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Influence of H_2O_2 Activation with Doped Catalyst for Treating Recalcitrant Textile Dyes

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Abstract

The sono-hybrid degradation process of a dye derivative Bismarck Brown was investigated under sonication bath integrated with UV light irradiation with the influence of TiO_2 and H_2O_2 under a variety of conditions. The degradation was studied by monitoring the change in dye concentration employing UV spectroscopic technique as a function of irradiation time. The degradation was studied under different conditions such as Fe, TiO_2, Fe doped TiO_2, reaction pH and dye initial concentration assisted with the activation of hydrogen peroxide (H_2O_2). The degradation rates were found to be strongly influenced by all the above parameters. H_2O_2 activated by the photocatalyst Degussa P_{25} in the sonophotocatalytic hybrid process gave higher degradation of the dye. 100% complete removal of the dye with a kinetic rate constant of 3.92×10^{-2} sec^{-1}. H_2O_2 was significantly improved by the influence of sonophotocatalysis for the complete mineralization of the dye. There was an existence of beneficial synergistic effect between the activation of H_2O_2 by the catalyst under the ultrasound and UV light irradiation. The experimental results revealed the tentative and positive correlation that cavitation process improving the H_2O_2 activity by the catalyst under the influence of ultrasound and providing the generation of more number of •OH active radicals for the complete degradation of the dye. The activity of the synthesized catalyst were compared with the commercial and the observed results show that the synthesized catalyst also enhances the activity of H_2O_2 and tentatively breaks down the dye leading to 96% and 92% degradation.

Keywords: Sonophotocatalysis; Dyes; Bismarck brown; Cavitation; TiO_2; H_2O_2

Introduction

The dye stuff released from the textile industry plays a key role in threatening the water resources. Treatment of the dye wastewater becomes a challenge to most of the researchers [1]. Many different types of dyes are used in textile industries they are classified into many types such as azo, reactive, basic and acid dyes [2]. Azo dyes contribute to about 70% of all used dyes, structural complexity and artificial synthesis of these azo dyes require a hybrid process for complete mineralization. The specific characterization of consisting nitrogen to nitrogen double bond (–N N–) paves key to its non-degradable nature. The color of dyes is due to azo bond and associated chromophores, so disposal of dyes into surface water not only affects the aesthetic but cause also biotoxicity [3]. The different conventional processes involving biological treatment process end up in forming various intermediates which are more toxic. The conventional process along with hybrid processes including membrane filtration [4,5], electrochemical technology and advance oxidation process (AOP) including photochemical oxidation [6], photocatalysis [7] and ultrasonic wave [8] helps in treating these recalcitrant dyes parent and intermediate molecules.

A rapidly developing field in advanced oxidation technologies for applications in environmental remediation is the use of cavitation (i.e., environmental sonochemistry), which is the application of ultrasound to destroy or accelerate the destruction of liquid-phase contaminants [9]. Cavitation science and engineering is a field involving the application of ultrasonic waves to chemical processing [10]. The application of sonochemistry in environmental remediation falls under three categories: (i) the use of cavitation alone. as a clean energy source; (ii) the use of cavitation to improve other treatments (e.g., advanced oxidation); and (iii) the use of cavitation to effect reduction in the amounts of chemicals required for conventional treatments (e.g., reduction in biocide levels) [11]. During cavitation process the bubbles collapse inside the aqueous medium with very high temperatures and pressure. This phenomenon hot spot where the solvent vapor inside the bubble at this condition go through pyrolysis process at the interface between the bubble collapse and solvent lead to high temperature and pressure gradient [12].

In aqueous solutions, the thermal dissociation of non-volatile solutes or formation of radicals to scavenge completely depend on the gas/solution accumulation. The accumulation exists under ambient temperature where there is an interference between growing micro bubble and bulk solution. The formed free radicals react with the solution and generate the final products according to the radiation chemistry. The various aromatic ring structure compounds and azo dye molecules are degraded to short chain ions, CO, CO_2, and H_2O as the final products in advanced oxidation process.

The sono-hybrid process mechanism enhances the generation of hydroxyl radicals and helps in the oxidation of polar organic compounds. The objective of this work is on investigation of ultrasound irradiation integration with the H_2O_2 activation by the photocatalyst in decolorization of textile wastewaters. For this purpose, model dye Bismarck Brown (BB) was chosen, as it is used in various tanneries, dyeing units, spinning mills and cannot be quickly

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degraded. The sonication was coupled with the H_2O_2 activated by the nanocatalyst. The process was optimized by various influencing parameters like pH, H_2O_2 concentration and initial dye concentration. Finally, the kinetic rate constant was calculate to find out the plausible degradation mechanism.

Materials and Methods

Materials

Bismarck Brown (BB), TiO_2 P_{25} Degussa (Specific surface area 35 m^2/g and particle size 21 nm) Hydrogen Peroxide (30%), Fe_2SO_4 were procured from Merck, India and were used as received. The molecular formula of BB is $C_{18}H_{20}Cl_2N_8$ and molecular weight was found to be 419.32 and absorbance was measured at λ_{max} 447 nm.

Synthesis of catalyst: The nano iron solution was prepared by mixing green tea solution (polyphenol extract) and 0.5 M Ferrous sulphate solution in the ratio 2:1 respectively. Then the solution was subjected to ultrasonic irradiation for 30 min. then the solution was centrifuged (12000 rpm, 30-45 min) to separate the nano iron that was formed. The precipitate was dried in a hot air oven upto 24 hrs at 100°C. finally the dry powder was grounded in mortar and pestle to get a fine nano iron powder. The morphological analysis and elemental analysis for the nano iron was carried out using a scanning electron microscope given in Figure 1.

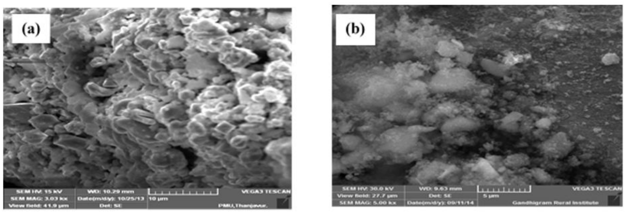

Figure 1: SEM of (a) Fe and (b) Fe doped TiO_2 synthesized by Sonochemical method.

Doping of TiO_2 (Degussa) with Fe(0) was done using sonochemical method. The same experimental procedure for synthesizing Fe(0) was followed and for doping the TiO_2 was added during the formation of Fe(0). By this way the added TiO_2 would get doped effectively on the Fe(0) by means of sonolysis. The sem picture (Figure 1b) shows that the TiO_2 were doped on the Fe(0) particle. The elemental analysis (EDS) composition of the respective compounds were depicted in Figures 2a and 2b.

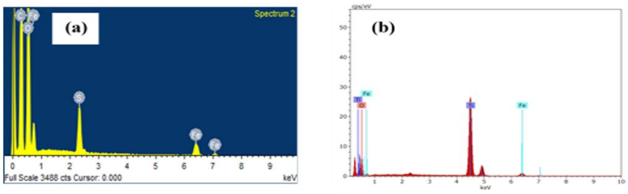

Figure 2: EDS of (a) Fe and (b) Fe doped TiO_2 by Sonochemical Method.

Irradiation procedure

Sono-hybrid process using synthesized catalyst zero valent iron, Fe(0)-TiO_2 doped and commercially available TiO_2 were experimented with a circular glass reactor having 149 cm^2 surface area. A sonication bath with 2 L capacity which emits ultrasound waves at 20 kHz and delivers a net power output of 100 watts is used for all the experiments. All the experiments were performed with 100 W set power. 4 W mercury vapor lamp was used to irradiate the dye solution. The wavelength peaks around 256 nm. Initially, the lamp irradiated before 10 min to reach constant output during the degradation studies. The photolytic or photocatalytic experiments were carried by inserting the lamp in a sealed photoreactor where the reaction mixture surrounds the lamp in open-air condition. The degradation experiments with an initial volume of 100 ml dye solution was used and the variation of pH of dye solution were adjusted either by adding dilute NaOH or dilute H_2SO_4. All the experiments were carried out for a time of 60 minutes. All the reported results were average of three trial experiments. The performance of the degradation study was evaluated by observing the absorbance value of the dye at 447 nm and using the formula given below.

$$\%Decolorization = \left(\frac{C_i - C_f}{C_i}\right) \times 100$$

Where C_f is the final dye concentration and C_i is the initial dye concentration.

Analytical methods

At definite time intervals the sample solution aliquots (5 ml) was taken out from the reactor and centrifuged. The catalyst free sample were analyzed for its absorbance by UV–vis spectroscopic technique (Merck) UV–vis spectrophotometer.

Results and Discussion

Effect of H_2O_2

Advanced oxidation process plays a key role in degradation of dyes. Hydrogen peroxide play as an essential parameter for dye decomposition in AOP technique, depending on its concentration and nature of anti-oxidant property. The anti-oxidant effect takes place in two different pathways producing hydroxyl radicals.

At conduction band reduction of H_2O_2 takes place

As a result of ultrasound irradiation H_2O_2 self-decompose into OH radicals.

$$H_2O_2 \leftrightarrow HO_2- + H^+ \qquad (1)$$

The decolorization of dye increases with an increase in the H_2O_2 concentration increases until the scavenging reaction takes place. However, recent researches succumbs that ultrasound irradiation can be used possibly for efficient generation of highly active •OH, HOO• and H• radicals [13]. At an increased concentration, H_2O_2 acts as a scavenger of valence bond holes and hydroxyl radicals causing a decrease in dye degradation. The resulting plots of dye removal percentage versus time implying the H_2O_2 effect are shown in Figure 3. The effect of ultrasonic irradiation combined with H_2O_2 observed to degrade dye slightly only when free radical attack is the controlling mechanism.

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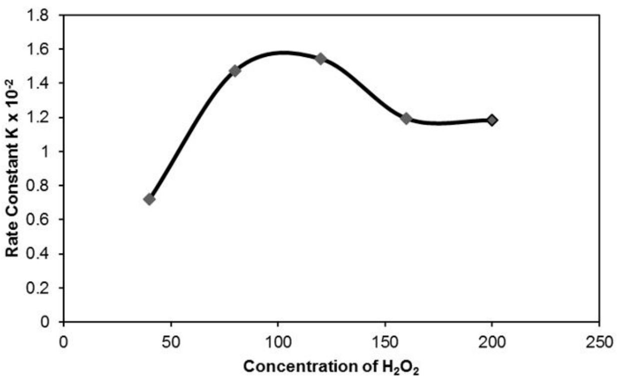

Figure 3: Varying concentrations of H_2O_2 and Rate constants.

Effect of pH and H_2O_2

In this experiment, the optimum value of the pH of 4.0 is maintained, with variation in the dosage of hydrogen peroxide in steps of 40 mM up to 200 mM. Here it was found to be at the optimum hydrogen peroxide dosage of 120 mM and at optimum pH of 4.0, the maximum decolourization occurs. Figure 4 shows the decrease in the degradation efficiency as the concentration of the anti-oxidant increases. The excess of OH radicals produced will have reverse reaction of forming H_2O_2 as following the equation 1.

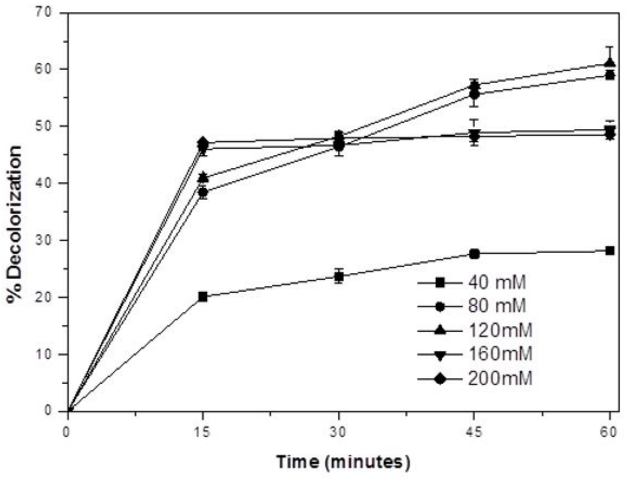

Figure 4: Decolourization of BB1 dye solution (25 ppm) with varying concentration of H_2O_2 at pH 4.

Effect of H_2O_2 and the bubble content

The decolourization value at the solution pH of 5.4 and with purging the gas for 5 minutes viz. Oxygen, Argon, Nitrogen and Air, from Figure 5 it was found that when argon gas was passed the maximum decolourization occurs. The hydroxyl radicals formation in the presence of argon were efficient when compared to other other gases. Also, when an inert mono atomic argon gas was passed the decolourization was found to be maximum. This is due to argon's high heat capacity ratio. It was found that with argon and 120 Mm of Hydrogen Peroxide showed the maximum decolourization.

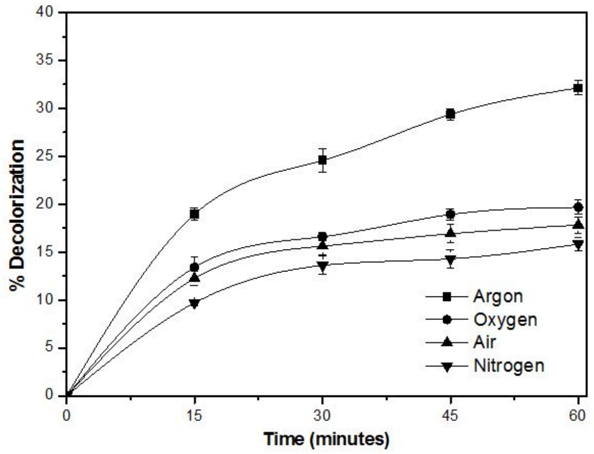

Figure 5: Decolorization of dye with purging of different gases with optimum H_2O_2 concentration: BB=25 ppm H_2O_2=180 Mm.

Effect of H_2O_2 and catalyst loading

The various catalysts like Fe0, Fe0-TiO_2 doped and TiO_2 were used. The sonophotocatalytic degradation was done for the dye with 25 ppm concentration with normal pH 5.4. After the sonophotocatalytic effect the pH of the final solution was checked to be around 3.68 such that the optimum pH was reached under which the maximum decolorization occurs.

In acidic medium oxidation at iron surface lead to form ferrous ions (Fe^{2+}). The alternate reaction between iron surface and oxidant H_2O_2 which are partially adsorbed on the iron surface cause the generation of Fe^{2+} ions. The reaction further continues with adsorbed Fe^{2+} ions and H_2O_2 generate hydroxyl radicals

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + \ldots\text{Surface} \qquad (2)$$

$$Fe^{2+} + \text{Surface} + H_2O_2 \rightarrow Fe^{3+} + HO. + HO- \qquad (3)$$

Further the extra Fe^{2+} ions which are not adsorbed, diffuse into the bulk of the solution and helps in the formation of hydroxyl anions. Initially, Fe0 oxidizes to Fe^{2+} by the loss of two electrons as depicted in Eq. (4). The electron acceptors like H_2O_2 react with those two electrons and form two hydroxide ions as shown in Eq. (5). By combining Eqs. (4) and (5) results in Eq. (6):

$$Fe^0 \xrightarrow{H^+} Fe^{2+} + 2e^-(4)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \qquad (5)$$

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \qquad (6)$$

The self-oxidation of Fe^{2+} ions happened by reaction with the oxidant molecules to generate free radicals and forming Fe^{3+} ions as in Eq. (7).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO. + OH^- \qquad (7)$$

The formation of Ferric ions (Fe^{3+}) were either by reacting with molecules of water or H_2O_2 as represented in the following way:

Reaction with water molecules results in an aqua complex Ferric ion (Fe^{3+}). Upon UV irradiation with this complex end in generation of Fe2+ ions and hydroxyl radicals

H_2O_2 reacts with Fe^{3+} ions form Fe^{2+} ions and hydroperoxyl radicals. Hydroperoxyl radicals reduced by Fe^{3+} ions into hydroxyl radicals.

The overall efficiency controlled by the regeneration of Fe^{2+} ions on iron surface. An oxidant going through sonolysis and Photolysis lead to the formation of various ions and highly oxidative reactive radicals contributing for the enhancement of process efficiency.

TiO_2 gets excited by UV light at a faster rate and initiate the degradation process of the aqueous dye solution. The generation of electron/hole pair upon TiO_2 excitation by absorbing the light.

$TiO_2 + hv \rightarrow TiO_2(ecb- + hvb+)$ (8)

$H_2O_2 + hv \rightarrow 2OH^-$ (9)

$TiO_2(e-) + H_2O_2 \rightarrow TiO_2 + 2OH^-$ (10)

It has been shown in sonophotocatalysis integration with the hydrogen peroxide activation enhances the degradation kinetics, probably via reaction (10). The catalyst surface was adsorbed by the organic compounds where the generated hydroxyl radicals degrades the dye compounds, resulting in oxidation. As for the US/UV/ TiO_2 system, the generation of OH radicals can arise because of reduction of the positive holes in the TiO_2 surface by electron donating species such as H_2O and OH.

Process	**BB1 concentration**	**Percentage Degradation**	**Rate constant x (10^{-2} / sec)**
Fe0/UV/US/H_2O_2	25	92	2.83
	50	68	1.78
	100	53	0.95
TiO2/ UV/US/H_2O_2	25	100	3.92
	50	88	2.67
	100	74	1.94
Fe0-TiO_2/UV/US/H_2O_2	25	96	2.94
	50	77	1.86
	100	61	1.14
Experimental condition: [Fe0] / [TiO_2] / [Fe0-TiO_2]=10 mg/100 ml, [BB]=25 ppm, [HP]=40 Mm and pH 5.4.			

Table 1: Percentage degradation and rate constant for different initial concentration of BB using HP oxidant and various catalyst.

Effect of H_2O_2 and dye concentration

In the sonophotocatalytic process, the initial dye concentration influences the degradation process significantly. Therefore, investigation on the dye concentration with keeping all other experimental constant. The percentage degradation and the rate constant were calculated for different initial concentration of the dye with the oxidants concentration are shown in the Table 1. The optimum concentration (25 ppm) was found, such that further increase in the dye concentration (100 ppm) decreases degradation to 53 percent. This can be attributed by the fact that the dye concentration increased and the hydroxyl radicals available is not increased proportionally. High dye concentration prevents the hydroxyl radical generation. The intense color solution by higher dye concentration can act as inner filter preventing the UV light photons reaching the surface of the photocatalyst. Thus, inhibiting the cyclic photo-Fenton reactions resulting and reduces the kinetic rate in degradation.

Effect of H_2O_2 and volume variation

The experimental results showed in Figure 6 the decolorization efficiency decreased with the increase in initial dye concentration. When the dye samples were treated with the sonophotolytic effect there is not much degradation in the dye concentration. After the addition of antioxidants and photocatalyst the degradation percentage increases. When the initial dye volume was (25 ppm) 100 ml, the complete decolorization reaching 100% in 60 min in the presence of catalyst, but when initial dye solution volume was enhanced to 500 ml, the decolorization decreased to 58%. Enhanced volume of aqueous dye solution provides interferences which inhibited degradation. Figure 6 clearly depicts that the degradation efficiency of the dye solution at regular time intervals.

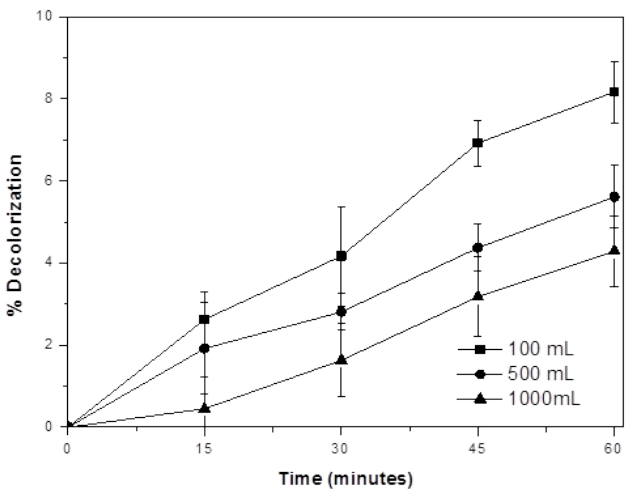

Figure 6: Percentage degradation of BB1 with varying volume at normal pH.

Conclusion

The study show that H_2O_2 activated by nanocatalyst hybrid process (sonophotocatalysis with H_2O_2) an efficient treatment process for degradation of an aqueous azo dye BB solutions. The decolorization of an aqueous dye BB solution was strongly depended on the pH such that an acidic medium favours efficient degradation. Additionally, the initial lower concentration of the dye favors higher dye removal. Also, the presence of oxidants helps in enhanced degradation efficiency which can be understood from its varied concentration effect. The presence of catalyst also gives an additional increment in degradation reaction and transforms the recalcitrant dye molecules into desirable results.

References

1. Zollinger H (1987) Synthesis, properties and application of organic dyes and pigments. In: Eblel HF, Brenzinger CD (eds.), Colour Chemistry, VCH, Inc., New York, USA.
2. Song S, Ying H, He Z (2007) Mechanism of decolorization and degradation of CI Direct Red 23 by ozonation combined with sonolysis. J Chen Chemosphere 66: 1782-1788.
3. Tan X, Kyaw NN, Teo WK, Li K (2006) Decolourization of dye-containing aqueous solutions by the polyelectrolyte-enhanced ultrafiltration (PEUF) process using a hollow fibre membrane module. Purify Technol 52: 110-116.
4. Lee JW, Choi SP, Thiruvenkatachari R, Shim WG, Moon H (2006) Submerged microfiltration membrane coupled with alum coagulation/ powdered activated carbon adsorption for complete decolorization of reactive dyes. Water Res 40: 435-444.
5. Chidambara CBR, Quen HL (2005) Advanced oxidation processes for wastewater treatment: Optimization of UV/H2O2 process through a statistical technique. Chemical Engineering Science 60: 5305-5311.
6. Gupta AK, Pal A, Sahoo C (2006) Photo catalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using Ag+ doped TiO2. Dyes and Pigments 69: 224-232.
7. Wang Y, Zhao Y, Ma W, Chen C, Zhao J (2008) Enhanced Sonocatalytic Degradation of Azo Dyes by Au/TiO2. Environ Sci Technol 42: 6173-6178.
8. Torok B, Balazsik K, Felfoldi K, Bartok M (2001) Asymmetric reactions in sonochemistry. Ultrasonics Sonochemistry 8: 191-200.
9. Suslick KS (1998) Kirk-Othmer Encyclopedia of Chemical Technology. Wiley & Sons 26: 517-541.
10. Yusuf GA (2005) Sonochemistry in Environmental Remediation Combinative and Hybrid Sonophotochemical Oxidation Processes for the Treatment of Pollutants in Water. Environ Sci Technol 39: 3409-3420.
11. Abbasi M, Razzaghi NA (2008) Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO2 and H2O2. Journal of Hazardous Materials 153: 942-947.
12. Dinesh GK, Gangwar TS, Anandan S, Sivasankar T (2016) Sonophotocatalytic Degradation of Scarlet Red dye using Fe-Bi2O3 Catalyst and its Process Optimization by Response Surface Methodology. Journal of Catalyst & Catalysis 3: 14-32.
13. Dinesh GK, Sivasankar T, Anandan S (2016) Metals Oxides and Doped Metal Oxides for Ultrasound and Ultrasound Assisted Advanced Oxidation Processes for the Degradation of Textile Organic Pollutants. Handbook of Ultrasonics and Sonochemistry, pp: 1-27.