Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 1328-1336

(International Peer Reviewed Journal)

Use of Solid Supported Photo-Fenton and Photo-Fenton like Reagents in Degradation of Bismarck Brown-R

Khushboo Salvi[1]*, Kanchan Kumari Jat[1] and Suresh C. Ameta[2]

1. Department of Chemistry, M.L.Sukhadia University, Udaipur-313002 (Raj.), **INDIA**
2. Department of Chemistry, PAHER University, Udaipur-313003 (Raj.), **INDIA**

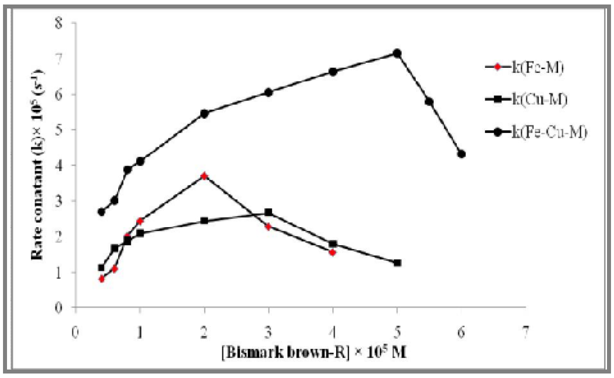
Email: khushisalvi1601@gmail.com

Accepted on 16th April, 2019

ABSTRACT

Performance of Fe-montmorillonite (Fe-M), Cu-montmorillonite (Cu-M), and (Fe-Cu) montmorillonite (Fe-Cu-M) in degradation of Bismark brown-R in presence of hydrogen peroxide was evaluated. Optimum conditions obtained for photo-Fenton degradation of Bismark brown-R are: {Fe-montmorillonite}: pH=7.5, [Bismark brown-R]=2.0×10^{-5} *M, amount of composite=0.10 g and light intensity=50.0 mW* cm^{-2}*,* H_2O_2*=0.392 M; {Cu-montmorillonite}: pH=7.5, [Bismark brown-R] =*3.0×10^{-5} *M, amount of composite = 0.10 g and light intensity=60.0 mW* cm^{-2}*,* H_2O_2*=0.235 M; {Fe-Cu montmorillonite}: pH=7.0, [Bismark brown-R]=*5.0×10^{-5} *M, amount of composite=0.10 g and light intensity =70.0 mW* cm^{-2}*,* H_2O_2*=0.196 M. It was concluded that composite showed Fe-Cu-montmorillonite composite is better for wastewater treatment as compared to Fe- montmorillonite composite, and Cu-montmorillonite composite.*

Graphical Abstract



Effect of concentration of Bismark brown-R.

.

Keywords: Photo-Fenton, Photo-Fenton like reagent, Bismark brown R, Copper sulphate, Ferrous sulphate, Montmorillonite.

INTRODUCTION

Water is highly essential for the life of living organisms, but it is being rapidly polluted as a result of effluents thrown in our natural resources. Chemicals, food and beverages, textile, pesticides and insecticides, dyeing and printing industries, etc. are among major culprits causing water pollution. Dye effluents originating from production and application industries, pose a threat to surrounding ecosystems, because of their toxicity, recalcitrant nature and potentially carcinogenic nature in some cases. There is an increasing demand of clean water all over the globe. Colored solutions containing dyes from industrial effluents may cause harmful effects on human beings, animals and plants, due to photosensitization and photodynamic damage. The color in the wastewater is an obvious indicator of water pollution due to dyes and pigments [**1, 2**] and therefore, the removal of dyes from wastewater becomes utmost necessary.

Fenton reagent has been used for oxidative decomposition and transformation of organic substances. In this process, ferrous ion reacts with hydrogen peroxide generating hydroxyl radical, which is very active oxidizing agent. The pH of the resultant solution is also increased due to hydroxyl ions. As a result, ferric hydroxide is also precipitated making the removal of sludge necessary. This problem is better solved by using this reagent in the presence of light, i.e., Photo-Fenton. The presence of light helps in regenerating ferrous ion and maintaining pH of the medium. Ferric ion so formed will react with water in presence of light to regenerate ferrous ion along with hydroxyl radical and a proton. This proton will maintain the pH of the reaction while hydroxyl radical is utilized for oxidative purpose; thus, making the process cyclic. Photo-Fenton reaction is also considered as one of the Advanced Oxidation Processes (AOPs).

The untreated dyes in effluent from dyeing factories and leather industries are a group of hazardous chemicals as well as major sources of water pollution [**3, 4**]. Water pollution due to discharge of these dyes is one of the major environmental concerns in the world today and different strategies have been developed based on physico-chemical [**5, 6**] and biological methods [**7**] in order to degrade and remove these dyes. Chemical oxidation processes is an alternative technology that can be successfully applied for the degradation of a broad spectrum of organic compounds [**8, 9**]. Among these, AOPs environmental remediation technologies are gaining importance for degradation of most of the organic pollutants as environmental remediation technologies [**10**].

Aye *et al*. [**11**] reported that 15% of the dyes is lost in the synthesis, processing of colorants, dyeing, printing and finishing. This invariably corresponds to a release of about 615 tons per day into the environment and ecological system. Brown and De Vito [**12**] reported that dyes are hazardous to the environment and can cause serious carcinogenic effects even if these are present in very low concentrations. Because of the high levels of aromatics present in these molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation [**13**].

Neamtu *et al.* [**14**] reported that physico-chemical methods such as coagulation/flocculation, activated carbon adsorption and reverse osmosis techniques have been developed in order to remove the color. Sreedhar and Kotaiah [**15**] opined that color removal from textile dyeing effluents had been the target of a great attention in the last few years due to its aesthetic effect, even at lower concentrations. Fang *et al*. [**16**] were of the opinion that the conventional biological treatment processes are ineffective, whereas adsorption [**17**] and coagulation processes resulted in secondary pollution. These include biodegradation [**18, 19**] Fenton/photo-Fenton degradation [**20-23**], UV/Visible light driven photocatalytic degradation process [**24**], etc.

MATERIALS AND METHODS

Preparation of Fe-montmorillonite, Cu-montmorillonite, and Fe-Cu montmorillonite composite: Solutions A, B, and C were prepared separately. In beaker A, 13.9 g ferrous sulphate was taken in 250 mL distilled water and 25 g montmorillonite clay and few drops of dil. H_2SO_4 were added to this solution. In beaker B, 18.66 g copper sulphate was taken in 250 mL distilled water and 25 g montmorillonite clay and few drops of dil. H_2SO_4 were added to this solution, Similarly, in beaker C, 6.95 and 6.22 g ferrous sulphate and copper sulphate were taken in 250 mL distilled water and 25 g montmorillonite clay and few drops of dil. H_2SO_4 were added. A, B and solutions C were stirred for 5-6 h. The product was filtered and washed with distilled water 6-7 times. It was dried in an oven at 100°C for 4-5 h.

Photo-Fenton degradation Process: Stock solution of 1.0 x 10^{-3} M concentration was prepared by dissolving 0.0461 g of Bismark brown-R in 100 mL of doubly distilled water. It was used as a stock solution. This stock solution was used to prepare working solutions during the further experiments.

- The first beaker containing Bismark brown-R solution was kept in dark.
- The second beaker containing Bismark brown-R solution was exposed to light.
- The third, fourth and fifth beakers containing Bismark brown-R solution and 0.1 g composite, (Fe-M, Cu-M, and Fe-Cu-M) and H_2O_2 were kept in dark.
- The sixth, seventh and eighth beakers containing Bismark brown-R solution and 0.1 g composite, (Fe-M, Cu-M, and Fe-Cu-M) H_2O_2 were exposed to light.

After exposing these beakers for 3 h, absorbance of solution of each beaker was measured with the help of a spectrophotometer. The absorbance of the solution of first five beakers was found almost constant, but the solution of the sixth, seventh and eighth beakers showed a decrease as compared to initial value of its absorbance. It is clear from all these observations that the degradation required both; light and Fe-montmorillonite, Cu-montmorillonite, or Fe-Cu montmorillonite composite. The desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. About 3 mL aliquot was taken out after fixed time interval to measure absorbance with the help of a spectrophotometer (Systronics Model 106) at λmax = 350 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture and it was measured by Suryamapi (CEL model SM 201). It was observed that the absorbance of the solution decreases with increasing the time of exposure.

RESULTS AND DISCUSSION

Typical runs of Fe-montmorillonite, Cu-montmorillonite, and Fe-Cu montemorillonite composite, is graphically represented in figure 1. The rate constant for degradation was calculated with the help of equation:

$$k = 2.303 \times \text{slope} \qquad \ldots(1)$$

The rate constants in presence of Fe-montmorillonite, Cu-montmorillonite and Fe-Cu montmorillonite composite were found to be 3.71×10^5, 2.68×10^5, $7.15 \times 10^5 s^{-1}$ respectively, at optimum values of operational parameters; pH=7.5, 7.5, 7.0; Fe-montmorillonite, Cu-montmorillonite, Fe-Cu montmorillonite composite = 0.10 , 0.10 , 0.10 g ; [Bismark brown-R] = 2.0×10^{-5}, 3.0×10^{-5}, 5.0×10^{-5} M, Light intensity = 50.0, 60.0 , 60.0 mW cm^{-2}; H_2O_2 = 1.5, 1.2, 1.0 M.

Different rate affecting parameters were studied to obtain the optimum values for the maximum rate of reaction for photo-Fenton degradation of Bismark brown-R.

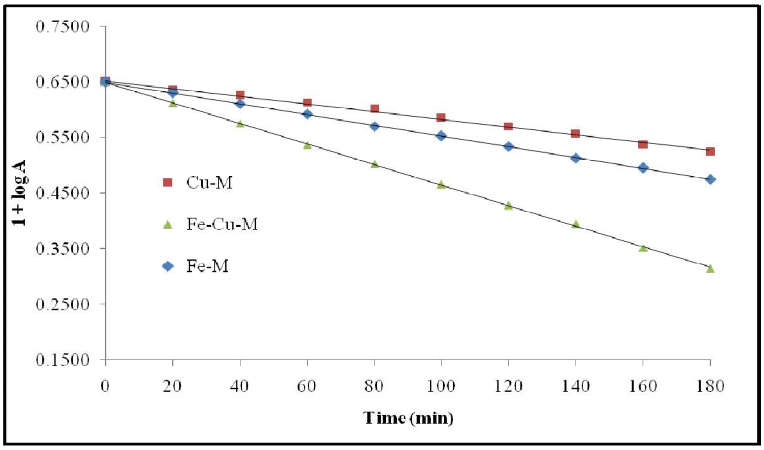


Figure 1. Typical runs.

Effect of pH: The pH of the solution may affect the degradation of Bismark brown-R. The effect of pH on the rate of degradation of Bismark brown-R was investigated in the pH range 5.0-9.0. The results are graphically reported in figure 2. It was observed that the rate of photocatalytic degradation increased with increase in pH up to 7.5, 7.5 and 7.0, in presence of Fe-montmorillonite, Cu-montmorillonite, and Fe-Cu montmorillonite composites, respectively but rate of the reaction gradually goes declined on increasing pH above optimum pH.

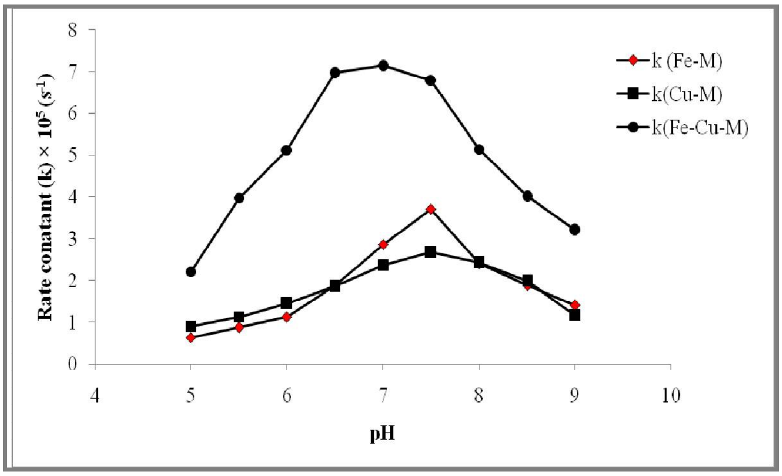


Figure 2. Effect of pH.

This increase in rate of reaction may be due to availability of more $^{-}$OH ions in solution. After a certain pH (in alkaline range), there was a decrease in reaction rate, because cationic molecules are present in their neutral or almost neutral forms, and therefore, there will be no attraction between neutral dye molecules and –ve charged surface of composite. On the other hand, there was also a decrease in acidic range because of the repulsion between cationic dye molecules and positively charged surface of the composite due to adsorption of protons, which will not permit the dye molecules to come into the contact of surface of the composite.

Effect of concentration of dye: The effect of dye concentration on rate of photo-Fenton degradation was observed by taking different concentrations of Bismark brown-R. The results are represented in figure 3.

It was observed that the rate of photo-Fenton degradation increased with increase in concentration of Bismark brown-R of Fe-montmorillonite, Cu-montmorillonite, and Fe-Cu montmorillonite composite up to 2.0 x 10^{-5}, 3.0 x 10^{-5}, and 5.0 x 10^{-5} M, but any increase in concentration above this limit resulted in a decrease in rate of the reaction. This observation may be explained by the fact that with an increase in concentration of dye; there is an increase in number of dye molecules for excitation and energy transfer. As a result, the rate of photo-Fenton degradation increased significantly. A decrease in rate of degradation may be attributed to the fact that after a certain dye concentration, the dye starts acting as an internal filter itself for incident light, and hence, it will not allow the required light intensity to reach the surface of the composite. As a consequence, a decrease in rate of photo-Fenton degradation was observed.

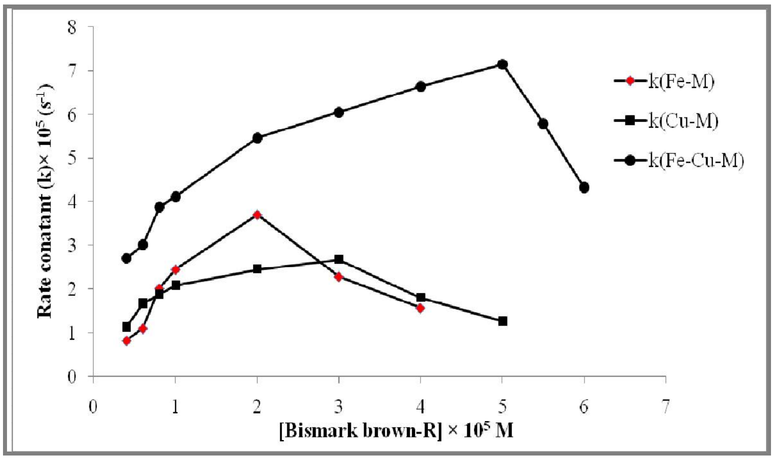


Figure 3. Effect of concentration of Bismark brown-R.

Effect of amount of composite: The effect of dose of composite on the dye removal was also studied. It was observed that rate of dye removal increases as amount of adsorbent was increased upto a certain amount of composite, 0.10 g in all these cases; after that the rate of reaction decreases. The results of effect of adsorbent dose on the removal of Bismark brown-R are given in figure 4. Highest rate of reaction was observed at 0.10 g, and hence, it was taken as optimum value for further studies.

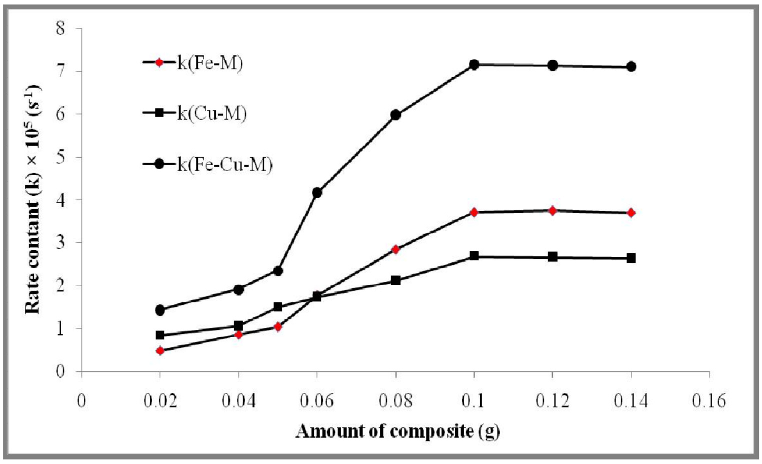


Figure 4. Effect of amount of composite.

Such variation may be due to the fact that as the amount of composite was increased, the exposed surface area of the composite increases, but after 0.10 g, there was almost a saturation like behaviour as there was no or insignificant effect on rate of degradation on increasing the amount of composite. It is all because of the fact that an increase in the amount of composite, it will only increase the thickness of layer of the composite and not its exposed surface area.

Effect of light intensity: The light intensity was varied by changing the distance between the light source and the exposed surface of composite. It was observed that the rate of photo-Fenton increases up to 50.0, 60.0, and 70.0 mW cm^{-2} in presence of Fe-M, Cu-M, and Fe-Cu-M, respectively and then decreases with further increase in light intensity. The results of observation are graphically presented in figure 5.

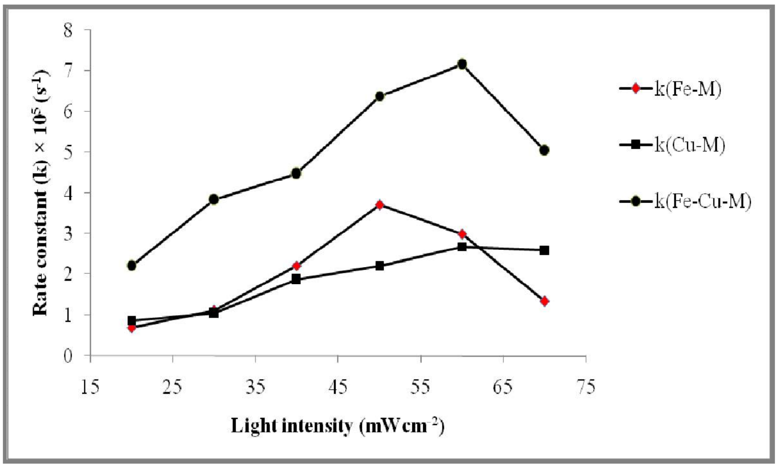


Figure 5. Effect of light intensity.

This can be explained on the basis that as the light intensity was increased, number of photons striking per unit area per unit time increases, which leads to higher rate of degradation of dye. Further increase in the light intensity may cause some other thermal side reactions and as a consequence, the rate of the reaction is decreased. Therefore, higher light intensities of avoided were avoided.

Effect of H_2O_2: The effect of H_2O_2 was observed by taking different concentrations of of H_2O_2. The results are represented in figure 6.

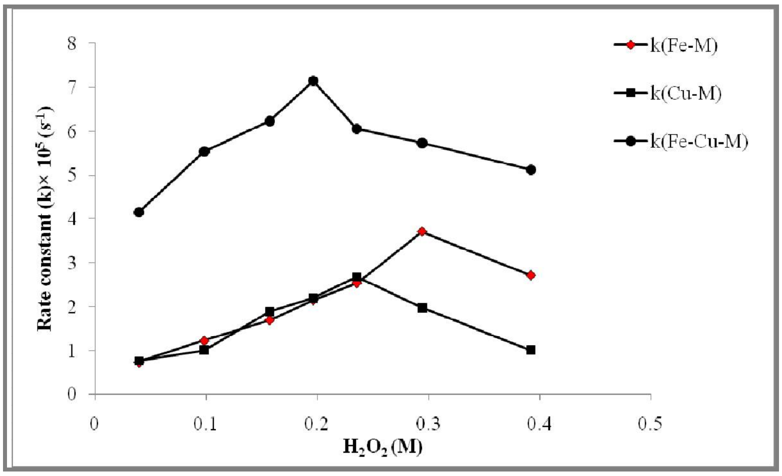


Figure 6. Effect of H_2O_2.

It was observed that the rate of photo-Fenton degradation of Bismark brown-R increased with increase in amount H_2O_2 up to 0.392, 0.235 and 0.196 M, in case of Fe-M, Cu-M and Fe-Cu-M, respectively, but any increase in H_2O_2 above this limit resulted in a decrease in rate of the reaction. This observation may be explained by the fact that with the increase in H_2O_2 of dye; there is an increase in number of hydroxyl radicals produced. As a result, the rate of photo-Fenton degradation increased. A decrease in rate of degradation may be attributed to the fact that after a certain concentration of H_2O_2 , the reactive $^{\bullet}OH$ radicals could be consumed by H_2O_2 resulting in the generation of less reactive $HO_2^{\bullet}$ radicals [24], as:

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \qquad \ldots (2)$$

Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and causes the decolorization rate to drop. It is important to control the initial concentration of H_2O_2 since the high concentration would be adverse to the decolorization of the dye and would increase the cost of the wastewater treatment also.

Mechanism: A tentative mechanism of photo-Fenton degradation of Bismark brown-R (BBR) in presence of Fe-montmorillonite, Cu-montmorillonite, and Fe-Cu montmorillonite composite may be proposed as:

$$^{1}\,BBR \xrightarrow{h\nu} {}^{1}BBR_{1} \qquad \ldots (3)$$

$$BBR_{1} \xrightarrow{ISC} {}^{3}BBR_{1} \qquad \ldots (4)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH \qquad \ldots (5)$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + H^{+} + {}^{\bullet}OH \qquad \ldots (6)$$

$$H_2O_2 + h\upsilon \longrightarrow 2\,{}^{\bullet}OH \qquad \ldots (7)$$

$${}^{\bullet}OH + BBR \longrightarrow \text{Leuco BBR} \qquad \ldots (8)$$

$$\text{Leuco BBR} \longrightarrow \text{Oxidized products} \qquad \ldots (9)$$

Bismark brown-R is excited to its first excited singlet state by absorbing light of suitable wavelength, which undergoes intersystem crossing to its corresponding triplet state. Ferrous and cuprous ions will react with H_2O_2 decomposing it into $^{\bullet}OH$ radicals, ^{-}OH ions and oxidizing itself to ferric or cupric ions. These ions in higher oxidation states will react with H_2O in presence of light; thus, regenerating ferrous/cuprous ions. Sidewise hydroxyl radical is generated along with a proton, which will assist in maintaining to pH of medium. These radicals will oxidize triplet state of Bismark brown-R to its leuco form, which will finally degrade to oxidized products.

APPLICATION

Photo-Fenton and Photo-Fenton like reagent has been reported by Bosco *et al.*[26] in degradation of ivermectin, a veterinary drug. Degradation of tetracycline by photo-Fenton process under solar irradiation was studied by Bautitz *et al.* [27]. Fenton's reagent has also been used to remediate diesel contaminated soils by Xu *et al.* [28]. The feasibility of use of photo-Fenton like method using nano zero-valent iron (nZVI/UV/H_2O_2) has been assessed by Dehghani *et al.* [29] in removing total petroleum hydrocarbons.

CONCLUSION

Photo-Fenton or photo-Fenton like process seems to be a promising method for treatment of pollutants present in contaminated water and takes care of environment also. It was also observed that montmorillonite can be used as a support for photo-Fenton or photo-Fenton like reagent. Observations indicate that Cu- and Fe- loaded montmorillonite has lower rate of degradation of Bismark brown-R than Cu-Fe loaded montmorillonite. This may be due to synergistic effect of photo-Fenton like reagent on photo-Fenton reagent. Thus, it is worthwhile to mineralize toxic dyes to their less toxic or almost harmless counter parts using photo-Fenton or photo-Fenton like reagents and better, a combination of two.

REFERENCES

[1]. A. Kumar, M. Paliwal, R. Ameta, S. C. Ameta, Oxidation of fast green FCF by the solar photo-Fenton process, *J. Iran. Chem. Soc.*, **2008**, 5, 346-335.
[2]. M. A. Rauf, S. S. Ashraf, Radiation induced degradation of dyes--An overview, *J. Hazard. Mater*, **2009**, 166, 6-16.
[3]. C. M. Whitaker, C. C. Willock, Dyeing with coal tar dyestuffs, *Tindal cox Bailliere*, **1949**, 5, 1-7.
[4]. L. Huang, D. Gu, L. Yang, L. Xia, R. Zhang, H. Hou, Photoreductive degradation of sulfur hexafluoride in the presence of styrene, *J. Environ. Sci.*, **2008**, 20, 183-188.
[5]. C. Radulescu, A. M. Hossu, I. Ionita, E. I. Moater, Synthesis and characterization of new cationic dyes for synthetic fibres, *Dyes Pigments*, **2008**, 76, 366-371.
[6]. A. S. Stasinakis, Use of selected advanced oxidation processes (AOPs) for waste water treatment, *Global Nest J*, **2008**, 10, 376-385.
[7]. S. Nam, P. G. Tratnyek, Reduction of azo dyes with zero-valent iron, *Water Res.*, **2000**, 34, 1837-1845.
[8]. A. B. Prevot, C. Baiocchi, M. C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO_2 suspensions. *Environ. Sci. Technol.*, **2001**, 35, 971-976.
[9]. Y. H. Lee, S. G. Pavlostathis, Decolorization and toxicity of reactive anthraquinone textile dyes under methanogenic conditions. *Water Res.*, **2004**, 38, 1838-1852.
[10]. O. Legrini, E. Oliveros, A. M. Braun, Photochemical processes for water treatment. *Chem. Rev.*, **1993**, 93, 671 -698.
[11]. T. Aye, W. A. Anderson, M. Mehrvar, Photocatalytic treatment of cibacron brilliant yellow 3G-P. *J. Environ. Sci. Health*, **2003**, 38, 1903-1914.
[12]. A. Brown, S. C. DeVito, Predicting azo dye toxicity. *Crit. Revs. Environ. Sci. Technol.*, **2003**, 23, 249-324.
[13]. M. Abbas, H. Robab, Ultrasonic degradation of rhodamine B in the presence of H_2O_2 and some metal oxide. *Ultrason. Sonochem.*, **2010**, 17, 168 -172.
[14]. M. Neamtu, I. Siminiceami, A. Kettrup, Kinetics of nitromusk compounds degradation in water by UV radiation and hydrogen peroxide. *Chemosphere*, **2000**, 40, 1407–1410.
[15]. R. S. Sreedhar, B. Kotaiah, Decolorization of simulated spent reactive dye bath using solar/TiO_2/H_2O_2. *Int. J. Environ. Sci. Tech.*, **2005**, 2, 245-251.
[16]. H. A. B. Fang, S. R. Venkata, A. B. Kambala, S. C. Madapusi, R. C. Dharmarajan, R. A. B. Naidu. Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review, *Appl. Catal. A: Gen,*. **2009**, 359, 25-40.
[17]. T. Nargawe, A. K. Rai, R. Ameta, S. C. Ameta, Adsorption study for removal of crystal violet dye using MMT-MWCNTs composite from aqueous solution, *J. Applicable Chem*., **2018**, 7(5), 1252-1259
[18]. L. Ayed, K. Chaieb, A. Cheref, A. Bakhrouf, Biodegradation and decolorization of triphenylmethane dyes by *Staphylococcus epidermidis*. *Desalination*, **2010**, 260, 137–146.

[19]. O. CInar, S. Yasar, M. Kertmen, K. Demiröz, N. O. Yigit, M. Kitis, Effect of cycle time on biodegradation of azo dye in sequencing batch reactor. *Process Safety Environ. Prot*., **2008**, 86, 455–460.

[20]. C. Bouasla, M. E. H. Samar, F. Ismail, Degradation of methyl violet 6B dye by the Fenton process. *Desalination*, **2010**, 254, 35–41.

[21]. M. Jangid, S. C. Ameta, A. Sharma, Photodegradation study of Evan's blue in presence of strontium chromate, *J. Applicable Chem*., **2018**, 7(5), 1291-1299.

[22]. A. Paliwal, R. Banu, R. Ameta, S. C. Ameta, Photocatalytic degradation of methylene blue using undoped and Co-doped bismuth ferrite, *J. Applicable Chem*., **2017**, 6(5) 967-975.

[23]. J. M. Monteagudo, A. Duran, I. S. Martin, M. Aguirre, Catalytic degradation of orange II in a ferrioxalate-assisted photo-Fenton process using a combined UVA/C-solar pilot-plant system. *Appl. Catal. B: Environ*., **2010**, 95, 120–129.

[24]. M. A. Rauf, M. A. Meetani, A. Khaleel, A. Ahmed, Photocatalytic degradation of methylene blue using a mixed catalyst and product analysis by LC/MS. *Chem. Eng. J.*, **2010**, 157, 373–378.

[25]. N. Kang, D. S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenol, *Chemosphere,* **2002**, 47, 915-924.

[26]. D. Bosco, M. Sandra, I. M. Barbosa, C. P. Fernando, M. Maniero, G. Rath, G. Susanne , R Jose, Degradation of ivermectin by fenton and photo-fenton and toxicity test using daphnia similis, *J. Adv Oxidation Techno*., **2011**, 14, 292-301.

[27]. I. Rossi Bautitz and R. F. Pupo Nogueira, *J. Photochem. Photobiol.* A: Chem., **2007**, 187, 33.

[28]. P. Xu, G. Achari, M. Mahmoud, and R. C. Joshi RC. Application of Fenton's reagent to remediate diesel contaminated soils. *Pract. Period. Hazard. Toxic. Radioact. Waste Manage.*, **2006**, 10, 19-27.

[29]. M. Dehghani, E. Shashsavani, M. Farzadkia, and M. R. Samaei , Optimizing photo-Fenton like process for the removal of diesel fuel from the aqueous phase. *J Environ Health Sci Eng*., **2014**, 12, 12-87.