. All sol-gel reactions were done at ambient conditions. The obtained gel was filtered and dried at 100 °C for 1 hr and finally calcined at 300 °C for 2 hrs (Carbolite furnace (RWF 11/23)).

Characterization

Powder X-ray diffraction (XRD) patterns of samples were determined by using Philips diffractometer (X'pert-MPD, Cu K α radiation). Crystallite sizes were calculated using the Debye-Scherrer equation according to Eq. (1) [4]:

$$B_{hkl} = \frac{K\lambda}{D_{hkl}\cos\theta_{hkl}} \quad (1)$$

where λ is the wavelength of incident X-rays = 1.54 Å for Cu K α , D_{hkl} is the full width at half maximum (FWHM) of the diffraction line, θ is the central diffraction angle of the peak, and K is a constant, which has been assumed to be 0.9 [4].

Fourier Transform Infrared spectra (FT-IR) of the synthesized -TiO₂ samples were conducted by KBr pellet method on Shimadzu (FTIR-8900) spectrophotometer in the range of 4000-400 cm⁻¹. The scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM) images of the synthesized-TiO₂ samples were photographed on scanning electron microscope (JEOL, JSM-7800F) and high resolution transmission electron microscope (FEI, TECNAI G2 20 S-TWIN), respectively. The Ultraviolet-Visible absorption spectra (200-800 nm) were determined on a Shimadzu (UV-1601) spectrophotometer.

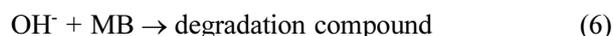
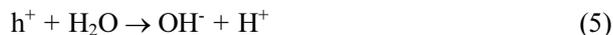
Photocatalytic activity

All degradations were performed in an open system with an open air circulation to provide enough oxygen for the oxidative degradation of pollutants. 10.00 mL of 6.25 × 10⁻⁶ M methylene blue in aqueous solution was photodegraded with loading 0.020%wt catalyst in ethanol at pH 4. Photodegradation studies were carried out using a rectangular quartz cell photoreactor with a

commercial germicidal UV lamp of 6 W (wavelength at 350 nm) from Sankyo denki Ltd. During irradiation, ~2.00 mL of the suspension was collected in regular time interval and the progress of photodegradation was monitored by observing the disappearance of the absorption peak of methylene blue at 663 nm in the UV-Visible absorption spectra on a Shimadzu (UV-1601) spectrophotometer. Mechanism for photodegradation of MB dye can be explained as follows. On illumination of catalyst surface with enough energy (equals or higher than the bandgap energy, E_{bg} , of the catalyst), it leads to the formation of a hole (h^+) in the valence band and an electron (e^-) in the conduction band. The hole oxidizes either pollutant directly or water to produce radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst. The activation of catalyst by UV light can be represented by the following steps:



In this reaction, h^+ and e^- are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as follows:



One of the major problems in the photocatalytic process is the electron-hole recombination. To avoid this problem, UV irradiation source stands up among other sources [5, 6]. The energy of UV irradiation is large compared to the bandgap energy of the catalysts. Hence, the problem of electron-hole recombination is not fully but largely avoided with UV source. The percentage efficiency of photodegradation was determined using the following equation [5, 7]:

$$X = \frac{C_0 - C}{C_0} \times 100 \quad (7)$$

where C_0 is the initial solution concentration of MB and C is the solution concentration of MB after degradation.

Results and Discussion

Characterization of the synthesized-TiO₂

The XRD patterns of the various the synthesized-TiO₂ samples are shown in Figs. 1-2. A series of characteristic peaks were observed at 2θ of 25.32, 37.84, 48.07, 55.11, 62.75, and 75.12 indicating the pure anatase structure according to JCPDS card 01-084-1286. The mean sizes

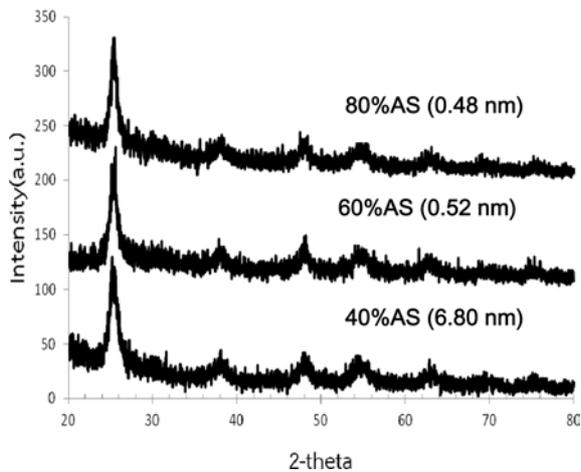


Fig. 1. XRD patterns of TiO₂ with 40%, 60% and 80%AS and sonicated time for 1 hr. The calculation crystallite sizes are in parentheses.

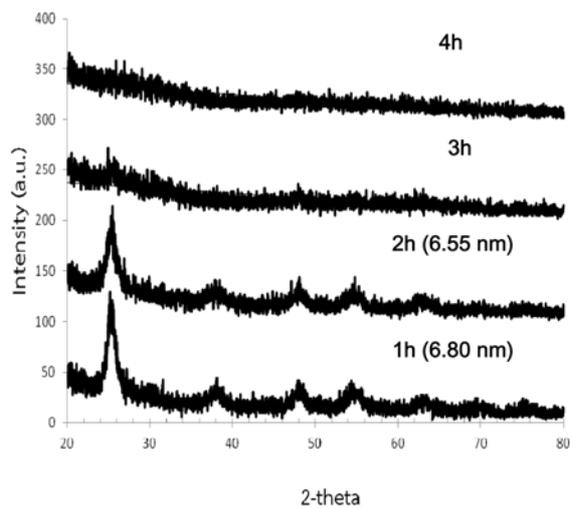


Fig. 2. XRD patterns of TiO₂ with 40%AS ultrasonic energy and sonicated time for 1-4 hrs. The calculation crystallite sizes are in parentheses.

of the synthesized-TiO₂ nanocrystals, as calculated by Debye-Scherrer's formula, are in the range of 0.48-6.80 nm for the samples ultrasound-treated at different %AS (Fig. 1). It can be also found that both the sonic energy and sonicated reaction time significantly affect the crystallinity of the synthesized-TiO₂. The sonicated reaction time from amorphous gel to crystal phase is about 4 hrs, 3 hrs, 2 hrs and 1 hr for the investigated TiO₂ crystallized at 40%AS (Fig. 2), revealing that the elevated sonic energy can shorten the time from amorphous gel to crystal phase. As the sonicated time or %AS increases, the mean size of TiO₂ nanocrystals decreases because of the shock waves are high pressure amplitude waves emitted by the bubble; nevertheless, microturbulence is continuous oscillatory motion of liquid induced by radial motion of cavitation bubble. In a case of sonocrystallization, shock waves lead to

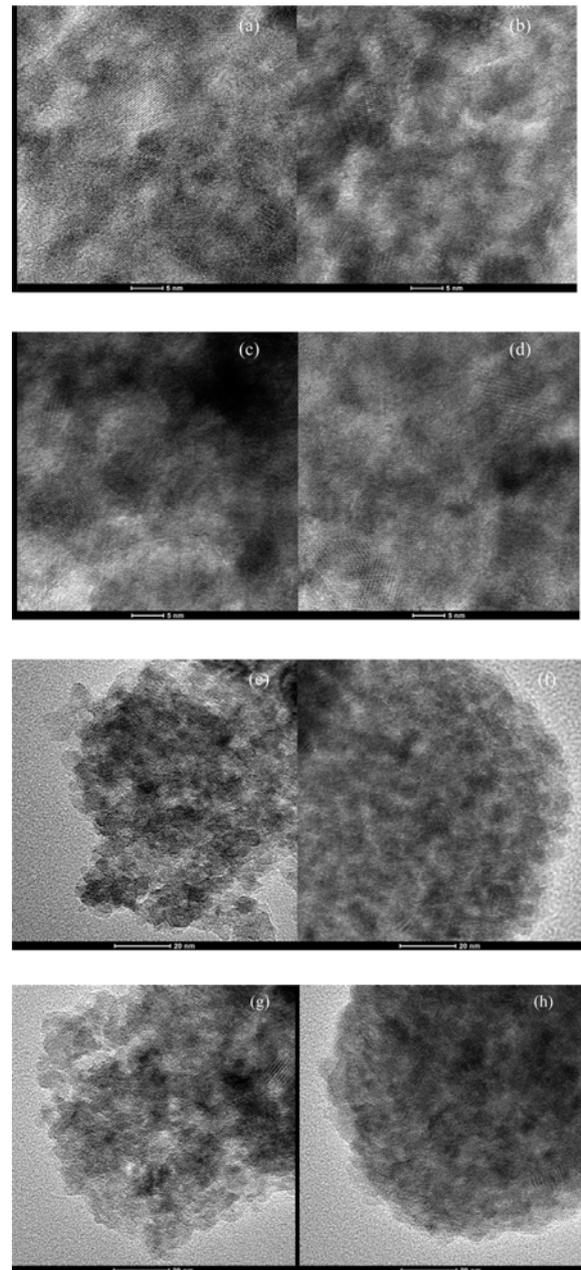


Fig. 3. HR-TEM images of the synthesized- TiO₂ at 40%AS ultrasonic energy and sonicated time for 1 hr (a,e), and for 2 hrs (b,f), 60%AS (c,g), and 80%AS (d,h) ultrasonic energy and sonicated time for 1 hr.

increasing the nucleation rate and microturbulence governs the growth rate [8]. However in this case either the increasing more and more sonic energy or the longer sonicate time leading to high pressure amplitude waves affected the crystalline size decrease to smallest or amorphous form [4]. The crystalline particle sizes of the synthesized-TiO₂ were confirmed by HR-TEM images as shown in Fig. 3. The SEM images of the synthesized-TiO₂ at different sonication energy as shown in Fig. 4. Synthesized-TiO₂ was found to be spherical-like in shape and uniformity with some agglomeration

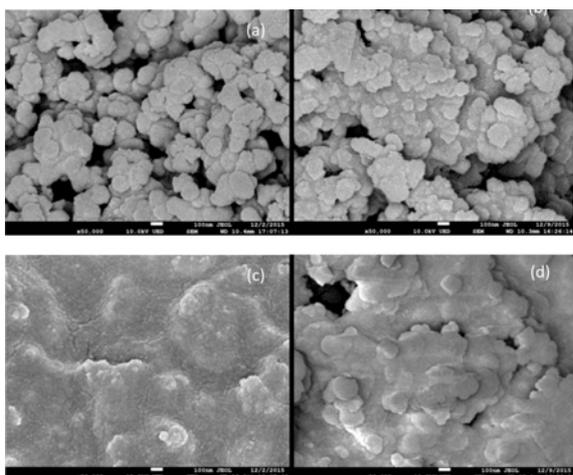


Fig. 4. SEM images of the synthesized- TiO₂ at 40%AS ultrasonic energy and sonicated time for 1 hr (a), and for 2 hrs (b), 60%AS (c), and 80%AS (d) ultrasonic energy and sonicated time for 1 hr.

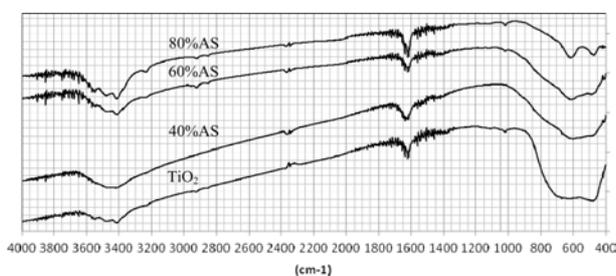


Fig. 5. FT-IR spectra of TiO₂ with 40% 60% 80%AS ultrasonic energy and sonicated time for 1 hr.

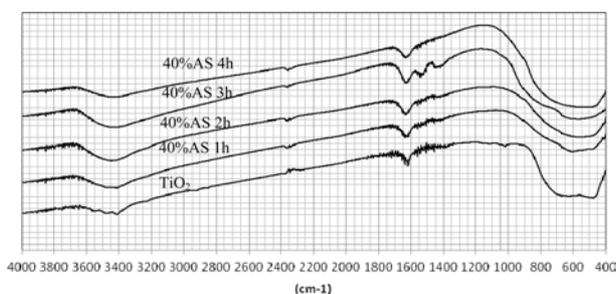


Fig. 6. FT-IR spectra of TiO₂ with 40%AS ultrasonic energy and sonicated time for 1-4 hrs.

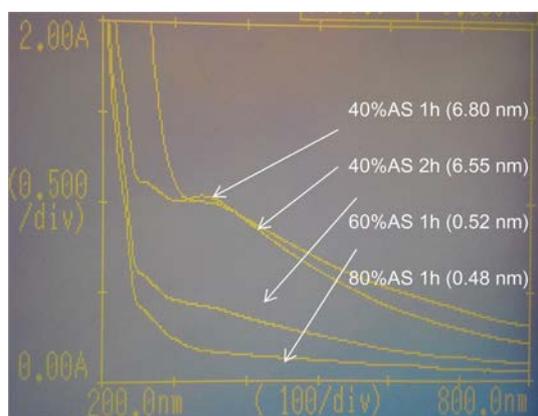


Fig. 7. UV-VIS absorbance spectra of the synthesized- TiO₂ at various % amplitude ultrasonic energy.

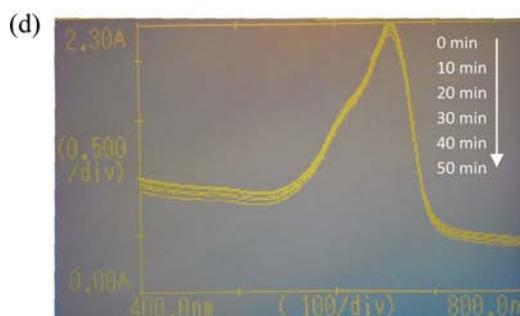
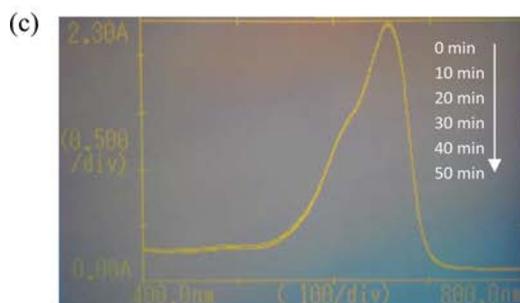
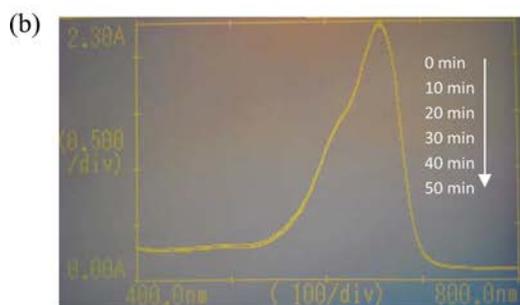
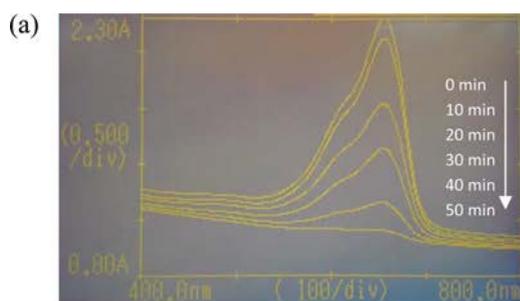


Fig. 8. UV-VIS spectra of methylene blue degradation under UV irradiation (λ 350 nm) with TiO₂ photocatalyst at 40%AS (a), 60%AS (b), and 80%AS (c) ultrasonic energy and sonicated time for 1 hr, and 40%AS ultrasonic energy and sonicated time for 2 hrs (d).

due to calcinations [5].

Figs. 5-6 show the FTIR spectra of the synthesized-TiO₂ with sonicated for different % AS and time, and comparing with commercial TiO₂ from Ajax Finechem Pty Ltd. In the typical spectra of the investigated TiO₂, some main characteristic peaks can be assigned as follows. The bands at 3400-3500 cm⁻¹ and 1639 cm⁻¹ are assigned respectively to the stretching and bending modes of hydroxyl group (-OH) or the adsorbed water on the TiO₂ surface. The bands at 2340 and 2360 cm⁻¹

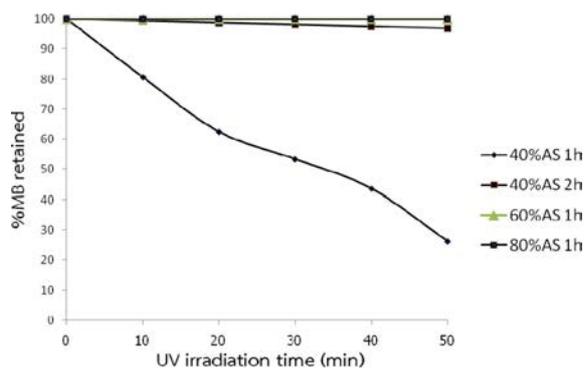


Fig. 9. %MB retained under UV irradiation (λ 350 nm) versus irradiation time with TiO_2 photocatalyst at different ultrasonic energy and sonicated reaction time.

represent the asymmetric stretching of CO_2 from atmosphere. The peaks appearing in the $1430\text{--}1541\text{ cm}^{-1}$ region can be attributed to combinations of C-H, O=C-OR, and OR groups linked to titanium, roughly ascribed to acetate-like compound [9]. The wide peak at $450\text{--}700\text{ cm}^{-1}$ corresponds to the Ti-O bending mode of TiO_2 . The above results show that some organic groups observed in the amorphous TiO_2 form.

Photocatalytic activity of the synthesized- TiO_2

Fig. 7 displays the UV-VIS spectra of the synthesized- TiO_2 at different sonic energy and sonicated reaction times indicating that the larger nano- TiO_2 size about 6.80 nm can be absorbed energy at wavelength 350 nm corresponded to 3.54 eV while other absorbed the high energy or lower wavelength. Photocatalytic degradation of MB in an ethanol suspension of the synthesized- TiO_2 was performed to evaluate their photocatalytic activity. Figs. 8-9 show the visible spectra (400-800 nm) for MB degradation and %MB retained under UV irradiation (λ 350 nm) versus different nano size TiO_2 versus UV irradiation time, indicating that the suitable nanosized- TiO_2 photocatalyst about 6.80 nm could be degraded the MB retained of 25% within 50 min as faster than reported in [10] as shown in Figs. 8(a) and 9. While the nanocrystal. size of photocatalyst samples lower than

6.80 nm, degradation process could not be done due to UV light not enough to activated the catalyst as shown in Fig. 7.

Conclusions

The nano- TiO_2 photocatalysts were successfully synthesized by ultrasound assisted sol-gel method, and the synergetic effect of % amplitude sonic energy and sonicated reaction time enhanced the nucleation and growth rate of crystallization significantly. The suitable nano- TiO_2 (6.80 nm) showed the degradation of MB in shorting UV irradiation time.

Acknowledgments

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References

1. Y. Wang, Y. He, Q. Lai, and M. Fan, *Journal of Environmental Sciences* 26 (2014) 2139-2177.
2. P. Nagarjuna, S. Roy, and R. Ganesa, *Microporous and Mesoporous Materials* 211 (2015) 1-8.
3. K.K. Latt, and T. Kobayashi, *Ultrasonics Sonochemistry* 15 (2008) 484-491.
4. K. Prasad, D.V. Pinjari, A.B. Pandit, and S.T. Mhaske, *Ultrasonics Sonochemistry* 17 (2010) 697-703.
5. A.K. Singh, and U.T. Nakate, *Journal of Nanoparticles* 310809 (2013) 1-7.
6. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, and V. Murugesan, *Journal of Hazardous Materials B* 89 (2002) 303-317.
7. S. Ghasemi, S. Rahimnejad, S. Rahman Setayesh, S. Rohani, and M.R. Gholami, *Journal of Hazardous Materials* 172 (2009) 1573-1578.
8. V.S. Nalajala, and V.S. Moholkar, *Ultrasonics Sonochemistry* 18 (2011) 345-355.
9. Q. Luo, Y. Chen, D. Wang, J. An, X. Li, R. Yin, and L. Shi, *Materials Research Bulletin* 67 (2015) 140-145
10. G.M. Madhu, M.A. Raj, and K. Pai, *Journal of Environmental Biology* 30 (2009) 259-264.