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# **Graphical Abstract**



# Sonophotocatalytic treatment of Bismarck Brown G dye and real textile

effluent using synthesized novel Fe(0) doped TiO<sub>2</sub> catalyst

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# Sonophotocatalytic treatment of Bismarck Brown G dye and real textile effluent using novel synthesized Fe(0) doped TiO<sub>2</sub> catalyst

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#### Abstract

Using the novel Fe(0)-TiO<sub>2</sub> doped catalyst, the degradation of bismarck brown G dye was compared by means of advanced oxidation processes such as sonolysis (13 mm and 25 mm probe tip diameter), photolysis (UV light) and sonophotolysis. The effect of initial dye solution pH, H<sub>2</sub>O<sub>2</sub> concentration, gas bubbling (Argon, Oxygen, Air and Nitrogen), dye concentration and reaction volume were studied. Understanding the degradation mechanism from these studies, the bismarck brown G dye treatment was further intensified by catalytic treatment such as commercial TiO<sub>2</sub>, synthesized Fe(0) and synthesized Fe(0) doped TiO<sub>2</sub> under sonolytic, photolytic and sonophotolytic irradiations. SEM, TEM, XRD and DRS characterization study of the sonolytically synthesized catalyst shows that they were of uniform in shape, nanoscale in size and good absorption properties. Among the processes studied, sonophotocatalytic treatment of bismarck brown G dye in presence of Fe(0) doped TiO<sub>2</sub> showed highest colour removal with lesser catalyst addition and for larger reaction volume. The practical applicability of the synergistic effects with real textile effluent signifies that the studied process is highly efficient for safer environment.

*Keywords:* Bismarck Brown G dye, Fe(0) doped  $TiO_2$ , Ultrasound, UV light, Real textile effluent treatment

#### 1. Introduction

The textile industry is one of the largest water consuming industries as there are different processes involved, which ultimately discharges wastewater with unconsumed dyes and other chemicals. Among textile dyes, azo dyes are well-known for carcinogenic organic substances wherein the reductive cleavage of its azo linkage produces aromatic amines that lead to cancer in human liver. The control and efficient removal of these dye pollutants from textile wastewater is an important measure of environmental protection [1]. Electrocoagulation, adsorption, biodegradation, chlorination and ozonation are the frequently used primary methods for the removal of dye compounds from wastewater [2-4]. However, these treatment processes are non-destructive as the pollutants are only transferred from one phase to another, thus requiring additional method to achieve the complete detoxification of the environment. Moreover, in general, the primary degradation products of azo dyes are aromatic amines, which are toxic, carcinogenic, and teratogenic [5,6]. Advanced oxidation processes (AOPs) emerge as an alternative that quickly, directly and non-selectively oxidizes a broad range of organic pollutants based on the generation of very reactive species for example, hydroxyl radicals (\*OH) [7,8].

In recent years, the application of ultrasonic energy for an AOP has drawn attention to solve problems associated with conventional non-destructive wastewater treatment. Cavitation science and engineering is a field involving the application of ultrasonic waves to chemical processing despite its high cost of electrical consumption [9]. Ultrasound (US) irradiation causes acoustic cavitation through which micro sized bubble grows and collapses causing intense local heating, high pressures, and very short lifetimes of bubbles; these transient, localized hot spots drive high-energy chemical reactions [10]. The result of it is the splitting of water molecules into homogeneous radicals (H<sup>•</sup> and <sup>•</sup>OH) within or out of the bubbles through cavitation [11-13].

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The efficiency of the AOP treatment methods depends on the rate of generation of free radicals and the degree of contact with the contaminants. When these two parameters are maximized the treatment efficiency would attain its maximum. In this view, process integration is conceptually advantageous in wastewater treatment since it can eliminate the disadvantages associated with each individual process [14,15]. Although photocatalysis and sonolysis have been extensively employed individually for the degradation of several organic species in water, the studies on their combined use (i.e. sonophotocatalysis) has been limited. Coupling of ultrasound irradiation with other AOPs such as  $TiO_2$  photocatalysis has produced a synergistic effect in those systems on formation of active species [16,17]. Researchers have used sonophotocatalysis in a variety of investigations i.e. from water decontamination to direct pollutant degradation. This process provides an excellent opportunity to reduce reaction time and the amount of reagents used without the need for extreme physical conditions. Given its advantages, the sonophotocatalytic process has a futuristic application from an engineering and fundamental aspect in commercial applications [18]. Several studies involving high frequency ultrasound have focused on the combinative or hybrid techniques (i.e., the methods of using ultrasonic irradiations in combination with other advanced oxidation methods and/or biological treatment) since such novel techniques have proven to be more advantageous than ultrasound alone in effectively degrading recalcitrant contaminants.

The mechanism of this sonophotocatalysis effect is attributed to (a) activation of the photocatalyst surface, (b) enhancement of the mass transport of organic compounds, and (c) aggregate breakage [19]. The degradation of azo dye in aqueous solution using zero valent iron represents a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems [20-22].

Mineralization and recovery of catalyst employed is more desirable than mere decolourisation in view of environmental safety. Unfortunately, most discoloration methods are unable to remove total organic carbon (TOC) efficiently.

In this work, commercial TiO<sub>2</sub>, green synthesized Fe(0) and Fe(0) doped TiO<sub>2</sub> has been used as a catalyst for sonophotocatalytic degradation of an azo dye, Bismarck Brown G (or Basic Brown 1). Various studies reveal that the addition of nanoparticles has enhanced the degradation of pollutants through oxidation path [23-27]. When employing a catalyst, both oxidation and reduction of the pollutant take place (H<sup>•</sup> mediated reduction pathway, sonolysis of noble metal ions to form noble metal nanoparticles) [10,28]. Initially, a series of experiments were carried out by varying initial dye solution pH, H<sub>2</sub>O<sub>2</sub> concentration, gas bubbling (Argon, Nitrogen, Oxygen and Air), dye concentration and reaction volume to understand the mechanism of degradation of the dye under ultrasonic and ultraviolet light irradiations. With the analysis of these experimental results, the dye treatment was performed with the said catalyst which could demonstrate that enhanced <sup>•</sup>OH mediated oxidation as well as H<sup>•</sup> mediated reduction play a significant role in the acceleration (sonophotolysis) of dye degradation. This study provides a way to increase the efficiency of sonophotocatalysis and also helps to understand the mechanism of degradation of the dye using catalyst. Further, the sonophotocatalytic study is extended with the application of the synthesized catalysts with real textile effluent collected from textile industry after preliminary physical treatment.

#### 2. Experimental

# 2.1. Materials

TiO<sub>2</sub> (Degussa P25, Germany) having a specific surface area of 57 m<sup>2</sup> g<sup>-1</sup> was used as a starting material to prepare Fe(0) doped TiO<sub>2</sub>. Bismarck Brown G (BBG) was obtained from Sigma-Aldrich and used as supplied. BBG is a certified biological stain, for microscopy, histology and cytology and also used in textile industries. High purity analytical reagents were used for the sample solution preparation: Hydrochloric acid (Merck), Sodium Hydroxide (Merck), Hydrogen Peroxide solution (30% w/w, Merck), Ferrous sulphate FeSO<sub>4</sub>.7H<sub>2</sub>O (Merck). All reagents used were of analytical grade and the solutions were prepared using Millipore water.

# 2.2 Synthesis of Sonocatalysts

#### 2.2.1 Zero Valent Iron

The green synthesis of zero valent iron using polyphenols as the reducing agent has been illustrated by many research works [29]. In this study, the reaction of ferrous sulphate with green tea extract as polyphenol source forms the basis for the preparation of zero valent iron. Green tea extract was brewed by heating green tea leaves to 80°C followed by vacuum filtration. Green tea synthesized nanoscale zero-valent iron (ZVI) was then prepared by mixing 0.5M FeSO<sub>4</sub>.7H<sub>2</sub>O and green tea in a 2:1 volume ratio, resulting in the final ZVI solution. Later, the solution was centrifuged for 10 min at 6000 RPM by which the pellet remained has been washed twice with deionised water. The resultant ZVI was then dried in hot air oven for 24 hrs at 105° C [22].

#### 2.2.2 Zero Valent Iron Doped TiO<sub>2</sub>

ZVI doped TiO<sub>2</sub> catalyst was prepared by sonication method. TiO<sub>2</sub> (P25 degussa) was mixed with the aqueous solution of  $FeSO_4 \cdot 7H_2O$  (5 atomic weight %). The mixture was sonicated for 30 mins to allow the penetration of ZVI (Fe(0)) ions on the titanium dioxide crystal matrix. The supernatant liquid (water) is evaporated by heating at 105°C over a time period of 24 hrs [30].

# 2.2.3 Characterization of synthesized catalysts

The morphological characteristics of synthesized ZVI and TiO<sub>2</sub> doped ZVI were studied using scanning electron micrograph (SEM) and transmission electron micrograph (TEM). The images were obtained using SEM with an accelerating voltage of 3 kV. The magnification was adjusted so as to visualize the shape of ZVI and also the effect of TiO<sub>2</sub> doping on ZVI. UV-Visible diffuse reflectance Spectra (DRS) for the catalysts, TiO<sub>2</sub>, Fe(0) and Fe(0) doped TiO<sub>2</sub> were recorded to understand the absorption capacity of the catalysts studied. The crystallite sizes of prepared catalysts were determined with the help of X-ray diffractometer. X-ray diffractometer (XRD) were recorded by the radiation source of Cu K $\alpha$  (40 kV, 30 mA) and NaI as the detector. The powder samples were analyzed in 20 range from 10° to 80°. The particle size (D) of ZVI and TiO<sub>2</sub> doped ZVI were found using the Debye–Scherrer formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad \text{eq.1}$$

Where,  $\lambda$  is the x-ray wavelength,  $\beta$  represents full-width half maximum (FWHM) obtained at a corresponding 20 angle.

# 2.3 Degradation study procedure

The experimental setup consists of a 100 ml glass reactor to hold the BBG dye solution with a water cooling jacket to keep the reactor contents at constant temperature ( $27 \pm 0.5$  °C). Sonication probe (SONICS Vibra-cell, VCX 500) with a titanium tip (13 and 25 mm dia.) which emits ultrasound waves at 20 kHz and delivers a set power output of 100W is used for all the experiments. For photolytic experiments, 4 W UV lamps emitting light at 256 nm was used.

1000 ppm of the BBG dye stock solution was prepared by dissolving 1 g of dye in 1000 ml of Millipore water and from the stock solution required concentration of BBG was prepared. The initial pH of the BBG solution was altered as 2, 3, 4, 5, 6, 7, 8, 9 and 10 by adding either 0.1 N hydrochloric acid solution or 0.1 N sodium hydroxide solution. For gas bubbling study, the BBG solution was purged with different gases such as Oxygen, Argon, Nitrogen and Air for a duration of 5 minutes in order to make the solution saturated with the respective gas nuclei prior to sonolysis or photolysis [31]. The initial dye concentration was varied as 10, 50 and 100 ppm. The reaction volume variation study was also performed to identify the effectiveness of the sonolysis, photolysis and sonophotocatalysis processes so that the studied process could be employed for field applications. Three different jacketed reactors of capacity 100, 500 and 1000 ml were used. The treatment of dye with catalysts was done by varying the load from 0.1 to 1 g. It needs to be mentioned that each of the experiments were done thrice and the mean of them has been reported.

Based on the experimental results of the model dye (i.e. BBG), efforts were made to employ the sonophotocatalytic process to real textile effluent treatment. For this, the textile effluent was collected from textile industry after preliminary treatment. The physical and chemical characteristics of the collected textile effluent were studied as per standard methods (APHA 1998). The decolourization of BBG and the textile effluent were monitored for every 15 min. with intermittent sampling.

#### **Analytical procedure**

The optical absorption spectra of the BBG dye solutions were recorded by JASCO UV-Visible spectrophotometer with a quartz cuvette of 10 mm path length. The maximum peak for the absorption spectra of BBG dye is 447 nm. In order to quantify the degree of degradation, COD (closed reflux method as per standard methods: APHA 1998) analysis of the treated textile effluent was performed.

#### 3. Results and Discussion

# 3.1. Effect of pH

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Decolourization of the BBG dye aqueous solution was carried out at various initial pH's (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 & 10.0). Figure 1 shows that the initial solution pH has a remarkable influence on the decolourization efficiency (BBG: 10 ppm, Reaction Volume: 100 mL, Treatment time: 60 min.). The UV-Vis spectral variation of BBG dye at different time interval under ultrasound irradiation (pH 4, 13 mm probe) is also shown in the figure. The decolourization of the dye is highest when the initial pH of the aqueous solution is 4.0 and lowest at an initial pH of 10 for all the conditions studied (13 mm, 25 mm and UV irradiation). Among all, 25 mm probe has resulted in giving highest colour removal of 66 % followed by 13 mm probe and it is lower for UV irradiation for all pH variations when compared to US treated dye solution. The factor that had influenced higher colour removal with US treated dye is the ultrasound power which is set as 100W whereas in the case of UV it is only 4W. Sonication probe with larger diameter (25 mm) have larger irradiating area and provides better energy

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dissipation than smaller diameter probe (13 mm). Also, for the same power output the ultrasound

intensity produced with 25 mm probe would be higher than with 13 mm probe. The number of cavitational events would be higher with larger areas of irradiating surface leading to increased 'OH radical production for the same conditions [32]. This helps in effective treatment of the BB1 dye solution as the 25 mm probe makes it cavitationally more active volume for the given input power than 13 mm probe. In acidic conditions the lone pairs of electrons present on the nitrogen atoms of amino groups of BBG dye would be protonated and it was reported that under this state the oxidation reaction was highly favoured at lower pH values and the oxidation reaction rate decreases at higher pH values [1]. It is observed that the decolourization rate had decreased with increased initial solution pH (beyond pH 4) for all the cases which is due to the deprotonation of lone pairs of electrons present on the nitrogen atoms of amino groups.

# **3.2.** Effect of hydrogen peroxide dosage

The addition of hydrogen Peroxide which can act as the activator and strong oxidant having an oxidation potential of 1.78 eV would result in the additional production of hydroxyl radicals upon ultrasound and UV irradiation. The resulting hydroxyl radicals (oxidation potential: 2.80 eV) are the major cause of the increasing oxidation reaction. The effect of hydrogen peroxide concentration on the removal of the BBG is shown in Fig. 2. Experiments are conducted by varying  $H_2O_2$  from 300 to 2100 ppm (BBG: 10 ppm, pH: 6.04, Reaction volume: 100 ml, Treatment time: 60min). When the concentration of  $H_2O_2$  is increased from 300 to 900 ppm, the decolourization efficiency has increased from 28 to 59 % for 13 mm probe and 33 to 70 % for the 25 mm probe. For UV treated aqueous solution the decolourization efficiency varied from 15% to 42% from 300 to 2100 ppm. Maximum decolourization is achieved at 900 ppm of

 $H_2O_2$  for US irradiation irrespective of the probe tip diameter and at 2100 ppm for UV irradiation. The addition of  $H_2O_2$  concentration exceeding 900 ppm and 2100 ppm reduced the decolourization efficiency for US and UV irradiation. This may be attributed to the auto decomposition of  $H_2O_2$  to oxygen and water, and the recombination of produced 'OH radicals [33]. Moreover, higher concentrations of  $H_2O$  act as free-radical scavenger itself, thereby decreasing the concentration of 'OH radicals and reducing compound elimination efficiency [27]. For UV treated aqueous solution, optimum  $H_2O_2$  concentration is on the higher side (2100 ppm) than US treated aqueous solution (900 ppm). US has the advantage over UV that mere sonication itself produces 'OH radicals in addition to the 'OH radicals produced through  $H_2O_2$  splitting whereas UV's only resource for producing 'OH radicals is  $H_2O_2$ .

#### 3.3 Effect of gas bubbling

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The gases Oxygen, Argon, Nitrogen and Air are bubbled one at a time for 5 minutes in the BBG aqueous solution (BBG – 10 ppm, pH – 6.04, Reaction volume – 100 ml, Treatment time: 60 min) prior to irradiation so as to make the solution saturated with the respective gas nuclei. The maximum decolourization was observed for argon bubbled dye solution for both sonolysis and photolysis treatment and the least decolourization occurs for nitrogen bubbled dye solution (Fig. 3). In sonolysis process dissolved gases form the nuclei for cavitation. Argon bubbled gas gave higher colour removal due to its inert nature and higher specific heat capacity ratio. At the time of cavitation bubble collapse higher temperatures and pressures are generated [9] with monoatomic gases with higher specific heat capacity ratio ( $\gamma$ ) than those with polyatomic gases with lower heat capacity ratio ( $\gamma$ ). Unlike other gases of study, argon bubbled nuclei doesn't undergo any radical scavenging reactions. In addition to thermal dissociation of

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oxygen molecule leading to generation of hydroxyl radicals in the oxygen bubbled dye solution, inside the cavitation bubble oxygen scavenges hydrogen atom to form hydroperoxyl radical which is an oxidizing agent. This radical causes a number other reactions to occur, resulting in the formation of H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, O and H<sub>2</sub> as products [34]. Formation of atomic nitrogen and oxygen, nitrogen fixation can occur in the cavity bubbled with an air bubbled dye solution. Whereas in nitrogen bubbled dye solution, nitrogen molecules inside the cavitation bubble may react at high temperature with hydroxyl radicals and oxygen atoms to give nitrous oxide and nitrogen oxide [35] thus reducing the activity of 'OH radical with BBG molecules. This leads to the reduced colour removal with nitrogen nuclei when compared with other gas nuclei. It also observed that gas bubbling has minimal effect on the simple photolysis process which is evident that in sonolysis process the gas content is the major drive for the production of 'OH radicals.

# 3.4 Effect of initial dye concentration and reaction volume variation

The decolourization efficiency for different initial dye concentrations shows (Fig.4A) that the efficiency gradually decreases with increase in initial dye concentration (pH - 6.04), Reaction volume – 100 ml, Treatment Time: 60 min.). This shows that the amount of 'OH radicals produced by individual processes were not sufficient enough to interact with increasing concentration of dye molecule. Sonolysis treatment has resulted in higher colour removal than photolysis treatment irrespective of dye concentration. In photolysis process, when the dye concentration was increased, the dye starts acting as an internal filter and as a result, the rate of decolourization of dye decreases. The increasing dye concentration leads to shield the entering photons in solution and as a result, the rate of decolourization decreases due to reduction in hydroxyl radical ('OH) formation [36].

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The study with varying reaction volumes of the dye solution is performed to understand the intensity of the treatment methods undertaken since for real time application of these systems needs to handle larger volumes of textile effluents. The decolourization efficiency for different volume of dye solution for the treatment time of 60 minutes is shown in Fig.4B (BBG -10 ppm, pH - 6.04, Treatment Time: 60 min). For mere sonolysis and photolysis treatment, the increase in the reaction volume of the dye had reduced the rate of decolourization. This shows that both sonolysis and photolysis were not effective when it comes to larger volumes. In the case of sonolysis, whether it is 13 mm probe or 25 mm probe, the effective irradiation area is restricted near to the surface of the probe tip. Also, the frequency used in this case is 20 kHz, the length of the frequency and its intensity is only 6 cm. This means that for the rest of the volume mere mixing occurs and that the volume of dye solution does not undergo cavitation reaction. This indicates that with the increase in distance from the irradiation source the intensity of ultrasound decreases. In the case of photolysis, the same concept holds good that the UV radiation can't reach the whole volume of the solution unless the solution is vigorously stirred to bring in effective contact of the solution with UV light. These reasons limits the effectiveness of production of <sup>•</sup>OH radicals required to act on the dye molecules and hence, these systems resulted in reduced decolourization efficiency for larger volume reactors.

#### Summary of the results

The pseudo first order rate constant values for the studies performed were listed in Table 1. From the above studies the following points were to be considered for efficient treatment of BBG dye:

- From pH study, it is understood that the BBG dye should be in hydrophobic form (or the BBG dye is more hydrophilic) to have effective an interaction between BBG molecule with the produced 'OH radicals at the point of the cavitation event or photolytic reaction.
- From H<sub>2</sub>O<sub>2</sub> study, it is understood that when the number of 'OH radicals are increased in bulk liquid medium upon H<sub>2</sub>O<sub>2</sub> splitting (either through US or UV irradiation) efficient colour removal is achieved. The colour removal achieved by this method is the highest among the parameters studied wherein the production of 'OH in the bulk liquid medium is instantaneous than compared to gas bubbling.
- From gas bubbling study, when the gas nuclei is monatomic (argon gas producing more 'OH radicals) there exists a good colour removal followed by other gas nuclei's (Oxygen, Air & N<sub>2</sub>). Again, this study shows the importance of 'OH radical production (or the availability of 'OH radicals in the bulk liquid medium) for better treatment.
- From the initial concentration study, with increase in initial dye concentration the available 'OH radicals for oxidation reaction has significantly reduced providing lower colour removal under the same experimental conditions. This is a further indication that the chosen dye is highly hydrophilic.
- From volume variation study, there is a reduced colour removal rate with increased volume of the dye solution showing the limitations of the US and UV treatment processes that individual processes can't hold good for larger volumes.

For efficient colour removal of BBG dye, it can be said that there should more of 'OH radicals in the bulk liquid medium and with the amount of energy spent and the chemicals used for both the processes, a better method is required to reduce the overall cost and at the same time to achieve better efficiency in a shorter duration. This is the motivation behind to undergo catalyst preparation for the processes studied for BBG dye colour removal.

#### 3.6 Catalyst characterization

#### **3.6.1 SEM and TEM analysis**

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The SEM and TEM images of ZVI showed clustered aggregates representing their crystalline cubic indices as visualised in Fig.5A & 5B. The doping of Fe(0) on the TiO<sub>2</sub> crystal matrix has been clearly identified by the homogenous distribution of TiO<sub>2</sub> with Fe(0). The agglomeration observed in both the images (ZVI doped TiO<sub>2</sub> and ZVI) is due to the Vanderwaals forces among the magnetic Fe(0) particles and higher band gap energy of TiO<sub>2</sub> particles. The high rate of Fe(0) doping is evident as the doping reaction takes place efficiently in a solution rather than in a solid state of Fe(0). The influence of doping on the particle size has been identified by XRD spectra and it is in good agreement with the SEM and TEM images.

#### 3.6.2 XRD analysis

XRD spectra of Fe(0) and Fe(0) doped TiO<sub>2</sub> as shown in Fig.5C represents that the doping of Fe(0) with TiO<sub>2</sub> has changed the crystalline behaviour and also the size. It was found that the doping of TiO<sub>2</sub> has caused the increase in particle size of the doped catalyst. From the scherrer equation, the grain size of synthesized Fe(0) was 13.9 nm which has been determined to

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be increased to 21.4 nm for Fe(0) doped TiO<sub>2</sub> owing to the doping effect. The peaks of Fe(0) representing the Miller indices of (110) and (211) are characteristics of Fe(0) which are found at the 2 $\theta$  angle of 28.75° and 45.76° respectively. However, TiO<sub>2</sub> doping has been clearly confirmed by the reduced Fe(0) characteristic peaks and also by high intensity anatase peaks (2 $\theta$  = 25.36°, 48.73°) with lesser rutile peaks (2 $\theta$  = 27.5°, 37.7°). The pure TiO<sub>2</sub> constitutes the most active anatase and also some of the other crystalline rutile phases [37]. The replacement of Fe(0) in the crystal framework of TiO<sub>2</sub> has been attributed to the reduction of the rutile phases thereby suggesting the active doping. It is also due to the reduction in the oxygen vacancies on the TiO<sub>2</sub> surface that inhibits the crystallization of other phases [38]. However, the formed Fe ion were not of complete metallic form (i.e. Fe(0)) based on XPS data (see the supplementary file) and much of the Fe were in oxidized state (i.e. Fe<sub>2</sub>O<sub>3</sub>). The grain size of Fe(0) and Fe(0) doped TiO<sub>2</sub> from the XRD spectra were calculated using Debye–Scherrer equation and were found to be 13.9 nm and 21.4 nm.

#### 3.6.3 UV-Vis DRS analysis

The UV-Vis diffuse reflectance spectra of the TiO<sub>2</sub>, Fe(0) and Fe(0) doped TiO<sub>2</sub> was shown in Fig.5D. The DRS analysis shows that the % transmittance is decreasing in the order of TiO<sub>2</sub>>Fe(0)>Fe(0) doped TiO<sub>2</sub>. It can be inferred from the spectra that Fe(0) doped TiO<sub>2</sub> exhibits a higher light absorption both in visible and ultraviolet range than TiO<sub>2</sub> and Fe(0). Similar kinds of results were reported by several authors [39-42].

#### 3.7 Decolourization study with Catalyst

The commercial  $TiO_2$  and the synthesized catalyst (Fe(0) and Fe(0) doped  $TiO_2$ ) were subjected to BBG dye colour removal under ultrasound and UV irradiations. The results were presented in the following sections.

3.7.1 TiO<sub>2</sub>

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TiO<sub>2</sub> catalyst has been widely as a semiconductor photocatalyst which under UV irradiation excites creating electron hole pair splitting the water molecules into H' and 'OH radicals. Adsorption of the pollutant also occurs with the addition of TiO<sub>2</sub>. Hence, the combined effect of adsorption of the pollutant on TiO<sub>2</sub> surface and the 'OH radical production leads to efficient degradation [43]. Fig.6 shows the decolourization of BBG dye upon US and UV irradiation with varying TiO<sub>2</sub> concentration (BBG - 10 ppm, pH - 6.04, Reaction volume - 100ml, Reaction time: 60 min). When compared to other treatment methods (i.e. initial pH variation, Gas bubbling,  $H_2O_2$  concentration variation and volume variation) the decolourization rate of UV irradiated solution showed lesser differences with US irradiation. But the decolourization efficiency showed a larger increase than with all the previous treatment methods studied. The decolourization efficiency has reached maximum with 0.75g TiO<sub>2</sub> addition and with further increase in TiO<sub>2</sub> the decolourization efficiency was nearly constant and it had slowly started to reduce with an increase in TiO<sub>2</sub> amount. After a certain concentration, the TiO<sub>2</sub> would form a cluster obstructing UV irradiation to pass through the whole liquid medium and with US irradiation it reduces the ultrasound intensity reducing cavitation activity. Apart from this, increased catalyst dosage can act as a hydroxyl radical scavenger (28). Again, maximum colour removal of 86% was achieved for 25 mm probe followed by 13 mm probe (81%) and UV irradiation (80%).

#### 3.7.2 n-Fe(0)

The synthesized zero valent iron powder (Fe(0)) is used as a catalyst and its effectiveness on colour removal upon US and UV irradiation (BBG: 10 ppm, pH: 6.04, Reaction volume: 100 ml, Treatment time: 60 min) is shown in Fig.7. There is a slight increase in the decolourization rate with US irradiation (87% for 25 mm and 82% for 13 mm – 1g catalyst) and there is a slight decrease in decolourization efficiency with UV irradiation (78% - 1g catalyst). Cavitation reaction is known to produce H<sub>2</sub>O<sub>2</sub> also upon recombination of 'OH radicals and the H<sub>2</sub>O<sub>2</sub> in reaction with the zero valent iron powder (Fe(0)) is corroded [44]. The corroded Fe(0) oxidizes from Fe(0) to Fe<sup>2+</sup>, which then reacts with H<sub>2</sub>O<sub>2</sub> in a Fenton's like process to generate 'OH radicals and Fe<sup>3+</sup>. The Fe(0) then reduces the Fe<sup>3+</sup> back to Fe<sup>2+</sup> and the cycle continues. The reactions were presented below:

$$Fe(0) + H_2O_2 \rightarrow Fe^{2+} + 2OH^{-}$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{-}$$

Whereas, UV treated samples lack this Fenton's reaction and hence only catalyst activity prevails for dye colour removal.

# 3.7.3 n-Fe(0) doped TiO<sub>2</sub>

It has been reported by several researchers [37,45] that iron doped TiO<sub>2</sub> results in higher UV light absorption [4,22,46]. Also, it is proved that doping of metals with TiO<sub>2</sub> narrows the band gap energy and enhances the separation of electrons and holes which is essential for photocatalytic activity [37]. This means that ZVI-TiO<sub>2</sub> doped catalyst could decompose the dye molecule at a faster rate. The effect of doped catalyst under different treatments (Fig.8) shows that (BBG: 10 ppm, pH: 6.04, Reaction volume: 100 ml, Catalyst: 0.1g, Treatment time: 60min)

doped catalyst activity is the highest than the undoped catalyst irrespective of the treatment methods with a lesser catalyst addition. In the presence of doped catalyst, the US and UV treated dve solution resulted in ~99% and 92% respectively.

# 3.8 Sonophotocatalytic treatment of BBG

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The synergistic effects of sonolysis and photocatalyis are well understood from their basic mechanisms of chemical effect (production of radicals by sonolysis and photolysis) for degrading pollutants and physical effect (microjets, shockwaves and microturbulence by sonolysis) for bringing in effective contact between pollutant and radicals. Apart from these, the combined processes have several other advantages such as regeneration of the catalyst surface, maintaining uniform dispersion of catalyst, mass transfer enhancement and disintegration of solid catalyst into smaller particles thus increasing the surface area. Since it was found that for 10 ppm BBG concentration had resulted in near complete colour removal with doped catalyst under the conditions studied (section 3.7.3), the chosen dye concentration was 25 ppm (System: 25 mm probe + UV, Reaction volume: 100 ml, pH: 6.04, Treatment time: 60 min) for various studies of the sonophotocatalytic treatment to have its visible effect. The results were shown in Fig.9. The synergistic effect of sonophotocatalytic process is clearly observed as the colour removal efficiency is more when compared with the individual sonolysis & photolysis processes. Inorder to validate the synergistic effect, simple sonolysis and photolysis experiments (System: 25 mm probe, UV, Reaction volume: 100 ml, pH: 6.04, Treatment time: 60 min) were performed with 25 ppm dye solution. It was observed that simple sonolysis and photolysis could result in ~15% and ~5% decolorization where as sonophotolytic treatment had resulted in ~36% decolourization. From the studies (3.1-3.3), it is understood that degradation of BBG dye occurs

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through the hydroxylation reaction in the bulk liquid medium. Since, BBG dye is hydrophilic in nature, it will remain in the bulk aqueous medium and the degradation of these pollutants depends on how far the produced 'OH radicals move to reach the pollutant molecules [47]. But these OH radicals are highly reactive, short lived and they try to recombine to form water molecule or hydrogen peroxide without reaching the pollutant molecule under normal conditions. These uncertainties would be eliminated when the photolysis (which can produce more number of radicals through UV light illumination in the presence of doped catalyst) and sonolysis (which can yield more number of 'OH radicals through cavitation) were applied together. UV light shielding by the catalyst and agglomeration of the catalyst were overthrown by the cavitational activity through microjets and microturbulence actions (6). These combined effects bring in an effective 'OH radical production and to have effective oxidation of BBG dye. These effects were reflected in experimental results that sonophotocatalysis of BBG dye in the presence of doped catalyst was highly efficient (98%) than other processes studied. The synergistic mechanism of ultrasound, ultraviolet irradiation and catalytic activities of Fe(0) doped TiO<sub>2</sub> were pictorially illustrated in Fig.10.

#### 3.9 Sonophotocatalytic treatment of textile effluent

The textile effluent was collected from Textile Industry (Clothing Company, Tirupur, Tamilnadu, India) after preliminary treatment. The physico-chemical characteristics of the textile effluent was tested [48] under the same conditions as it was received and were listed in Table 3. The sonophotocatalytic degradation studies were performed for the effluent with the following conditions: Reaction volume – 1000 ml, Catalyst (Fe(0) doped TiO<sub>2</sub>) – 0.1 g, H<sub>2</sub>O<sub>2</sub> – 900ppm, Gas bubbling – Air. Larger reaction volume of 1000 ml is chosen keeping in mind of practical

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applicability. It needs to be mentioned here that air is chosen as the bubbling gas as it is the less costly and for practical application air is the best suited gas which is readily available. Further, the catalyst and  $H_2O_2$  concentrations were based on the studies reported elsewhere in this report. The UV-Vis spectrum (Fig.11) of the sonophotocatalytically treated effluent at various time intervals shows that there is a drastic reduction in the colour removal of the effluent and the colour removal was evident after 15 min of treatment time itself. The spectrum of raw textile effluent exhibit characteristics peaks in the visible and UV region indicating the presence of dyes as well as other organic compounds. In accordance with the spectrum results, it is easily understood the present treatment methodology could degrade both dyes and other organic compounds present in textile effluent. The COD analysis was also performed for every 15 min time interval and the results were presented in Fig.11. Again, there was a drastic reduction in the COD value during the first 15 min of treatment time and it is in good agreement with the UV-Vis spectrum results. The decrease in COD value of the textile effluent from 2400 to 293.5 mg/l is further evident that the sonophotocatalytic treatment not only helps in complete colour removal but also degrades the complex compounds present in the textile effluent leading to efficient treatment.

#### Conclusions

In this experimental study, the decolourization of 10 ppm of Bismarck Brown G was investigated by varying several parameters with the application of ultrasound and UV light. Initial studies of Bismarck Brown G dye with pH, H<sub>2</sub>O<sub>2</sub>, gases (Oxygen, Argon, Nitrogen and Air), catalyst, dye concentration and variable volume proved to indicate that 'OH radical production is the key for effective colour removal. The oxidation reaction is through hydrolysis

in the bulk liquid medium either through US or UV. From the individual parametric study, pH

4.0 (US & UV), 900 ppm H<sub>2</sub>O<sub>2</sub> (US), 2100 ppm H<sub>2</sub>O<sub>2</sub> (UV), Argon gas bubbling (US & UV),

lower BBG dye concentration (US & UV) and lower reaction volume (US & UV) gave maximum decolourization efficiency. Further intense study with the nanocatalyst (Commercial TiO<sub>2</sub>, green synthesized Fe(0) and Fe(0) doped TiO<sub>2</sub>) proved effective for higher BBG dye colour removal with lesser catalyst quantity. Among the methodology adopted, sonophotocatalytic is the best treatment method for the BBG dye solution in the presence of Fe(0) doped TiO<sub>2</sub>. The sonophotocatalytic treatment of real textile wastewater further supports the claim that for practical applicability synergistic effects are more important that individual parametric effect to handle larger volumes of textile effluents.

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Fig.3 Decolourization of BBG dye solution with purging of various gases (a) 13 mm probe,(b) 25 mm probe & (c) UV irradiation

Fig.4 Decolourization of BBG dye solution. (A) varying BBG concentration and (B) varying volume

**Fig.5 A.** SEM images (a) Synthesized Fe(0) and (b) Fe(0) doped TiO<sub>2</sub>; **B.** TEM images (a) Synthesized Fe(0) and (b) Fe(0) doped TiO<sub>2</sub>; **C.** XRD spectra of Fe(0) and Fe(0) doped TiO<sub>2</sub>; **D.** UV-Visible diffuse reflectance Spectra (a) TiO<sub>2</sub>, (b) Fe(0) & (c) Fe-TiO<sub>2</sub>

Fig.6 Decolorization of BBG dye solution with TiO<sub>2</sub> Catalyst

Fig.7 Decolorization of BBG dye solution with Fe(0) Catalyst

Fig.8 Decolorization of BBG dye solution with Fe(0)-TiO<sub>2</sub> Catalyst

Fig.9 Sonophotolytic degradation of BBG with various parameters

Fig.10 Synergistic effect of the sonophotocatalytic process

Fig.11 COD variation and UV-Visible Spectrum of sonophotocatalytically treated textile effluent











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Fig.4



Fig.5



Fig.6



Fig. 7



Fig.8

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Fig.9



Fig. 10

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Fig.11

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Table 1 Pseudo first order rate constant for BBG dye solution with varying parameters

Table 2 Pseudo first order rate constant for BBG dye solution in presence of catalyst

Table 3. Physico-chemical characteristics of the textile effluent

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CL N	Parameter	Experimental	Rate Constant x 10 <sup>-2</sup> /min		
<b>SI.No.</b>			Dhotolysis	Sonolysis	
			1 110t01ys1s	13 mm	25 mm
1.	pН	4	1.032	1.651	2.011
2.	$H_2O_2$	2100 ppm for UV & 900 ppm for US	0.778	1.601	1.939
		Argon	0.245	0.543	0.569
2	Casas	$\frac{Oxygen}{Oxygen} = 0.170 \qquad 0.362$	0.379		
3.	Gases	Air	0.153	0.324	0.339
		Nitrogen	0.084	0.174	0.182
	DDC	10 ppm	0.295	0.327	0.356
4.	BBU	50 ppm	0.080	0.235	0.249
	Concentration	100 ppm 0.055 0.115	0.118		
	Reaction Volume	100 ml	0.250	0.325	0.338
5		500 ml	0.100	0.164	0.165
		1000 ml	0.077	0.131	0.136

# Table 1 Pseudo first order rate constant for BBG dye solution with varying parameters

CL N		Experimental	Rate Constant x 10 <sup>-2</sup> /min			
<b>SI.NO.</b>	Catalyst	Conditions	Photolysis	Sonolysis		Sononhotolysis
			1 1100019315	13 mm	25 mm	- Sonophotolysis
1.	TiO <sub>2</sub> , 0.75g	10ppm, pH=6.04	2.092	2.129	2.921	1.293
2.	Fe (0), 1g	for US & UV,	2.229	2.655	2.881	1.290
3.	Fe(0) doped	25ppm, pH=6.04				
	TiO <sub>2</sub> , 0.1g	for	3.732	7.358	7.582	5.665
		sonophotolysis				

 Table 2 Pseudo first order rate constant for BBG dye solution in presence of catalyst

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SI. No.	Characteristics	Value
1.	Color	Dark Blue color liquid
2.	pH	9.06
3.	Total Hardness as CaCO <sub>3</sub> (mg/l)	960
4.	Turbidity (NTU)	64
5.	Total dissolved solids (mg/l)	209031.0
6.	Conductivity (Micromho's/cm)	35600
7.	BOD <sub>5</sub> at 20° C (mg/l)	128 (VFL)
8.	COD (mg/l)	2400
9.	Total Alkalinity as CaCO <sub>3</sub> (mg/l)	4124

# Table 3. Physico-chemical characteristics of the textile effluent