

Original paper

Sequential effect of microwave-photocatalysis on degradation of Bismarck Brown -Y dye

Vitthal L. Gole*, Apurva Alhat

Department of Chemical Engineering, AISSMS College of Engineering, Kennedy Road, MS, India.

ARTICLE INFO

Article history:

Received 6 July 2016

Received in revised form 30 August 2016

Accepted 14 September 2016

Keywords:

Microwave
Photocatalysis
Bismarck Brown
Advanced Oxidation
Photocatalyst
Hydroxyl radicals

ABSTRACT

Advanced oxidation technologies based on microwave and photocatalysis have a higher potential for the treatment of environmental persistence and reclarant compounds. The present work investigates the treatment of Bismarck Brown dye using effects of photocatalysis (UV) and microwave (MW) and their sequential combination. It has been observed that the sequential combination of MW followed by UV (MW/UV) has shown the higher performance as compared to the effects of MW and UV alone. The maximum degradation for MW/UV observed is $(44.1 \pm 0.5 \%)$. It was much higher than UV $(9.2 \pm 0.08 \%)$, and MW $(30.8 \pm 0.6 \%)$. The process efficiency was further increased in the presence of the catalyst such as hydrogen peroxide, zinc oxide, and titanium dioxide. The highest degradation was observed in the presence of titanium oxide $(82.9 \pm 0.4 \%)$ as a catalyst loading of 0.1 g/L in 100 min. Total organic carbon (TOC) measured for quantification of mineralization of BB-Y. The maximum removal of TOC was $38.2 \pm 0.32 \%$ in a sequential combination of MW-UV (presence TiO_2).

© 2016 Razi University-All rights reserved.

1. Introduction

The demand for chemical products is increasing exponentially with changing facets of life and globalization. Dye industries have wide chemical applications in chemical and allied industries (Ki et al. 2016; Zahra 2016). It is one of the highest water consuming industry after the agricultural sector and produced a large amount of wastewater. Wastewater generated from these industries have a higher range of initial COD values (3000-4000 mg/L) (Gole and Alhat, 2017; Horikoshi et al. 2014). It cannot be treated with the conventional biological process (Riaz et al. 2016). Advanced oxidation techniques are considered as one of the best alternatives for treatment of reclarant and environmental persistence compounds present in dye pollutants.

Most commonly used oxidation techniques for wastewater are wet air oxidation, sonochemical and photocatalysis. Wet air oxidation has a major limitation of higher processing requirement and expensive catalyst. Sonochemical methods are producing a higher quantity of oxidizing radicals at ambient temperature and pressure conditions. However, requiring an enormous amount of energy and issues with scale-up aspects of the process (Wang and Wang 2016; Jung 2011). Photocatalysis is a well-known process of generation of holes and electrons producing the oxidants in the presence of low-cost photocatalyst like titanium dioxide, zinc oxide, etc. A significant advantage of photocatalysis process is lower energy requirement for irradiation of catalyst. The detailed mechanism of degradation and other design aspects of the photocatalytic reactor have been discussed by several researchers (Devi et al. 2011).

The microwave is one of the emerging technique of intensifying the rate of chemical processing on multi-fold basis and reduces the processing time requirement from hours to second (Horikoshi et al., 2004; Horikoshi et al. 2014). The interaction of microwave (MW) with any aqueous medium produced rapid dipolar molecular level rotations. These molecular level activity creates molecular level friction and exhibits higher heating rates, reduced activation energy, and improved energy efficiency. In addition to this, MW shows the selective and volumetric heating. These effects are not demonstrated by the

conventional heating (Klán and Vavrik 2006; Zhang et al. 2009). Microwave equipment used for intensifying chemical reaction classified into two types namely a mono mode and a multi-mode type. In the multimode type of microwave type reactor (like a domestic microwave) all the modes i.e. transverse electric, transverse magnetic and simultaneous transverse electric and magnetic are acting continuously. The wave pattern in the multimode type of reactor is complex nature, it transverse and reflect several time inside in microwave cavity before transfer into the reaction volume. The uniformity of energy in reaction volume is a major concern for multimode type reactor (Sarmiento and Miranda 2010; Sarmiento and Miranda 2014). Whereas, mono-mode type microwave reactor has smaller reaction volume than a multimode reactor. However, it overcomes the issues of non-uniformity of microwave irradiation. Monomode type reactor used for minuscule volume (0.2-50 mL) which is a major concern for scale up aspect of mono mode type of microwave reactor. The uniformity of microwave irradiation in multi-mode type reactor can be overcome by coupling with a suitable stirring mechanism (Horikoshi et al. 2004; Wang and Wang 2016).

MW and UV have the higher potential for enhancing the degradation of reclarant compounds, but their rate of degradation process hindered due to the limitations associated with individual effects. UV is producing higher $\cdot\text{OH}$ radicals but has the diffusion restrictions between the transfer of oxidation radicals from catalyst surface to pollutants. These effects can be overcome by the sequential combination of MW and UV (Horikoshi 2014a, b). The thermal and non-thermal effects of the microwave can overcome the diffusion limitation of UV. The combination of MW and UV required the electrodeless lamp for illumination in MW cavity. The readily available mercury lamps cannot be fit with the cavity of MW. There few studies reported on the expensive combination of microwave electrodeless discharge lamps with MW irradiation (Horikoshi and Serpone 2014a; Sarmiento and Miranda 2014). These lamps are filled with varying concentrations of noble gasses, nitrogen, mercury, etc. The efficiency of these lamps is varying due to the emission of light of different wavelengths which may result in non-uniform degradation. To overcome these limitations, the

*Corresponding author Email: vitthalgole@gmail.com

sequential combination of MW and UV will be useful for intensifying rate of degradation (Serponea et al. 2010; Zhang et al. 2009).

Present work investigates the degradation of Bismarck Brown (BB-Y). BB-Y is one of the diazo dye and has wide applications in staining of tissues, cells, bones, etc. The discharge concentration of diazo dye (BB-Y) in discharge waste stream is about 2-15% of total initial concentration use in the industries (Serponea et al. 2010; Wang and Wang 2010; Boczkaj and Fernandes, 2017). Photocatalytic degradation of BB-Y in the presence of ZnO, TiO₂, H₂O₂, potassium bromate and Fenton have been reported in the literature. These studies reported the initial concentration of 24 μM as an optimum initial concentration for degradation of BB-Y (Horikoshi et al. 2010; Devi et al. 2011; Hussien et al., 2010). This optimum concentration considered as initial concentration of BB-Y in the present investigation. The degradation of BB-Y investigated using effects MW, UV, and the sequential combination of MW and UV. Effect of a catalyst such as TiO₂, H₂O₂, and ZnO was studied. Total organic carbon was monitored to understand the effect of UV, MW, and additives on the removal of carbon from BB-Y wastewater.

2. Materials and methods

2.1. Materials

Bismarck Brown-Y (Color Index number: 21000, color: brown, molecular formula: C₂₁H₂₈N₈, molecular weight: 388.47 g mol⁻¹) purchased from Loba Chemicals Pvt. Ltd., Mumbai, India. The solution of Bismarck Brown-Y (BB-Y) prepared by dissolving dye in distilled water. Distilled water obtained from Millipore water distillation unit at AISSMS College of Engineering, Pune, India. The chemicals such as hydrogen peroxide (H₂O₂, 30% w/v), titanium dioxide (TiO₂ (IV), anatase phase, ≥99% purity), zinc oxide (ZnO, ≥99% purity), sulphuric acid (H₂SO₄, 98%), and sodium hydroxide procured from Merck Chemicals Ltd., Mumbai, India. Terephthalic acid, 2-hydroxyterephthalic acid (measurement of hydroxyl radicals) obtained from Sigma-Aldrich. All chemicals were gradient grade and used as received from suppliers.

2.2. Reactor details

The effect of MW on the degradation of BB-Y performed in a domestic microwave oven (Make: LG, Model No. MS-2029 UV) procured from the Medica Instrument Manufacturing Company, Pune, India. The capacity of the oven is 20 L, dimension: 455×260×320 mm, fixed frequency: 2450 MHz and power: 800 W. Calorimetric (power utilized to power input) study performed at the different microwave power input of 800, 640, 480, 320 and 160 W and volume of 50, 100, 150, 200, 250 and 300 mL. The maximum calorimetric efficiency (72.5%) was obtained at 160 W power and 250 mL as volume. All the experiments performed at these conditions. A hole of 3 mm in diameter drilled at the top of the oven for the introduction of a glass stirrer in microwave cavity (drilled part of oven brazed with an aluminum tube to avoid the microwave leakage). Stirring (speed: 400 rpm, Make: Remi, power: 120 W) was maintained for catalyst suspension, uniform distribution of microwave energy, and reaction-diffusion.

The experiments related to the effect of photocatalysis performed using two UV tubes (Make: Philips, Power: 11 W, and wavelength: 355-370 nm). The tubes placed on two adjacent sides of reactor cavity (dimension of the cavity around reactor: 100cm×100cm×100cm). To avoid diffusion of radiation from reactor assembly, the sides of reactor covered with a black sheet. A magnetic stirrer (make: Remi, power: 120 W, magnetic needle size: 1 cm) used for continuous stirring in the reactor (catalyst suspension and prevent the existence of mass transfer). The calorimetric measurement was performed to assess the power efficiency of UV reactor. The maximum calorimetric efficiency using two UV lamps and 250 mL of the volume was found to be 29.8%. The sequential experiments performed by exposing reaction mixture for several intervals under microwave and photolysis modes of study.

2.3. Experimental procedure

The 24 μM concentration of a BB-Y solution prepared by dissolving the quantity of dye in 250 mL of distilled water and stirred for 30 min. The pH of the solution adjusted using 1 N sulphuric acid and 1 N sodium hydroxide. A known amount of catalyst added in aqueous solution. Aqueous solution exposed to microwave and photolysis effects. The temperature of reaction mixture kept at 35±2°C. The temperature in microwave reactor maintained (operating under cyclic modes of 'on'

and 'off.')

An infrared thermometer (Make: Mextech, Model: DT-8811) used for measuring temperature in the reactor. Samples of 4 mL were withdrawn from the reaction mixture at fixed interval of time to record the progress of the degradation. The experiments were conducted for various concentration of catalysts and under the effects of UV, MW, sequential effects of MW followed by UV (MW/UV), and sequential effect of UV followed by MW (UV/MW). Initially, experiments were performed by varying catalyst concentration. Only results of optimum catalyst concentration loadings presented and discussed.

2.4. Analytical procedure

Chemito SPECTROSCAN UV 2600 spectrophotometer used for measuring the progress of degradation of BB-Y at 458 nm. The solutions with different concentrations over a range of 1-40 μM of BB-Y prepared for obtaining calibration curve and followed by analysis on a spectrophotometer. The concentration of unknown samples obtained from the calibration curve. Total organic carbon (TOC) of optimized conditions samples measured by using the Shimadzu TOC (Model: TOCLCPH) analyzer. The concentrations of hydroxyl radicals' production measured by a spectrophotometer. The procedure for measurement of TOC and hydroxyl radicals reported in earlier work (Gole and Alhat 2017).

3. Results and discussion

The experiments were performed by varying pH of the solution such as 2, 4, 6 and 8 for UV and MW. The results of degradation of BB-Y is shown in Fig.1. The maximum degradation obtained at pH 3 for both operations of microwave (MW) and photolysis (UV). The moles of BB-Y remaining for 180 min treatment at pH 3 was 21.8±0.21 μM (9.2±0.08%) and 16.6±0.15 μM (30.8±0.6%) for UV and MW respectively. The maximum degradation at lower pH related with zero-point charge (ZPC) (Boczkaj and Fernandes, 2017). With the increasing the pH of the solution, the adsorptions of the release of hydroxyl ion on the sites of targeted pollutant decreased compared to lower pH of the solution (ZPC for BB-Y: 3). Hydroxyl ions ('OH) are the main driving factor for degradation of BB-Y (Horikoshi et al. 2003; Devi et al. 2011). So, the pH 3 was considered as optimum for further studies. The concentration of hydroxyl radicals measured at pH 3. It has been observed that formation of 'OH radical' was higher for MW/UV effect compare to the individual effect of MW and UV. The moles 'OH radicals were 3.4 μM, 8.6 μM, 11.3 μM, and 10.4 μM for UV, MW, MW/UV, and UV/MW.

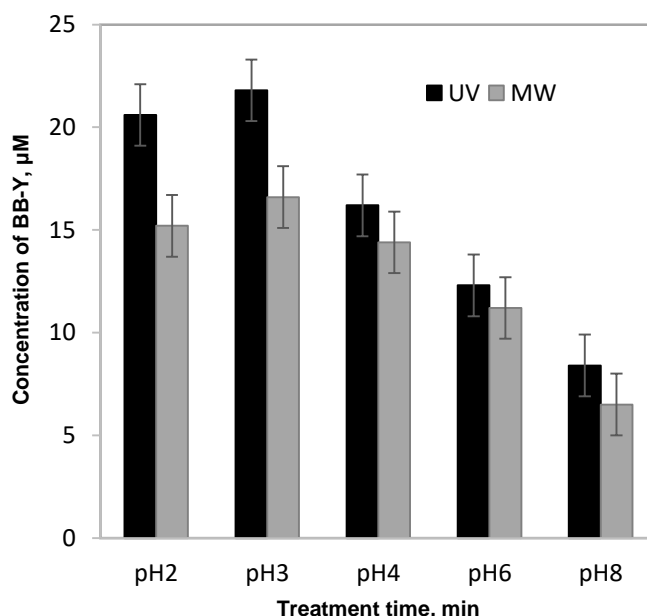


Fig. 1. Influence of photolysis (UV), microwave (MW), sequential combination MW followed by UV (MW/UV), and sequential combination of UV followed by MW on degradation of BB-Y.

3.1. UV, MW, MW/UV and UV/MW

Treatment of toxic pollutant depends on the formation of oxidants. The mechanism of generation of oxidants for both processes MW and UV is nearly same i.e. formation of holes and electrons (Horikoshi et al. 2014; Jung 2011). The efficiency of the process depends on the interaction/reaction of these oxidants with targeted pollutants (Zahra, 2017). The significant limitations associated with advanced oxidation process is a formation scavenging radicals and diffusion oxidation radicals from catalyst surface to the surface of targeted pollutants (Zhang et al. 2009). Comparative study of the performance of sequential combination with the single effect will be significant for intensifying the degradation of BB-Y.

The effect of UV, MW, MW/UV and UV/MW on the degradation of BB-Y studied (no catalyst), and results are illustrated in Fig. 2. Moles of BB-Y remaining in 140 min was $21.8 \pm 0.21 \mu\text{M}$ (9.2±0.08% removal), $16.4 \pm 0.15 \mu\text{M}$ (31.7±0.6% removal), $13.4 \pm 0.13 \mu\text{M}$ (44.1±0.5% removal), and $15.8 \pm 0.14 \mu\text{M}$ (34.2±0.6% removal) for UV, MW, MW/UV and UV/MW respectively. The results indicate that degradation rate is maximum for MW/UV compared to other effects. TOC removal at these conditions for UV, MW, MW/UV, and UV/MW was $3.1 \pm 0.03 \mu\text{M}$ (4.0±0.03% removal), $10.8 \pm 0.11 \mu\text{M}$ (14.1±0.14%), $12.6 \pm 0.14 \mu\text{M}$ (16.4±0.15% removal), and $11.5 \pm 0.15 \mu\text{M}$ (14.9±0.13% removal) respectively. The degradation of BB-Y is proportional to the rate of formation of oxidizing $\cdot\text{OH}$ radicals. The formation of these radicals depends on the mechanism of formation of radicals and subsequent reaction with targeted pollutants. The generation of $\cdot\text{OH}$ radicals resulted from the rapid interaction microwave with an aqueous solution. The rapid rotation of dipolar activity under microwave field and specific effects of microwave ('hot spot') increase the rate of $\cdot\text{OH}$ radical formation and other possible oxygen species (Zhang et al. 2009). Other effects of microwave such as superheating, polarization, nuclear spin rotations and spin alignment contribute to enhancing oxidation species. Non-thermal effects of microwave also contribute to increasing the reactant mobility and diffusion elimination between the target pollutant and hydroxyl radicals (Klán P. and Vavrik 2006; Wang and Wang, 2016). Generation of hydroxyl radicals during the photolysis process is well-known phenomena of generation of holes and electrons. The efficiency of photolysis process depends on the number of pairs of holes and electrons. The percentage degradation for UV is less than MW due to a lesser number of $\cdot\text{OH}$ radical formation and its subsequent reaction with BB-Y molecules. The major limitation associated with photolysis process is a recombination of $\cdot\text{OH}$ radicals which resulted into lower oxidation potential oxidation/scavenging radicals. The sequential combination of MW/UV and UV/MW can overcome the limitation associated with UV. The combination effect MW and UV is useful for reducing the recombination of hydroxyl radicals, and thus more oxidation radicals are available for degradation of BB-Y. The mechanism of formation of $\cdot\text{OH}$ radical formation depends on the combinational effect of MW and UV. For MW/UV effect, the molecular forces between H and $\cdot\text{OH}$ radicals became weak or relax more under rapid microwave field followed by dissociated under UV field. While in the case of UV/MW field, the lower penetration depth of UV, formed oxidation radicals may be recombined to formed scavenging radicals and may be resulted in lower degradation of BB-Y. Literature findings support our results, degradation of phenol for the combined effect of MW and UV increased by 21 times (compare to UV alone) and 13 times (compare to MW alone) (Klán and Vavrik. 2006).

3.2. Effect H_2O_2

The degradation efficiency of the process depends on the formation of oxidizing radicals. Hydrogen peroxide has strong oxidizing potential (Jung 2011). It quickly dissociated into the two moles of $\cdot\text{OH}$ radicals and other oxidizing radicals. The formation of these radicals depends on the O-O bond cleavage ($\text{H}_2\text{O}_2 + h\nu = 2\cdot\text{OH}$) and subsequent reaction with targeted pollutants. Thermal effects and rapid dipolar rotations of MW contribute to the dissociation of H_2O_2 molecules (Klán & Vavrik 2006). The mechanism of $\cdot\text{OH}$ radicals (effects of MW and UV) is a complex degradation chemistry.

Results of the effect of hydrogen peroxide on the degradation of BB-Y shown in Fig. 3. Results trends indicate that concentration of BB-Y decreased with time during initial of the phase of operation (100 min) and a further decrease in concentration was marginal. The degradation was highest for sequential combination approach of MW followed by UV compared to other methods. The moles of BB-Y remaining in 140 min for UV, MW, MW/UV, and UV/MW was $10.6 \pm 0.11 \mu\text{M}$ (55.8±0.5%

removal; catalyst concentration: 1 g L^{-1} , $13.7 \pm 0.14 \mu\text{M}$ (42.6±0.6%; catalyst concentration: 1.5 g L^{-1}), $7.5 \pm 0.08 \mu\text{M}$ (68.8±0.3% removal; catalyst concentration: 1.5 g L^{-1}), and $13.9 \pm 0.1 \mu\text{M}$ (45.4±0.5% removal; catalyst concentration: 1.5 g L^{-1}). The formation of hydroxyl radicals during UV, MW and combinational effect is highly dependent on the loadings of H_2O_2 . The higher catalyst loadings are required for MW and combination of MW and UV is due to the molecular level interaction of MW and higher dissipation of MW energy in for MW compared to UV. It results in higher degradation for MW, MW/UV and UV/MW compare to UV (Klán and Vavrik 2006; Jung 2011; Wang and Wang 2016). The similar trend observed for TOC removal. Moles of TOC removal in 140 min was $20.4 \pm 0.21 \mu\text{M}$ (26.5±0.27% removal), $14.5 \pm 0.16 \mu\text{M}$ (18.8±0.19% removal), $24.5 \pm 0.24 \mu\text{M}$ (31.9±0.3% removal), and $14.5 \pm 0.16 \mu\text{M}$ (18.8±0.19% removal) for UV, MW, MW/UV, and UV/MW respectively. The similar trend observed for degradation rate, the first order degradation rate constant was $(7.1 \pm 0.07) \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.92$), $(4.8 \pm 0.04) \times 10^{-3} \text{ min}^{-1}$ ($R^2=0.96$), $(11.6 \pm 0.1) \times 10^{-3}$, and $(5.2 \pm 0.05) \times 10^{-3}$ ($R^2=0.95$) for UV, MW, MW/UV, and UV/MW respectively. Increased in degradation for MW and MW/UV relates with dielectric properties of the distilled water and addition of hydrogen peroxide. The dielectric loss factor (represents dissipation of absorbed MW energy) for hydrogen peroxide is more than twice that of distilled water (Jung 2011). The addition of hydrogen peroxide increased the absorption of dissipated energy in an aqueous solution. In UV process cleaving of -O-O- bonds depends on absorption of UV radiation (Klán and Vavrik 2006; Sarmento and Miranda 2014). UV absorption of H_2O_2 is $\epsilon_{254} = 2850\text{-}3000 \text{ M}^{-1} \text{ cm}^{-1}$ which result in lower amount $\cdot\text{OH}$ radical formation with a quantum yield of 0.50 at 254 nm (Wang & Wang 2016). The formed radicals have a very short residence time in the range of picosecond (Gole and Alhat 2017). The nonthermal effects of MW can overcome the diffusion limitations between the $\cdot\text{OH}$ radicals and targeted pollutant, and they observed higher degradation for the MW/UV (Jung 2011). The lower degradation for MW may be due to quick evaporation of hydrogen peroxide (Serponea et al. 2010). The degradation studies of bisphenol-A observed that the sequential effect of MW/UV resulted in ~100 % degradation compared to effects of UV and MW. The enhancement in degradation for combinational effects was three times compare individual effects of MW and UV (Horikoshi and Serpone 2014b).

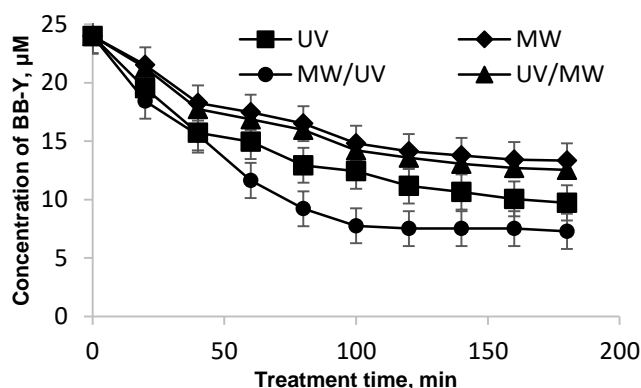
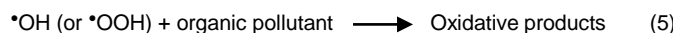
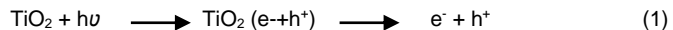


Fig. 2. Influence of photolysis (UV), microwave (MW), and sequential combination MW followed by UV (MW/UV) on degradation of Bismarck Brown - Y in the presence of hydrogen peroxide (initial concentration of BB-Y: $24 \mu\text{L}$, pH of the solution: 3, concentration of hydrogen peroxide for UV: 1 g L^{-1} , MW: 1.5 g L^{-1} , and MW/UV: 1.5 g L^{-1}).

3.3. Effect of TiO_2

TiO_2 is considered as a most versatile catalyst for enhancing the efficiency of photocatalysis process. It provides the higher surface area for increasing the activities of formation of holes and electrons which are useful for improving rate of the $\cdot\text{OH}$ radicals (Zahra 2017). Process efficiency of photocatalytic and microwave in the presence of TiO_2 depends on the number of active sites available for generation of hydroxyl radicals. With prolonged use of a catalyst, the active sites of TiO_2 surface blocked and decrease in the degradation of process observed (Ki et al. 2016). Sequential use of MW and UV may be useful for overcoming the limitation. The results of the effect of TiO_2 catalyst on the degradation of BB-Y have shown in Fig. 4. Results trends indicated that degradation of BB-Y decreased exponentially with time. Effect of MW and MW/UV have shown higher degradation in 100 min

then increase degradation was marginal. The moles of BB-Y remaining for UV, MW, MW/UV, and UV/MW in 140 min was $6.7 \pm 0.06 \mu\text{M}$ (71.9±0.3% removal; catalyst concentration: 0.1 g L^{-1}), $8.3 \pm 0.08 \mu\text{M}$ (65.5±0.3% removal; catalyst concentration: 0.5 g L^{-1}), $4.0 \pm 0.04 \mu\text{M}$ (83.3±0.4% removal; catalyst concentration: 0.1 g L^{-1}), and $6.6 \pm 0.07 \mu\text{M}$ (72.1±0.7% removal; catalyst concentration: 0.1 g L^{-1}). Photocatalytic degradation depends on the catalyst concentration, the presence of higher concentration of catalyst provides the additional surface area/active sites for the formation of hydroxyl radicals (Ki et al. 2016). Whereas, the presence of higher concentration of TiO_2 during microwave may increase the scattering effect and results in lower degradation (Zahra 2017). The similar trend observed for removal of TOC, moles of TOC removal in 140 min was $26.6 \pm 0.22 \mu\text{M}$ (34.6±0.31% removal), $22.8 \pm 0.19 \mu\text{M}$ (29.6±0.26% removal), $29.4 \pm 0.25 \mu\text{M}$ (38.2±0.32% removal), and $25.8 \pm 0.28 \mu\text{M}$ (33.6±0.28% removal) for UV, MW, MW/UV, and UV/MW respectively. The increase in the performance of process for sequential approach of MM/UV approach may be due to a) synergy effect between MW and UV, b) more hydroxyl radicals or oxidants generated for MW and UV compare to individual effects, and c) improved performance of the catalytic activity (Ki et al. 2016). When TiO_2 particle was illuminated by wavelengths larger than the bandgap energy of TiO_2 , then valence band electrons are excited to the conduction band, and holes are produced in the valance band. The life span of formed electron-hole pair in picoseconds and the recombination of the probability of pairs is much higher (Sarmento and Miranda 2014; Gole and Alhat 2017). Generated holes and electrons have the higher reactive oxidation and reduction potential. Anatase TiO_2 crystals have a bandgap of 3.20 eV which means UV source shorter than 387 nm wavelength creates an electrons-hole pair (Gole and Alhat 2017). Some of the generated holes may migrate to the surface and react with surface bound water molecules and formed hydroxyl radicals (reaction 2). The electron may react with dissolved electrons to yield to anions like $\text{O}_2^{\cdot-}$ (reaction 3) which on protonation to formed hydroperoxyl radicals $\cdot\text{OOH}$ (reaction 4). Photooxidation of BB-Y depends on the concentration of $\cdot\text{OH}$ radicals and $\cdot\text{OOH}$ radicals (Horikoshi and Serpone 2014a).



The mechanism of formation of hydroxyl radicals for UV and MW is nearly same, but the radical formation of $\cdot\text{OH}$ increased on the multifold basis compared to the effect of UV or MW (Horikoshi and Serpone 2014b). Study on the measurement of $\cdot\text{OH}$ radical in the presence of anatase TiO_2 showed that 30 % increase compared to UV effects and radical formation augmented to 40% with an increase in microwave power from 6 W to 16 W (Horikoshi et al. 2003). Improved in the efficiency of TiO_2 relates with the specific effects of the microwave. It is well-known that the rapid molecular interaction of MW led to frictions between the molecules ('hot spot') and released an enormous amount of heat. This effect contributes to the generation of oxidants and hydroxyl radicals. The specific effects of MW such molecular orientations, and change in the vibrational energies of molecules (useful for reducing the diffusion limitation), known as non-thermal effects of the microwave. These results are increasing the activity of TiO_2 catalyst or increasing the degradation of BB-Y (Horikoshi and Serpone 2014 a, b). The pseudo first order rate constant was $9.2 \pm 0.08 \text{ min}^{-1}$ ($R^2=0.97$), $10.9 \pm 0.09 \text{ min}^{-1}$ ($R^2=0.98$), $16.8 \pm 0.16 \text{ min}^{-1}$ ($R^2=0.96$), and $11.4 \pm 0.11 \text{ min}^{-1}$ ($R^2=0.94$) for UV, MW, MW/UV, and UV/MW respectively. Literature work supports our findings, degradation of 4- chlorophenol for MW, UV and MW/UV in the presence of TiO_2 as catalyst reported that degradation efficiency increased multi-fold basis compared to the individual effect of MW and UV. The pseudo-first order degradation constant of degradation of 4-chlorophenol for MW, UV and MW/UV was $0.0563 \times 10^{-2} \text{ min}^{-1}$, $0.052 \times 10^{-2} \text{ min}^{-1}$, and $2.755 \times 10^{-2} \text{ min}^{-1}$ respectively (Ki et al. 2016).

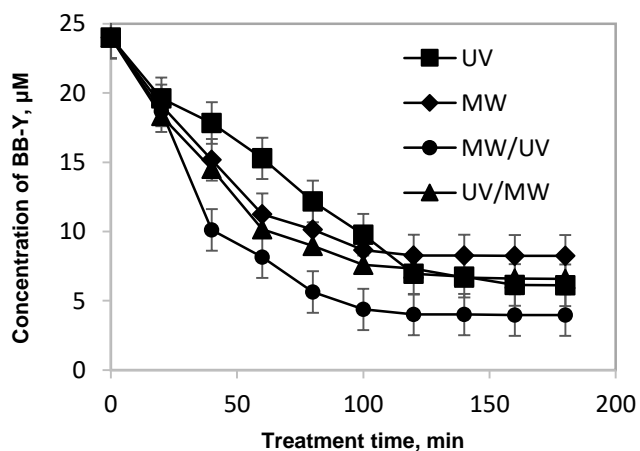


Fig. 3. Influence of photolysis (UV), microwave (MW), and sequential combination MW followed by UV (MW/UV) on degradation of Bismarck Brown - Y in the presence of titanium dioxide (initial concentration of BB-Y: $24 \mu\text{L}$, pH of the solution: 3, concentration of titanium dioxide for UV: 0.1 g L^{-1} , MW: 0.5 g L^{-1} , and MW/UV: 0.1 g L^{-1}).

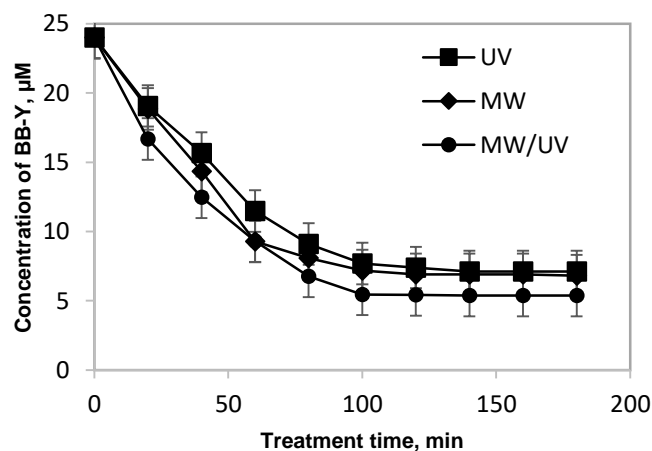
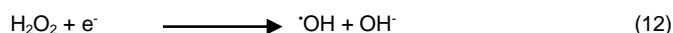
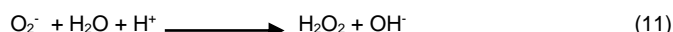
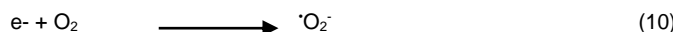
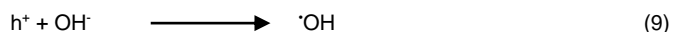
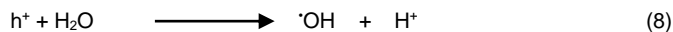
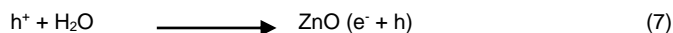
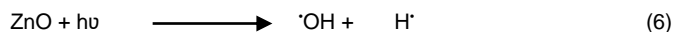


Fig. 4. Influence of photolysis (UV), microwave (MW), and sequential combination MW followed by UV (MW/UV) on degradation of Bismarck Brown - Y in the presence of zinc dioxide (initial concentration of BB-Y: $24 \mu\text{L}$, pH of the solution: 3, concentration of zinc peroxide for UV: 0.15 g L^{-1} , MW: 0.125 g L^{-1} , and MW/UV: 0.1 g L^{-1}).

3.4. Effect of ZnO

The photocatalytic efficiency is depending on the band gap energy and electron mobility on the catalyst surface (Ki et al. 2016). Zinc oxide has higher band gap energy (3.37 eV) compare to TiO_2 (3.2 eV). Zinc oxide had similar properties like TiO_2 and considered as more stable than photocatalyst than TiO_2 . ZnO has certain advantages over TiO_2 such as electron mobility of ZnO ($\sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is several order higher than that of TiO_2 ($> 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Mechanism of formation of electron and holes in the presences of ZnO is similar to TiO_2 . Equations 6-12 show the formation of oxidant/hydroxyl radicals formation (Horikoshi and Serpone 2014a; Riaz et al. 2016).



Experiments were conducted for various loadings of zinc oxide, and results of optimum loading of catalyst have shown in Fig. 5. The concentration of BB-Y is exponential decreasing with time, the maximum decrease in concentration occurred in first 100 min of operation further decrease in concentration was marginal or constant. The moles of BB-Y remaining in 140 min were $7.1 \pm 0.07 \mu\text{M}$ (70.3 \pm 0.7% removal; catalyst concentration: 0.15 g L^{-1}), $6.9 \pm 0.06 \mu\text{M}$ (71.3 \pm 0.6% removal; catalyst concentration: 0.125 g L^{-1}), $5.4 \pm 0.05 \mu\text{M}$ (77.6 \pm 0.5% removal; catalyst concentration: 0.1 g L^{-1}), and $6.3 \pm 0.06 \mu\text{M}$ (72.5 \pm 0.6% removal; catalyst concentration: 0.1 g L^{-1}) for UV, MW, and MW/UV respectively. The degradation of BB-Y highly depends on the concentration of zinc oxide, degradation increased with the optimum loading of zinc oxide and further increased in loading results in lower degradation. Higher loadings increased the scattering effect of UV light, the similar effect observed for the MW (Riaz et al. 2016). The removal of TOC was marginally same for individual operations of UV and MW and more for MW/UV. Moles of TOC removed for UV, MW, and MW/UV and UV/MW was $24.2 \pm 0.21 \mu\text{M}$ (31.5 \pm 0.34% removal), $24.8 \pm 0.22 \mu\text{M}$ (32.3 \pm 0.36% removal), $28.3 \pm 0.29 \mu\text{M}$ (36.8 \pm 0.32% removal), and $26.1 \pm 0.27 \mu\text{M}$ (33.9 \pm 0.28% removal). When results compared based on the rate of degradation, it has been observed that rate of degradation was maximum for MW/UV operation compare to MW and UV operations. The pseudo first order rate constant was $11.7 \pm 0.11 \text{ min}^{-1}$ ($R^2=0.99$), $13.2 \pm 0.13 \text{ min}^{-1}$ ($R^2=0.97$), $15.4 \pm 0.15 \text{ min}^{-1}$ ($R^2=0.99$), and $14.1 \pm 0.16 \text{ min}^{-1}$ ($R^2=0.99$) for UV, MW, MW/UV, and UV/MW respectively. The increase in degradation of BB-Y relates with the increased activity of the catalyst surface. The efficiency of UV and MW process depends on the activity of ZnO, and it decreases with prolonged use of a catalyst. The sequential combination of MW/UV is useful for production of oxidants in the presence of zinc oxide. The thermal and non-thermal of microwave effects are useful for increasing activity of catalyst (Riaz et al. 2016; Horikoshi and Serpone 2014a, b). A study on treatment of AR dye in the presence of zinc oxide reported the higher degradation for MW than UV. Under same loadings of ZnO and irradiation of MW and UV, the pseudo-first order rate constant was 0.005 min^{-1} and 0.052 min^{-1} for UV and MW respectively (Riaz et al. 2016).

The results confirmed that MW/UV sequential combination gives higher percentage degradation compare the effect of MW and UV. The degradation increased further in the presence of a catalyst such as H_2O_2 , TiO_2 , and ZnO. Analyzing the results in the presence of a catalyst with respective to effects of UV, MW, MW/UV, and UV/MW will be interesting. Comparative results of the effect of catalyst and UV, MW, MW/UV, and UV/MW showed in Figure 6. It has been observed that degradation in the absence of catalyst gives higher degradation for MW/UV followed MW, UV, and UV/MW. In the presence of catalyst higher degradation was observed. The efficiency process increased in the presence of photocatalyst (TiO_2 and ZnO) compare to the addition of hydrogen peroxide. H_2O_2 remains in the bulk of the solution, and maximum degradation occurred between the targeted pollutants and hydroxyl radicals' due to dissociation of H_2O_2 (Klan et al. 2006; Wang and Wang 2016). The formation of 'OH radicals during UV/ H_2O_2 system is highly sensitive to the pH of the solution (Horikoshi et al. 2004; Ki et al. 2016).

The possible reasons for increased degradation in the presence of photocatalyst are a) the process remains insensitive to the variation of

pH, b) MW affects the catalyst surface morphology (additional defects on catalyst surface), c) increment in catalyst surface hydrophobicity, and d) 'hot spots' generation on the photocatalyst surface due to the non-thermal effects of MW which may results in higher degradation of BB-Y under the ambient temperature conditions (Horikoshi & Serpone 2014; Riaz et al. 2016; Klan et al. 2006). The difference in degradation in the presences of TiO_2 and ZnO is due to different morphological properties of the photocatalyst, photocatalytic activity, catalyst concentration, and behavior of this catalyst under MW and UV. TiO_2 shown the higher degradation for UV and MW/UV compare to MW (Hussien et al. 2010; Ki et al. 2016). The degradation was greater for MW/UV, UV/MW and MW than UV in the presences of ZnO.

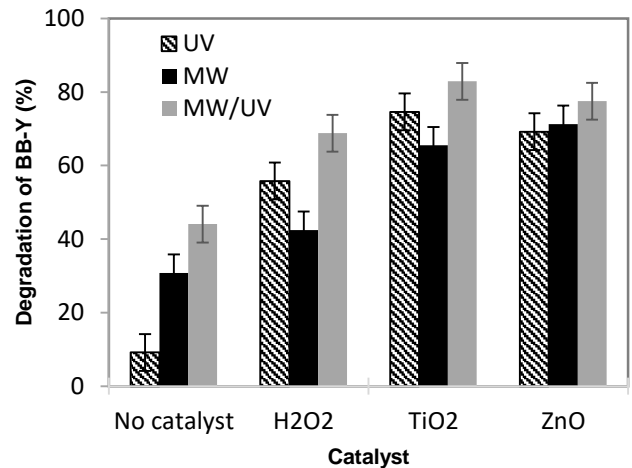


Fig. 5. Effect of catalyst and UV, MW and MW/UV on degradation of Bismarck Brown - Y in presence of zinc dioxide (initial concentration of BB-Y: $24 \mu\text{L}$, pH of the solution: 3, concentration of hydrogen peroxide for UV: 1 g L^{-1} , MW: 1.5 g L^{-1} , and MW/UV: 1.5 g L^{-1} ; concentration of titanium dioxide for UV: 0.1 g L^{-1} , MW: 0.5 g L^{-1} , and MW/UV: 0.1 g L^{-1} ; concentration of zinc peroxide for UV: 0.15 g L^{-1} , MW: 0.125 g L^{-1} , and MW/UV: 0.1 g L^{-1}).

4. Conclusions

Present work confirms that inexpensive technology based on a sequential combination of MW and UV is highly useful for enhancing the rate of degradation of BB-Y. The degradation rate was further increased in the presence of a catalyst. The highest degradation rate obtained was in the presence of TiO_2 (degradation: $82.9 \pm 0.4\%$, and rate constant: $16.8 \pm 0.16 \text{ min}^{-1}$) compared to ZnO (degradation: $77.5 \pm 0.5\%$, and rate constant: $15.4 \pm 0.15 \text{ min}^{-1}$), and H_2O_2 (degradation: $68.8 \pm 0.3\%$, and $11.6 \pm 0.1 \text{ min}^{-1}$). Synergic effects of MW and UV was found to be more beneficial for enhancing the rate of degradation. Present work will be highly useful for the development of technologies for the treatment of environmental persistence compounds.

References

- Devi L.G., Raju K.S. A., Kumar S.G., Rajashekhar K.E., Photodegradation of di azo dye Bismarck Brown by advanced photo-Fenton process: Influence of inorganic anions and evaluation of recycling efficiency of iron powder, Journal of Taiwan Institute of Chemical Engineers 42 (2011) 341-349.
- Gole V. L., Alhat A., Treatment of malachite green dye using combined oxidation techniques based on different irradiations, Korean Journal of Chemical Engineering 34 (2017) 1393-1399.
- Horikoshi S., Hidaka H., Serpone N., Hydroxyl radicals in microwave photocatalysis. Enhanced formation of OH radicals probed by ESR techniques in microwave-assisted photocatalysis in aqueous TiO_2 dispersions, Chemical Physics Letters 376 (2003) 475-480.
- Horikoshi S., Tokunaga A., Hidaka H., Serpone N. Environmental remediation by an integrated microwave/UV illumination method VII. Thermal/non-thermal effects in the microwave-assisted photocatalyzed mineralization of bisphenol-A, Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 33-40.
- Horikoshi S., Serpone N., On the influence of the microwaves' thermal and non-thermal effects in titania photoassisted reactions, Catalysis Today 224 (2014) 225-235.
- Horikoshi S., Serpone N., Coupled Microwave/Photoassisted Methods for Environmental Remediation, Molecules 19 (2014) 18102-18128.
- Hussien F.H., Halbus A.F., Hasssan H.A.K., Hussein W.A.K. Photocatalytic Decolourization of Bismarck Brown-G Using Irradiated ZnO in Aqueous Solution, E- Journal of Chemistry 7 (2010) 540-544.
- Jung S.C., The microwave-assisted photo-catalytic degradation of organic dyes, Water Science and Technology 63 (2011) 1491-1498.

- Ki S.J., Jeon K.J., Park Y.K., Jeong S., Lee H., Jung S.C., Improving removal of 4-chlorophenol using a TiO₂ photocatalytic system with microwave and ultraviolet radiation, *Catalysis Today* 293-294 (2016) 15-22.
- Klán P., Vavrik M. Non-catalytic remediation of aqueous solutions by microwave-assisted photolysis in the presence of H₂O₂, *Journal of Photochemistry and Photobiology A: Chemistry* 177 (2006) 24–33.
- Riaz U., Ashraf S. M., Budhiraja V., Aleem S., Kashyap J. Comparative studies of the photocatalytic and microwave assisted degradation of alizarin red using ZnO/poly (1- naphthylamine) nanohybrids, *Journal of Molecular Liquids* 216 (2016) 259-267.
- Sarmiento S.M. and Miranda J.T.G., Kinetics of the atrazine degradation process using H₂O₂-UVC, *Water Science and Technology* 69 (2014) 2279-2286.
- Serponea N., Horikoshi S., Emeline A.V. Microwaves in advanced oxidation processes for environmental applications. A brief review, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 11(2010) 114-131.
- Shaykhi Mehrabadi Z., Performance of advanced oxidation process (UV/O₃/H₂O₂) degrading amoxicillin wastewater: A comparative study, *Journal of Applied Research in Water and Wastewater* 5 (2016) 222-231.
- Wang N., Wang P. Study and application status of microwave in organic wastewater treatment - A review, *Chemical Engineering Journal* 283 (2016) 193-214.
- Zhang L., Su M., Liu N., Zhou X., Kang P. Degradation of malachite green solution using combined microwave and ZnFe₂O₄ powder, *Water Science and Technology* 60 (2009) 2563-2569.