Treatment of malachite green dye using combined oxidation techniques based on different irradiation

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Abstract−We investigated the treatment of malachite green (MG) dye using sonocatalytic, photocatalytic and sono-photocatalytic techniques. The percentage of decolorization for sonophotolysis (65.5±3.3%) was much higher than the individual effects of sonolysis (55.2±2.4%) and photolysis (52.1±2.6%). The efficiency of the sonophotocatalytic process increased in the presence of photocatalysts such as anatase TiO_2 (82.2±4.1%) and ZnO (75.7±3.8%). The decolorization rate further enhanced in the presence of nano-TiO_2 (anatase, rutile ratio 75 : 25 and particle size ≤100 nm). The enhancement in decolorization was marginal for sonophotocatalysis (95.9±4.8%) as compared to sonocatalysis (93.0±4.3%) and photocatalysis (93.2±4.6%). The intensification of decolorization in the presence of nano-TiO_2, due to lower recombination of hydroxyl ions on the photocatalytic surface and nano-particle size of a catalyst, increased cavitational activity. The total organic carbon was found to be maximum for sonophotocatalytic in the presence of nano-TiO_2 (67.1±3.3%).

Keywords: Degradation MG, Advanced Oxidation, Sonocatalysis, Photocatalysis, Sonophotocatalysis, Mineralization

INTRODUCTION

Treatment of environmental persistence, hazardous and toxic compounds is creating growing concern worldwide because of long-term impacts on human beings and eco-systems. Textile and dye industries require a large volume of water for processing. These industries are the second major sector in the terms of consumption of water and generate massive quantities of the wastewater. Initial COD of wastewater is immense (4,000-10,000 mg/L) and needs to be treated before discharge to the surface water. The majority of aromatic, organic compounds present in wastewater are non-biodegradable or less persistent with conventional biological or municipal sewage treatment [1-4]. The advanced oxidation process is considered as the suitable method for treatment of waste-water. Sonochemical and photocatalysis are the most substantial methods for treatment of wastewater containing complex organic compounds and bio-refractory materials.

Sonochemical is a cavitation-driven mechanism. Cavitation is a phenomenon of the formation, growth and subsequent collapse of cavities (micro-bubbles) for a short life span of time (milliseconds). Collapsing cavities release a significant amount of energy over a small location, and such events occur in millions of parts of the reactor (life span of cavitational activity is in picosecond range). During the collapsing conditions of the cavity, a high magnitude of pressure and temperature (4,000-8,000 K) is induced inside the cavity. At the higher elevated temperature condition, water molecules split into the H• and •OH inside the bubble ($H_2O \rightarrow H• +$

•OH). The higher temperature (bubble collapsing state) is sufficient to pyrolyze H˙ radical and ˙OH radicals diffuse out after bubble collapse. These generated •OH radicals have strong oxidation potential for degradation of pollutants like MG dye. The efficiency of a sonochemical reactor depends on the number of molecules near the vicinity of collapsing bubble or adhering to the bubble surface during the collapse. Sonochemical efficiency increases with increasing the number of collapsing cavities known as a cavitational activity. These cavities are enhanced in the presence of solid catalyst particles and further increase with a reduction in the size of particles [5,6]. Photocatalytic is a process of photoexcitation of electrons from valence to conduction band in the presence of semiconductor materials such as titanium dioxide, zinc oxide, and so on. The promotion of electrons creates a deficiency or hole in the valance band. Holes in the valence band react with a water molecule to form hydroxyl radicals or may trap targeted pollutants or organic compounds. The efficiency of the photocatalytic process depends on the formation of holes or active sites on the catalyst surface. The activity of photocatalyst depends on the catalyst surface morphology, band gap, and size of the particles [7-9]. The efficiency of sonochemical and photocatalysis increases with the combination of these processes [18]. Synergistic effects of a combined process attributed:

a) enhancement of activity of photocatalyst (cleaning and sweeping of catalyst surface) via physical effects of cavitation like acoustic streaming,

b) more mass transport of the reactants and product on catalyst surface due to shock wave propagation of cavitation,

c) fragmentation or pitting of catalyst surface during cavitation increases the surface of the catalyst, and

d) bubble turbulence during cavitation enhances the rates of

desorption of intermediate products from catalyst which helps for continuous cleaning of catalyst surface.

The rate of hydroxyl radical formation during sonophotocatalysis process depends on catalyst characteristics and cavitational activity [5]. Titanium dioxide and zinc oxide are the most attractive photocatalysts due to numerous advantages of less hazard, environmental stability, surface stability, and band gap. The activity of these catalysts is further augmented by doping or mixing of two catalysts [10,11].

In the present work, malachite green (MG) dye was considered as a model compound for degradation using photocatalysis, sonochemical and sonophotocatalytic methods. MG is a class of triarylmethane of synthetic dye that has an outstanding commercial application such as coloring agent, disinfectant and dying process [4,11]. The contaminated food (fish) or water of MG may cause carcinogenic, mutagenic and teratogenicity effects on human beings. US food and drug administration has nominated it '1' as a priority chemical for carcinogenicity. Degradation of MG was reported by numerous researchers using oxidation techniques based on ozonation, Fenton oxidation, photocatalysis, sonochemical and electrochemical [12,21]. Reported studies have been based on using the single effect of photocatalyst/sonochemical method using a different catalyst. Berberidou [4] reported sonophotocatalytic degradation of MG in the presence of photocatalyst (TiO$_2$ and Fenton) and the effect of dissolved gasses such as argon, air, and oxygen on the sonochemical degradation of MG. The study is limited to only a few 'mL' of operation and the focus of the study is limited to exploring the efficacy of sonochemical degradation.

We investigated the degradation of MG using sonochemical, photocatalysis and sonophotocatalysis for 3 L of operation. The effectiveness of the process was further explored in the presence of photocatalysts, such as anatase phase titanium dioxide, zinc oxide and a nano titanium dioxide (a mixture of anatase and rutile phases). Total organic carbon was measured to study the mineralization of the MG.

MATERIALS AND METHODS

1. Materials

Malachite green (MG) dye was procured from M/s Loba Chemicals Pvt. Ltd., Mumbai, India. An aqueous solution of required for the experiment was prepared by using distilled water. Fresh distilled water was used for all the experiments obtained from Millipore distillation apparatus. Terephthalic acid, 2-hydroxyterephthalic acid and Nano-titanium dioxide, a mixture of anatase and rutile phase of the ratio 75 : 25 (particle size <100 nm (BET), <50 nm (XRD)) were purchased from Sigma-Aldrich. Merck India Limited supplied titanium (IV) dioxide (15 m^2/g) and zinc oxide (15 m^2/g). All these chemicals were used as received from the suppliers.

2. Reactor Configuration

An ultrasonic bath (Max power: 120 W and frequency: 20 kHz) with three transducers (triangular pitch type arrangement) attached at the bottom of the reactor used as the sonochemical reactor in the present work (Fig. 1). Dimensions of the bath are 250×175× 100 mm with maximum capacity as 3.5 L, procured from M/s Oscar Ultrasonics Pvt. Ltd., Mumbai, India. Bath is made up of
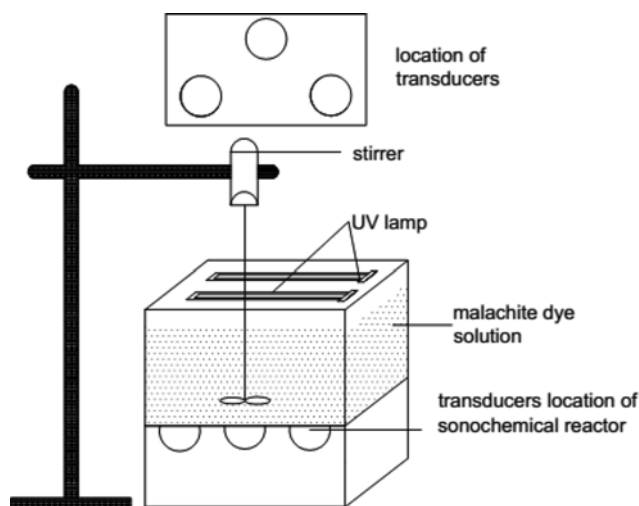

Fig. 1. Sonophotocatalytic reactor for degradation of MG.

stainless steel material, and there is a control panel for adjusting the temperature and time knobs. Frequency and power intensity have a significant effect on the efficiency of sonochemical degradation. With increasing power the intensity of cavitational activity increases. It is directly propositional to the volume of the reaction [5,6,8]. In present work, the volume of the reaction was optimized based on a calorimetric study (amount of energy dissipated to the reaction volume/energy supplied) and found to be optimum for 3 L (36.7%) of the solution. The studies were conducted at the maximum dissipation of sound energy in the reaction volume. So, all the experiments were carried out at 3 L volume. The frequency of operation relates to cavitational activity in the sonochemical reactor. The formation of oxidation radicals for degradation of dye depends on the temperature conditions inside the collapsing bubble. More violent temperature conditions inside bubble are useful for enhancing rate of oxidation/hydroxyl radicals. Maximum temperature inside the bubble was decreasing with increasing the frequency of operation [8,9]. So, the experiments were conducted at a lower frequency of operation with an objective of maximizing rate of degradation of dye.

The photocatalysis experiments reactor were performed in the sonochemical reactor, and the sonochemical reactor was in 'off' mode. The reactor was covered with a wooden board and two fluorescents tubes attached to the board. Specifications of the tube are Make: Philips, power: 18 W, initial lumen: 1,200 lm, chromaticity coordinate X: 440, chromaticity coordinate Y: 405, correlated color temperature: 3,000 K, luminous efficacy: 67 lm/m, color rendering index: 82 and wavelength: 274.6 nM. The board was covered with a black sheet to avoid radiation. Stirrer (Make: Remi, Power: 120 W, Speed: 400 rpm) was introduced at the center of the reactor, to maintain the uniform concentration of irradiation effect in the reactor and suspension of solid of the catalyst.

3. Experimental Procedure

An aqueous solution of the dye prepared by adding the known quantity of MG dye was added in the distilled water. The solution was stirred for 15 min using stirrer at 400 rpm to mix to the solid dye particles in water. All the experiments were performed at nat-
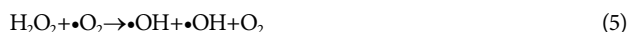
ural pH of the dye of solutions and 3 L of volume. The operating temperature of $25\pm2\,^{\circ}C$ was kept constant for all experiments by running reactor cyclic operation of 'on' and 'off' mode. Samples were taken at regular intervals of time and quenched immediately in the ice bath to stop degradation reaction. Samples were filtered to remove the traces of catalyst and solid particles. The progress of degradation was monitored using a UV Spectrophotometer. During sonolysis/sonocatalysis experiments the ultrasonic bath was in 'on' mode, photolysis/photocatalysis experiments fluorescents tubes were on 'on' mode, and sonophotolysis/sonophotocatalysis experiments ultrasonic bath and fluorescents tubes were on 'on' mode. Stirring at constant 400 rpm was maintained for all the experiments to keep an even concentration of MG in the reactor.

4. Analysis

The analysis of samples collected at a definite interval of time was performed by using double beam UV 2600 spectrophotometer (Make: Chemito). Samples were analyzed at a fixed wavelength of MG dye at 647 nm. Calibration curve of known concentration and absorbance was prepared. The concentration of unknown samples was analyzed based on the calibration curve. Mineralization of dye solution was measured regarding the total organic carbon (TOC). TOC of optimized conditions samples was measured using the Shimadzu TOC (Model: TOCLCPH) analyzer. Lucia and coworkers [13] reported a procedure for measurement of TOC. The concentration of •OH radicals was analyzed using a spectrophotometer. The procedure for measurement of •OH radicals used is described in [13].

RESULTS AND DISCUSSION

Efficacy of sonochemical and photocatalytic reactors depends on the number of hydroxyl radicals (•OH) per unit volume in the reactor and subsequent reaction with the targeted pollutants. Sonochemical degradation depends on the number of factors such as frequency of operation, physicochemical properties: surface tension, viscosity, temperature, so on [19,20]. While degradation kinetics of photocatalysis is the generation of holes and electron transfer phenomena and depends on physicochemical properties of the aqueous medium, catalyst surface area, the penetration depth of UV light [5,6]. The formation of hydroxyl radicals during the sonophotocatalysis shown by following reaction schemes (Eqs. (1)-(5)) [8].

$$H_2O+))) \rightarrow \bullet OH + H^{\bullet} \tag{1}$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{2}$$

$$H_2O_2 + H \bullet \rightarrow H_2O + \bullet OH \tag{3}$$

$$H_2O_2 + h\upsilon \rightarrow 2\bullet OH \tag{4}$$

$$H_2O_2 + \bullet O_2 \rightarrow \bullet OH + \bullet OH + O_2 \tag{5}$$

))): indicates interaction of sound energy with water

The experiments were performed with distilled water for measuring the concentration of •OH radicals for US, UV, US-UV, and 10 mg/L of aqueous solution of MG for US-UV operation. The radicals at the end 120 min for US, UV and US-UV operations

were $15.8\pm0.6\,\mu M$, $12.6\pm0.5\,\mu M$, and $22.2\pm0.8\,\mu M$, respectively. It clearly indicates that the rate of •OH radicals formation increased for a combination of US-UV operation compared to US and UV alone. The concentration of •OH radicals ($0.2\pm0.05\,\mu M$) decreased significantly during the US-UV treatment of MG (initial concentration: 27.4, natural pH). It clearly indicated that formed •OH radicals/H_2O_2 was utilized for degradation of MG. Our results are closely related to literature findings [13,22].

The efficacy of US-UV is dependent on the selection of optimum catalyst. The effect of catalyst concentration and oxidation processes (sonocatalysis (US), photocatalysis (UV), and sonophotocatalysis (US-UV)) on decolorization of MG was studied. All the experiments were performed at optimal initial concentration 27.4 μM and natural pH of the aqueous solution. The objective of work was to compare the efficacy of US, UV, and US-UV, so the result of optimum catalyst concentration was presented and discussed.

1. Sonolysis, Photolysis, and Sonophotolysis

The experiments were performed in the absence of a catalyst, 27.4 μM as initial concentration of MG and at natural pH of aqueous of solution using US, UV, and US-UV. The results of the change in the concentration of MG are shown in Fig. 2. Results indicate that the concentration of MG decreases linearly with the time for first 90 min of operation; a further reduction in the concentration with time was marginal. The decolorization was maximum for sonophotolysis compared to sonolysis and photolysis. The concentration of MG remaining at the end of 120 min of operation was $12.3\pm0.3\,\mu M$, $13.2\pm0.3\,\mu M$, and $9.6\pm0.3\,\mu M$ for sonolysis, photolysis, and sonophotolysis. MG decolorization depends on the removal of the color-bearing group (chromophore) and auxochromes (color substituent) from the benzene rings (chromogen). The structure of MG consists of three benzene rings (chromogen), azo group (-N=N-) a color bearing group and color substituent chloride group (Cl^-). The decolorization increased with the breaking of azo group and chloride group from the benzene rings [14]. Sonochemical degradation depends on the reaction between the hydroxyl radicals liberated (after bubble collapse) with targeted pollutants. The degradation rate is higher when the contaminants lie near
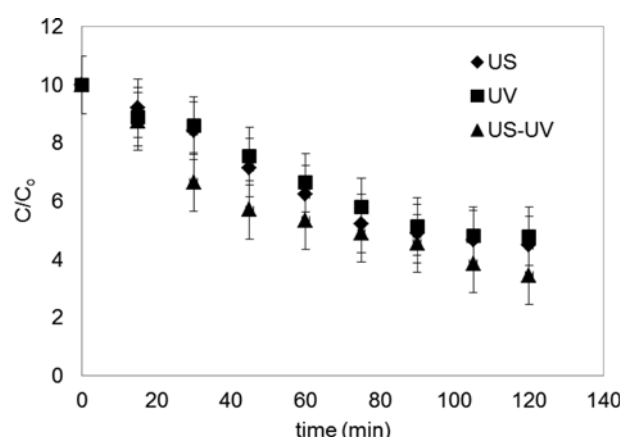

Fig. 2. **Effect of sonolysis (US), photolysis (UV) and sonophotolysis (US-UV) on degradation of MG (C_o: initial concentration of MG: 27.4 μM, C: concentration of MG at any time 't', pH: natural, temperature: $25\pm2\,^{\circ}C$).**

vicinity of bubble or adhere to the surface of the bubble. It depends on the hydrophobic nature of compounds; these compounds were quickly deposited on the surface of the bubble [5]. MG dye is hydrophilic and remains in the bulk of the solution. The degradation of MG increases with increase in the rate of hydroxyl radical's generation or increase in collapsing events. The formation of oxidation/hydroxyl radicals during photolysis depends on the number of active sites generation. When ultraviolet light interacts with the water molecules, it dissociates into radicals •O, •OH, •H [10]. These radicals have strong oxidation potential for degradation of MG molecules. Results of decolorization show that the synergic combinations of both the oxidation process are useful for enhancing the decolorization. However, the rate of decolorization does not show any additive effects for sonophotolysis. The percentage of decolorization of MG for sonolysis, photolysis and sonophotolysis was 55.2±2.4%, 52.1±2.6%, and 65.5±3.3%, respectively. The kinetic rate constant of sonophotolysis (9.4×10^{-3} min^{-1}) was higher as compared to distinct effects of sonolysis (7.4×10^{-3} min^{-1}) and photolysis (7.4×10^{-3} min^{-1}). The oxidation radicals have very high oxidation potential, and rate of recombination of these radicals is more. Recombination of hydroxyl radicals hampered the oxidation potential of radical. Another possible reason is as the decolorization progress; the concentration of MG decreases, which results in the lower concentration of MG near the vicinity of bubble or the oxidation radicals. These radicals may be utilized for complete mineralization of MG [1-3]. The mineralization of MG was analyzed based on measurement of TOC. The percentage TOC removal of MG for US, UV, and US-UV was 33.1±1.4%, 31.6±1%, and 64.3±2.2% respectively.

The obtained results correlate with the reported work. The decolorization of Orange II dye using photolysis, sonolysis, and sonophotolysis was 6.5%, 28.9 and 47.8% respectively [1]. The study of treatment of phenol using sonophotolysis reported that TOC removal rate was maximum for sonophotolysis (44.9%), as compared to individual operations of sonolysis (26.8%) and photolysis (36.8%) [2]. The first-order degradation rate constant of 2,4,6 trichlorophenol was maximum for sonophotolysis (0.2875 min^{-1}) as compared to the single operation of sonolysis (0.2397 min^{-1}) and photolysis (0.2347 min^{-1}) [3].

2. Presence of Titanium Dioxide

Presence of solid particles during the sonochemical process increased the surface cavitational activity. It provides additional nuclei for the growth of bubbles population, which results in cavitational events leading to higher production of the hydroxyl radicals. Higher dosing of solid particles leads to attenuation of the sound wave (scattering of the sound), which also hampers the rate of cavitational activity [5,6,11]. During photocatalysis the presence of the semiconductor materials like TiO_2 absorbs UV radiation equal to energy or higher energy than the band gap of TiO_2 (3.2 V for anatase). The absorption of ultraviolet light results in the formation of free electrons in the conduction band and holes in the valence band. This process results in extremely reactive and short-lived hydroxyl radicals [7-9]. These short-lived, highly reactive radicals either react with MG molecules or recombine. The formation of hydroxyl radicals highly depends on some of the particles and loading of TiO_2. Higher loading of the particles may lead to agglomer-
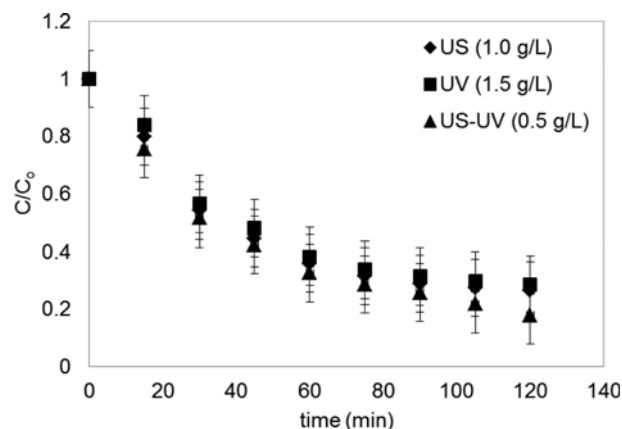

Fig. 3. Effect of titanium sonophotocatalysis dioxide on degradation of MG using sonocatalysis (US), photocatalysis (UV) and (US-UV) (C_o: initial concentration of MG: 27.4 μM, C: concentration of MG at any time 't', pH: natural, temperature: 25±2 °C).

ation and reduce the active sites in the aqueous medium [5,17].

The experiments were performed at various loadings (0.25 g/L to 2 g/L) of TiO_2. Results of degradation of MG for optimal TiO_2 loading of 1.0 g/L (US), 1.5 g/L (UV) and 0.5 g/L (US-UV) are shown in Fig. 3. The decolorization of MG was nearly the same for US (73.6±3.2%) and UV (71.5±3.6%). The combination of US and UV (82.2±4.1%) shows the higher decolorization. The concentration of MG remaining after 120 min treatment was 7.1± 0.2 μM, 7.6±0.3 μM and 5.8±0.2 μM for US, UV, and US-UV, respectively. A similar trend was observed for the kinetic rate of decolorization of MG in the presence of TiO_2; the pseudo-first-order kinetic rate constant for US, UV and US-UV was 13.4 min^{-1}, 12.5 min^{-1} and 15.6 min^{-1}, respectively. It is interesting to understand the role of TiO_2 for mineralization of MG. TOC removal was higher for US-UV (50.4±2.5%) as compared to US (44.2±2.2%) and UV (42.9±2.2%). As discussed earlier, in the presence of TiO_2 the higher decolorization rate of US was due to higher production of hydroxyl radical's formation and subsequent reactions with targeted pollutants. At higher concentration loading of TiO_2 during US leads to a lower rate of decolorization of MG. The degradation of MG during UV is due to the hydroxyl radicals formed during photoexcitation on the hydroxylated semiconductor surface and may be attributable to direct oxidation of MG molecules under UV radiation [7,18,19]. There may be more possibilities of formation hydroxyl radicals by both methods simultaneously which leads to higher degradation of MG. The process of formation of hydroxyl radicals occurred immediately after the reduction of absorbed oxygen of species on a semiconductor material or electron acceptors available in the aqueous MG solution [5,6]. The decolorization of MG is not only higher for US-UV, but also at a lower concentration of TiO_2 as compared to both methods. The beneficial advantages of combination of US and UV in the presence of TiO_2 are higher numbers of hydroxyl radicals, increase in the mass transfer between MG molecules (liquid phase) and catalyst surface, higher excitation of catalyst surface due the US induced luminescence effects in broad spectrum of wavelength and increased

activity of TiO_2 due to cleaning of catalyst surface and de-aggregating catalyst due to ultrasound, which results in higher particles size for photocatalysis [4,15-19].

A study of the degradation of MG reported that the rate of decolorization of MG increased with TiO_2 loading from 0.1 g/L to 0.5 g/L and bubbling of argon gas and combination of US and UV operations. The pseudo-first order kinetic rate constant for decolorization of MG for US, UV, and US-UV was 25.8 ± 0.90 min^{-1}, 96.2 ± 5.83 min^{-1}, and 149.0 ± 6.84 min^{-1}, respectively, and synergic index of 18 ± 0.02 [4]. Similar trends were reported for degradation of phenol (initial concentration: 40 mg/L, pH: 5.5) in the presence of TiO_2 (loading 0.1 g/L). The maximum degradation of phenol at the end of 120 min operation was 7%, 46% and 65% for US, UV, and US-UV, respectively [15]. A study on sonophotocatalytic treatment of paracetamol in the presences of TiO_2 (1 g/L) reported that kinetic rate constant was higher for a combination of US and UV (40.2×10^{-7} M min^{-1}) compared to the individual approach of US (8.3×10^{-7} M min^{-1}) and UV (30.2×10^{-7} M min^{-1}) [16].

3. Presence of Zinc Oxide

Titanium dioxide and zinc oxide are the most commonly used for photocatalytic and sonophotocatalytic degradation. They have the same band of the gap of 3.2 mV and show the similar photocatalytic performance [12-14]. The difference between these catalysts is due to morphology, surface interaction, and charge transfer dynamics. There are certain characteristics (electron mobility, quantum yield) of zinc oxide which are considered as an alternative for titanium dioxide [7,19,20]. Activities of zinc oxide during of US and UV are same as that of TiO_2. The difference in the morphological structure of zinc oxide may affect the decolorization of MG.

The results of decolorization of MG in the presence of optimal loading (US: 1 g/L, UV: 1.5 g/L and US-UV: 1 g/L) of zinc oxide shown are in Fig. 4. MG decolorization was marginally lower in presence of zinc oxide as compared to TiO_2. The concentration of MG remaining at the end of 120 min of operation for US, UV, and US-UV operation was 8.2 ± 0.2 μM ($69.2\pm2.8\%$), 8.5 ± 0.3 μM ($68.6\pm3.4\%$) and 6.6 ± 0.2 μM ($75.7\pm3.8\%$), respectively. The pseudo-
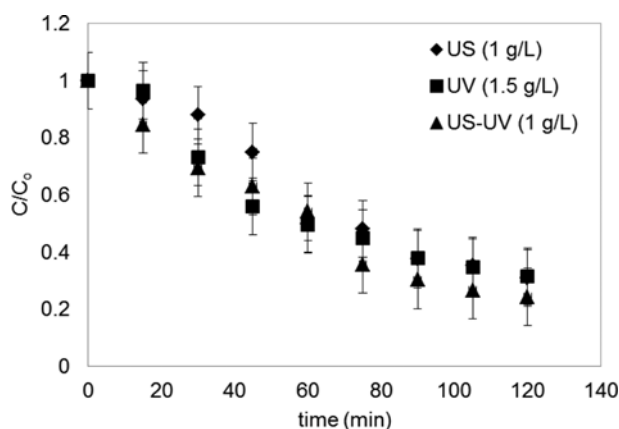

Fig. 4. **Effect of zinc oxide on degradation of MG using sonocatalysis (US), photocatalysis (UV) and sonophotocatalysis (US-UV) (C$_o$: initial concentration of MG: 27.4 μM, C: concentration of MG at any time 't', pH: natural, temperature: 25± 2 °C).**

first order kinetic rate constant for degradation of MG was maximum for US-UV (12.3×10^{-3} min^{-1}) as compared to US (9.9×10^{-3} min^{-1}) and UV (9.4×10^{-3} min^{-1}). Lower degradation of MG was in the presence of ZnO-related with nature of ZnO particle under pH conditions. During degradation of MG, chloride salt releases and more amount of Cl• ion in solution results in a decrease in pH of the solution. At lower pH, ZnO (UV operation) was readily dissolved in ionic form and resulted in lower degradation, while it favors the degradation for US process. Cavitational activity increased at lower pH due to increase in attractive forces between the negatively charged bubble and targeted pollutant. Also, tiny amount of zinc particles favors sonication process due to greater numbers of nuclei sides being available for increasing cavitational activities. Thus, the degradation of MG was less for UV than US in the presence of ZnO. TOC removal was marginally lower in zinc oxide for US and US-UV operations, but higher for UV operation as compared to the TiO_2. The percentage removal of TOC for US, UV, and US-UV operations was $38.1\pm1.9\%$, $41.2\pm2.1\%$, and $46.2\pm2.2\%$, respectively. Higher TOC removal rate for UV than US was due to lower recombination of hydroxyl radicals rate or higher number of hydroxyl radical's formation in the presence of ZnO as compared to TiO_2. Higher decolorization for combined approach was due to the same advantages in the presence of TiO_2.

The study of degradation of phenol in the presence of ZnO reported that removal of phenol (initial concentration: 40 mg/L, pH: 5.5, catalyst loading: 1 g/L and irradiation time: 120 min) was more for US-UV (85%) compare to US (13.7%) and UV (55%) [15]. ~90% degradation of phenol (initial concentration: 40 mg/L and pH: 5.5) reported for US-UV in the presence of ZnO (loading: 100 gm/L), which is more than degradation of phenol for UV (~55%) and US (~13%) [8].

4. Presence of Nano-titanium Dioxide

Sonophotocatalytic decolorization efficiency of MG depends on the catalyst surface area, catalyst activity and interaction of solid particles with irradiation medium. The combined effects of these activities were on the production of hydroxyl radicals (radicals used for degradation of targeted pollutants) [18,19]. The anatase TiO_2 is recommended due to higher photocatalytic activity, surface chemistry, and potentially high conduction band edge energy compared to rutile TiO_2. The anatase TiO_2 has the limitation of higher recombination rate of hydroxyl radicals. The rutile TiO_2 has greater stability in the critical process conditions, minor issues of recombination of hydroxyl radical due to surface morphology and band structural properties and more efficiency for the scattering of white light. A mixture of anatase and rutile can overcome the limitations of individual phases, and efficiency of the catalyst can be further increased using lower particle size [7-10].

The experiments were performed using a mixture of anatase and rutile (75 : 25) phase TiO_2, particle size ≤100 nm (BET), and ≤50 nm (XRD). The results trends indicate that decolorization of MG was maximum as compared to the effect of anatase TiO_2 and ZnO for all US, UV, and US-UV. The optimum catalyst concentration for US, UV, and US-UV was 1 g/L, 1.5 g/L, and 1 g/L, respectively. The decolorization was marginally higher for US-UV (95.9 ± 4.8) as compared to US (93.0 ± 4.6) and UV (93.2 ± 4.3), and efficiency of UV was marginally higher as compared to US (Fig.
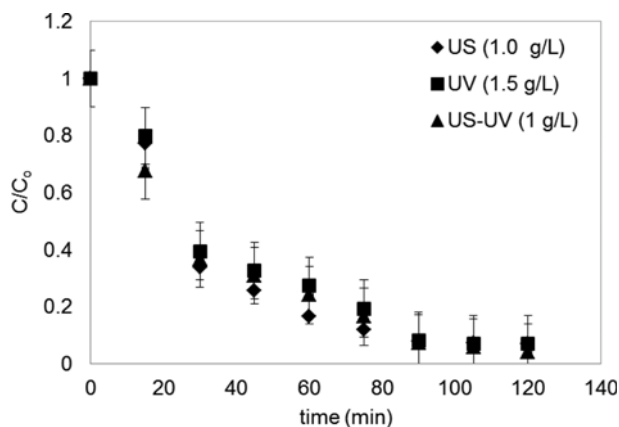
Fig. 5. Effect of nano-titanium dioxide on degradation of MG using sonocatalysis (US), photocatalysis (UV) and sonophotocatalysis (US-UV) (C_o: initial concentration of MG: 27.4 µM, C: concentration of MG at any time 't', pH: natural, temperature: 25±2 °C).

5). The pseudo-first order rate constant was $25.9 \pm 1.3 \, \text{min}^{-1}$, $25.1 \pm 1.3 \, \text{min}^{-1}$ and $26.9 \pm 1.4 \, \text{min}^{-1}$. Moles of MG remaining after 120 min of treatment was 1.9±0.1 µM (US), 1.86±0.1 µM (UV), and 1.1±0.04 µM (US-UV). TOC removal was maximum in the presence of nano-TiO_2 as compared to other approaches. Mineralization of MG was less for US (56.8±2.8%) as compared to UV (60.6±3.1%) and US-UV (67.1±3.3%). Results confirm that decolorization and mineralization were more in the presence of nano-TiO_2. Higher rates of decolorization for US were due to increasing in cavitational activity in the presence of nano-TiO_2, which helps in increasing the surface cavitational activities. Smaller catalyst particles provide more nuclei sites for increasing in the cavitational events and increase the rate of hydroxyl radicals for degradation of targeted pollutants [5]. The mixture of two phases of TiO_2 (anatase and rutile) increased the numbers of hydroxyl radicals as compared to anatase phase of TiO_2, and recombination rate of hydroxyl radicals may be lesser. It may be useful for increasing the interaction between the hydroxyl radicals and targeted pollutants. Another advantage of nano-TiO_2 is higher surface area increased more active sites for generation of hydroxyl radicals, and the presence of rutile phase increased the stability of catalyst [7-10]. These advantages are useful for increasing the number of active interactions between the hydroxyl radicals and targeted pollutants. US-UV combination in the presence of nano-TiO_2 does not show additional benefit for increasing the decolorization of MG [18-20]. It may be due to the diminishing of the initial concentration of the targeted pollutants with time.

The study of US degradation of methyl orange reported nearly 100% in the presence of nanometer anatase TiO_2, far greater than degradation of 54.16% in the presence of nanometer rutile TiO_2 and 18.24% with the absence of any catalyst [9]. The efficiency of photocatalytic degradation of 2, 4-dichlorophenol increased in the presence of nano-composite TiO_2. The removal efficiency of 2,4-dichlorophenol at the ambient temperature conditions (pH: 11 and time: 120 min) was 87% and 93% of solar and UV radiation, respectively [10].

CONCLUSIONS

Present work confirms the efficacy of decolorization of MG (malachite green) dye using a sonophotocatalytic reactor for 3 L of operation. The decolorization and demineralization of MG dye increased for combined effects of sonolysis and photolysis. It depends on the number of hydroxyl radical's formation and interaction with MG molecules. The rate of decolorization further increased in the presence of photocatalysts like anatase TiO_2 and ZnO. It was marginally higher in the presence of TiO_2 compared to ZnO due to the difference in surface morphology and band structure of catalyst particles. The rate of decolorization in the presence of nano-TiO_2 was nearly the same for sonocatalysis, photocatalysis and marginally higher for the combined effects of sonocatalysis and photocatalysis. The presence of nano-TiO_2 enhances the surface cavitational activity due to smaller particle size and a mixture of two phases (anatase and rutile) of TiO_2 reduce the recombination rate of hydroxyl radicals during photocatalysis. The maximum decolorization and mineralization of MG were 95.9±4.8% and 67.1±3.3%. Present work confirms that the combination of advanced oxidation processes has the potential for intensification of degradation of environmentally toxicant compounds. The study is useful for the development of scale-up aspects of the sonophotocatalytic reactor.

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