

Decolorization of Reactive Azo Dye Remazol Black B by Using Advanced Oxidation Processes (AOPs)

Nabeela Firdous, Irfan Ahmed Shaikh and Rukhsana Shahid

College of Earth and Environmental Sciences, University of the Punjab, Lahore, Pakistan.
textilemaster@gmail.com*

(Received on 19th July 2017, accepted in revised form 6th April 2018)

Summary: This study was carried out to ascertain the effect of photochemical and non-photochemical AOPs (O_3 alone, O_3/H_2O_2 , UV alone, UV/ H_2O_2 and Fenton's process) on the decolorization of sulphatoethylesulphone reactive group azo dye (Remazol Black B). All experiments were performed on a laboratory scale set-up and room temperature. Initial results showed that decolorization by UV alone were not effective because dye was photolytically stable and resistant to direct UV irradiation. However, the addition of appropriate amount of H_2O_2 improved color removal efficacy and the dye degradation. The research results showed that color removal efficiencies by O_3/H_2O_2 , UV/ H_2O_2 of synthetic dye solution containing 100 mg/l concentration were found efficient. Ozone assisted hydrogen peroxide (O_3/H_2O_2) treatment yielded about 98% decolorization at pH 9 and 25 minutes ozone exposure time. At 15 minutes of UV exposure with 4.4 mM H_2O_2 dose, 99% color removal efficiency was achieved. It is evident from results that the addition of H_2O_2 in the O_3 and with UV irradiation accelerated the decomposition and degradation of synthetic dye solution through an increased rate of hydroxyl radical ($HO\bullet$) generation which has high oxidation potential. Fenton's process (H_2O_2/Fe^{+2} reagent) showing remarkable results (99.9%) in terms of color removal in just 5 minutes at pH 3 while keeping optimal iron (Fe^{2+}) dose of 0.25 mM and hydrogen peroxide (H_2O_2 , 30% w/w) concentration 2.2 mM in effluent. Ultraviolet (UV) assisted with H_2O_2 also proved promising technique after Fenton's process. There was about 99% color removal in 15 minutes UV exposure time at pH 5 value. Findings of the study clearly revealed that synthetic dye (Remazol Black B) effluent was degraded successfully by all examined advanced oxidation processes (AOPs) except UV alone irradiation at feasible treatment time, initial pH and adequate H_2O_2 dose value.

Keywords: Ozone (O_3); Fenton; Ultraviolet (UV); Degradation; Decolorization.

Introduction

Textile industry uses large amount of water in different processes from gray to finished fiber products, especially in wet processes such as bleaching, mercerizing, dyeing, and printing [1]. Among all wet processes, dyeing is the main source of color in the effluent, and thus removal of color becomes a serious challenge [2]. It is estimated that annually 2.80×10^5 tons of spent dyes are being discharged to the receiving water bodies along 6.9×10^3 chemicals and salts [3, 4]. Color in the effluent not only damages the esthetic nature of water, but also reduces light penetration which affects photosynthesis process of aquatic biota of receiving bodies [5]. Even a minor concentration of dye is highly visible and intolerable in water [6]. Many of these hydrolyzed reactive dyes form toxic and aromatic by products and complexes which may be carcinogenic as well as mutagenic to living organism [7, 8].

Several treatment strategies including chemical, biological and physical by adsorption such as magnetic mesoporous clay (MSEP) as well as activated carbon (MAC) have been employed for the removal of color from wastewater [9-11]. But, all

these conventional treatment processes are incapable of complete decolorization and degradation of dyes from the effluent [12]. Sludge generation, operational problems, high retention time and cost ineffectiveness are also major hurdles in the implementation of these techniques [13].

Advanced oxidation is an endowed alternative of conventional treatment methods. These processes have great potential in treating pollutants with high efficiency on low operational cost and detention time [14]. AOPs processes include ozonation, fenton's oxidation, photo-Fenton oxidation, UV, H_2O_2 and their combinations. Also Fenton like degradation with carbon-based nano materials such as activated carbon (AC) have been studied [15].

All these have ability to generate free oxidation radicals through a series of reaction which substantially have higher oxidation potential [16]. Especially, hydroxyl radical ($OH\bullet$) plays important role in the decolorization of synthetic dye because it quickly cleavage double bond ($-N=N-$) of chromophoric group [17].

*To whom all correspondence should be addressed.

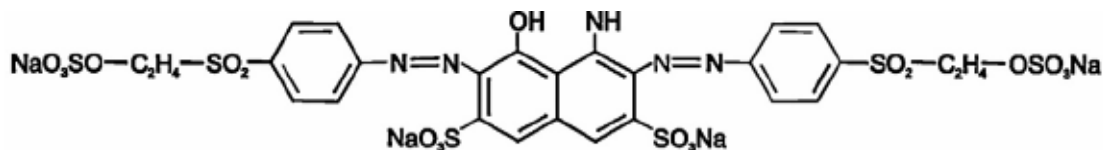


Fig. 1: Dye Remazol Black B chemical structure.

This research study is an attempt to investigate the influence of process conditions such as pH, treatment time and hydrogen peroxide dose on the performance of various advanced oxidation processes and their combination for the decolorization of synthetic solution containing reactive azo dye (Remazol Black B).

Experimental

Hydrogen peroxide (H_2O_2) of analytical grade (30% w/w) and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) were obtained from Merck, Germany. Synozol C.I Reactive Black 5 (Remazol Black B) was obtained from Clariant, Pakistan. Distilled deionized water (DDW) was used for preparing synthetic aqueous solution of dye. The stock solution of dye having 1000 mg/L concentration was prepared, and all the experiments were carried out on 100 mg/L dye solutions. (Fig. 1)

Experimental set up for AOPs

A cylindrical glass bubble column reactor was used to carry out ozone experiments. Internal diameter of reactor was 33mm. The ozone generator (JQ-6M, PURE TECH) was employed to feed ozone to untreated aqueous dye solution by means of porous diffuser. The gas output rate was 1.1 L/min. (Fig. 2 and 3)

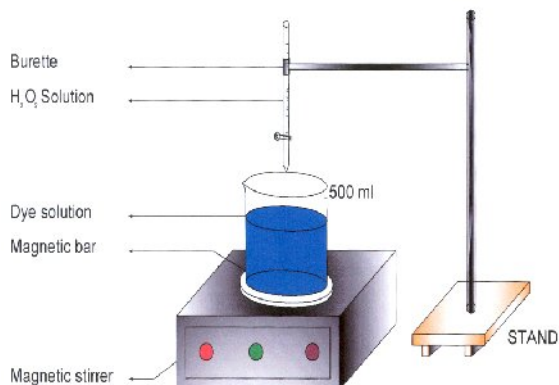


Fig. 2: Experimental set up for fenton's process.

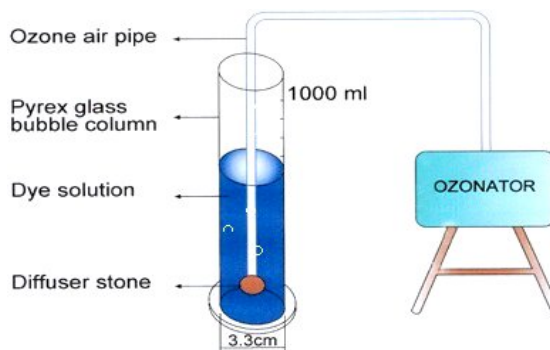


Fig. 3: Schematic Diagram of Ozonation Process.

The UV light source (Wavelength: 254 nm) was a mercury vapor lamp (3SC9 PENRAY UPLAND - USA). The UV radiation intensity was 5 mW/cm^2 . In order to enhance the absorbance of UV irradiation all related experiments were carried out in wrapped aluminum (Al) foil. Various concentrations (2.2 – 8.8 mM) of hydrogen peroxide were used for its optimal dose determination.

A lab scale Fenton set up was used consisting of a pyrex glass beaker coupled with a magnetic stirrer. The percentage of dye color removal was determined by using an UV/Visible Spectrophotometer (MN-Micron 970) at the wavelength of 597 nm. All experiments were carried out at room temperature.

The percentage color degradation was obtained as follows equation:

$$\text{Dye Removal (\%)} = (C_i - C_t / C_i) * 100$$

Where C_i was the concentration of untreated dye sample and C_t was the concentration of the respective AOPs treated sample.

Results and Discussion

The effects of pH and treatment time of AOPs on color removal efficiency

Table-1 displays the effect of variables such as initial pH values and contact time on color

removal of synthetic dyes by advanced oxidation processes (AOPs such as O_3 , O_3/H_2O_2 , UV, UV / H_2O_2 and Fe^{+2} / H_2O_2). The initial pH effect was assessed by varying pH from 3 to 9.

Ozonation process: The results demonstrated that ozone worked very well in the basic medium, and a colour removal efficiency of 89% was achieved at pH 9 for 25 minutes ozone exposure. Highest color removal was accompanied by ozone destabilization and decomposition into secondary free oxidation radicals ($HO\cdot$, $HO_3\cdot$, $HO_2\cdot$) through a series of reaction in highly alkaline medium. During ozonation, hydroxyl radical ($HO\cdot$) is especially important in the decolorization process because of its high oxidation potential [18] which quickly cleavage double bond ($-N=N-$) of chromophoric group of synthetic dye [19]. The color removal efficiency of 75% was observed at pH 3 for 20 minutes ozone contact time. In acidic pH, low oxidation potential and ozone decomposition performance caused reduced decolorization. The results showed that there was no appreciable progress in color removal efficiency by increasing ozone exposure time. (Fig. 4)

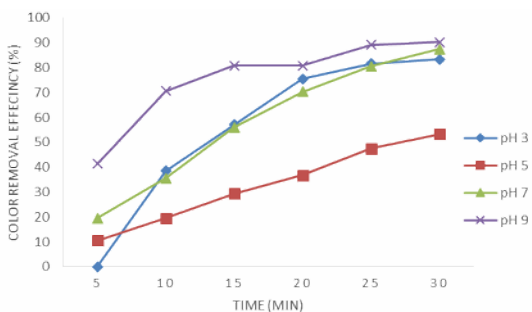


Fig. 4: Color removal of dye by ozone alone at various pH.

Ozone assisted with hydrogen peroxide (O_3/H_2O_2) treatment resulted 99% decolorization at pH 9 and 25 minutes ozone exposure time. Comparison of the results with color removal efficiency of ozone alone showed that there was almost 10 % increase in the color removal efficiency of H_2O_2/O_3 at the same ozone exposure time (25 min). It appears that addition of H_2O_2 in the O_3 has accelerated the decomposition of ozone, which resulted in an increased rate of hydroxyl radical ($HO\cdot$) generation [20]. (Fig. 5)

The UV alone effect on dye decolorization is given in Fig.6. At pH 7 and irradiation time of half an hour, only 26% color removal was observed. This deficiency of color removal can be explained as the

direct photolysis of organic compounds has complex reaction mechanism, so it can be predicted that during UV light contact, dye might have undergone intermolecular transformations process. Generation of oxidizing radical species did not occur when further decomposition of excited molecules of dye reaction took place. However, compared to other advanced oxidation processes, longer irradiation period (1 h) seems to be required. (Fig. 6).

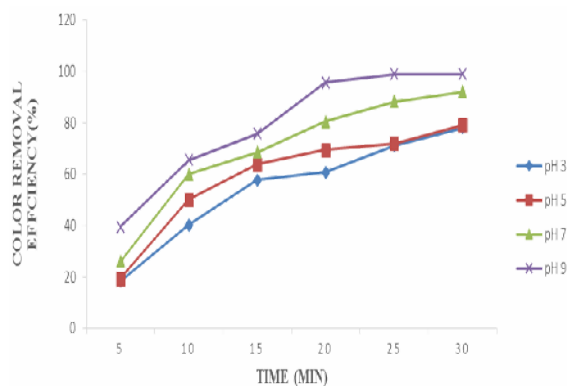


Fig. 5: Color Removal of dye by ozone and hydrogen peroxide (O_3/H_2O_2) at various pH.

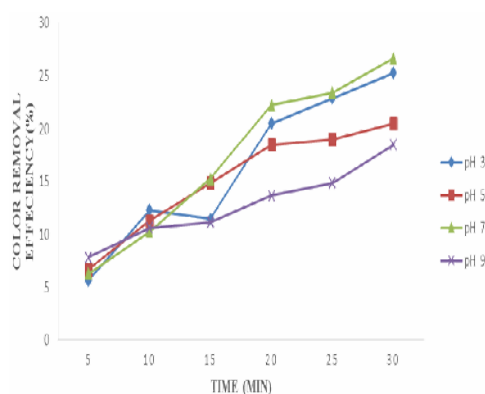


Fig. 6: Color removal of dye by UV alone at various pH.

Fig.7 reveals color removal efficiency of a combined system of UV and H_2O_2 of synthetic dye solution of 100 mg/l concentration. Results demonstrated that on 15 min of UV exposure with 4.4 mM H_2O_2 dose, there was 97% color removal efficiency. There was 100% color removal for 20 minutes exposure at pH value 5 of same dye concentration. Hydrogen peroxide decomposition yields hydroxyl radicals ($HO\cdot$) and other species under UV radiation. However, efficiency substantially decreased by increasing the solution pH value and remained at 70 and 85% for pH value 7 and 9, respectively, on the same exposure time and H_2O_2

dose. This can be attributed to the reduction of hydroxyl radicals' level due to the fact that under alkaline conditions hydrogen peroxide decomposes into water and oxygen rather than hydroxyl radicals. (Fig. 7)

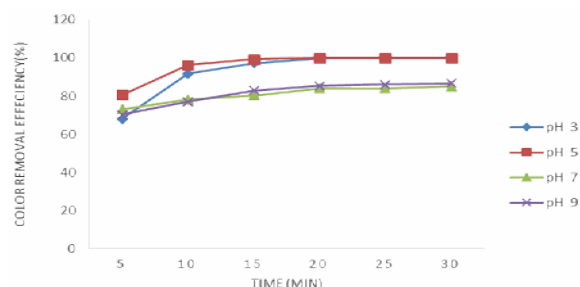


Fig. 7: Color removal of dye by UV and hydrogen peroxide (UV/H₂O₂).

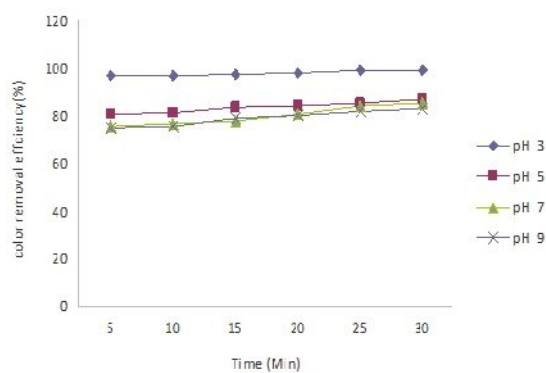


Fig. 8: Color removal of dye by Fenton's process (Fe²⁺/H₂O₂) at various pH.

Table-1: Effect of Initial pH and contact Time on the color removal efficiency through AOPs Processes.

| Treatment Type | pH | Color removal efficiency(%) with respect to Contact time (min) | | | | | |
|--|----|--|--------|--------|--------|--------|--------|
| | | 5 min | 10 min | 15 min | 20 min | 25 min | 30 min |
| Ozone Alone (O ₃) | 3 | n.d [†] | 38.60 | 57.02 | 75.44 | 81.58 | 83.38 |
| | 5 | 10.63 | 19.50 | 29.39 | 36.89 | 47.47 | 53.27 |
| | 7 | 19.50 | 35.53 | 55.99 | 70.32 | 80.56 | 87.38 |
| | 9 | 41.33 | 70.66 | 80.89 | 80.77 | 89.20 | 90.2 |
| O ₃ / H ₂ O ₂ | 3 | 18.48 | 40.31 | 57.70 | 60.77 | 71.34 | 78.17 |
| | 5 | 19.50 | 50.19 | 63.84 | 69.64 | 72.02 | 79.19 |
| | 7 | 25.98 | 60.09 | 68.62 | 80.55 | 88.40 | 92.15 |
| | 9 | 39.62 | 65.55 | 75.78 | 95.74 | 98.90 | 99.06 |
| UV Alone | 3 | 5.65 | 12.34 | 11.46 | 20.52 | 22.91 | 25.30 |
| | 5 | 6.70 | 11.31 | 14.89 | 18.48 | 19.02 | 20.52 |
| | 7 | 6.32 | 10.29 | 15.26 | 22.23 | 23.45 | 26.66 |
| | 9 | 7.86 | 10.63 | 11.15 | 13.70 | 14.86 | 18.48 |
| UV/ H ₂ O ₂ | 3 | 67.94 | 91.81 | 97.27 | 99.66 | 99.70 | 99.80 |
| | 5 | 80.55 | 96.25 | 99.32 | 100.0 | 99.20 | 99.12 |
| | 7 | 73.05 | 78.17 | 80.22 | 83.97 | 84.12 | 85.00 |
| | 9 | 70.32 | 77.15 | 82.95 | 85.33 | 86.14 | 86.70 |
| (Fe/H ₂ O ₂) | 3 | 96.93 | 97.03 | 97.61 | 98.29 | 98.98 | 98.98 |
| | 5 | 80.56 | 81.58 | 83.63 | 84.31 | 85.67 | 87.38 |
| | 7 | 75.78 | 76.80 | 78.17 | 80.55 | 83.97 | 85.67 |
| | 9 | 74.89 | 75.43 | 79.08 | 80.13 | 81.97 | 83.06 |

Table-2: The effect of H₂O₂ concentration on the decolorization of O₃/ H₂O₂, UV/ H₂O₂ and Fe²⁺/H₂O₂ Processes.

| Treatment Type | H ₂ O ₂ Concentration (mM) | Color removal efficiency(%) with respect to Contact time (min) | | | |
|---|--|--|--------|--------|--------|
| | | 5 min | 10 min | 15 min | 20 min |
| O ₃ / H ₂ O ₂ | 2.2 | 50.29 | 64.99 | 81.86 | 85.93 |
| | 4.4 | 67.98 | 87.77 | 91.29 | 93.98 |
| | 6.6 | 70.05 | 86.74 | 97.17 | 98.06 |
| | 8.8 | 72.32 | 92.13 | 97.06 | 98.13 |
| UV/ H ₂ O ₂ | 2.2 | 54.29 | 84.99 | 93.86 | 96.93 |
| | 4.4 | 69.98 | 89.77 | 98.29 | 98.98 |
| | 6.6 | 73.05 | 88.74 | 97.27 | 98.98 |
| | 8.8 | 70.32 | 91.13 | 97.61 | 98.63 |
| Fe ²⁺ /H ₂ O ₂ | 2.2 | 85.67 | 89.43 | 92.84 | 93.18 |
| | 4.4 | 95.91 | 96.25 | 97.61 | 98.64 |
| | 6.6 | 96.25 | 96.59 | 97.27 | 98.98 |
| | 8.8 | 96.93 | 95.91 | 97.61 | 98.98 |

Experimental results in table-1 show that at pH 3, solution underwent 97% decolorization in the first 5 minutes oxidation. An increase in pH value

from 3 to 9 decreases the decolorization from 97% to 74% respectively. So the optimum pH to achieve the highest color removal efficiencies was found to be 3.

Several researchers have also reported pH 3 as an optimum pH for Fenton process [21, 22].

Effects of various concentrations of H₂O₂ on AOPs

Table-2 shows that 4.4 mM dose of H₂O₂ and ozonation exposure of 20 minutes gave 85% color removal. Higher dose of H₂O₂ (6.6 mM) yielded 98% color removal at the same oxidation time (20 min). However, beyond this dose, the color removal efficiency started declining.

In O₃/H₂O₂ combination, H₂O₂ dose 2.2 mM and O₃ irradiation of 15 minutes gave 84% color removal. Higher dose of (4.4 mM) H₂O₂ gave 98% color removal at the same oxidation time (15 min). However, beyond this dose, the color removal efficiency again started to decrease. Addition of H₂O₂ in dye solution accelerates the photodecomposition resulting into increased production of hydroxyl radicals for dye oxidation. But when the H₂O₂ amount, relative to that of the dye in the mixture, is increased than the “most effective level” which yields the highest dye degradation, H₂O₂ acts as a scavenger of highly reactive free radicals (•OH) forming other inactive radicals such as peroxy and oxygen. HO•₂ are much less reactive and reduces the efficiency of the decolorization process. Furthermore, hydroxyl radicals (HO•) generated at high concentration will readily be converted into H₂O₂ [23].

The effect of H₂O₂ dose on treatment efficiency was investigated by varying H₂O₂ concentration while keeping optimal Fe²⁺ does of 0.25 mM at pH 3 as presented in table- 2. Increasing H₂O₂ concentration from 2.2 mM to 4.4 mM increased the color removal efficiency from 86% to 96 % in first 5 minutes. The addition of hydrogen peroxide (H₂O₂) increases the decolorization rate because of increased hydroxyl radical concentration in dye solution. Beyond 4.4 mM of H₂O₂ dose, marginal improvement in color removal was observed. For instance, increasing the H₂O₂ dose from 4.4 mM to 6.6 mM showed an improvement from 96% to 96.2% decolorization. This negligible improvement in decolorization efficiency is due to the fact that at higher H₂O₂ concentrations, scavenging of hydroxyl radical occurs that resulted in the formation of per hydroxyl radicals HO•₂ which are significantly less reactive than hydroxyl radicals. In addition, recombination of hydroxyl radical (•OH) also occurs, and thus these two reasons decline the overall efficiency of decolorization [24]. Hence, 4.4 mM of H₂O₂ dosage yielding 96% color removal at initial 5 min appears as an optimal.

Conclusion

The present work investigated the effectiveness of various AOPs in the decolorization of Remazol Black B dye. All AOPs used in this study appeared to be capable of completely decolorizing the azo dye Remazol Black B within feasible reaction time, ranging from few minutes to 30 minutes, except UV alone as the dye seemed to be resistant to direct photolysis. Fenton’s process was found to be a suitable and promising treatment method as compared to other AOPs. It gave complete decolorization of synthetic dye Remazol black B in relatively short reaction time such as 96% in 5 minutes at optimal process conditions (pH 3 and 4.4 mM H₂O₂ dose). O₃/H₂O₂ combination also proved promising technique and gave more than 98% color removal in 25 minutes exposure time. However the direct application of ozone (O₃) gave 89% color removal in 25 minutes exposure time. Exposure of UV alone proved that dye was photolytically stable. However, addition of H₂O₂ tremendously improved the efficiency of the system and gave 99% decolorization at H₂O₂ dose of 4.4 mM at 15 minute irradiation. A dose of H₂O₂ higher than 4.4 mM per liter corresponded to an unsuccessful consumption of hydrogen peroxide due to the scavenging effect of excess H₂O₂ and hydroxyl radicals.

References

1. S. M. Imtiazuddin, M. Mumtaz and K. A. Mallick, Pollutants of wastewater characteristics in textile industries, *J. Basic Applied Sci.*, **8**, 554 (2012).
2. D. M. K. Iqbal, S. Ahmed, D. S. Alam and D. M. Ahmed, Sustainable management of textile waste water of Pakistan, *World Water Day.*, 96 (2011).
3. A. Asghar, A. A. A. Raman and W. M. A. W. Daud, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment, *J. Clean Prod.*, **87**, 826 (2015).
4. A. Hazrat, K. Mehtab, I. Muhammad and A. J. Sohail, Biological decolorization of crystal violet by *Alternaria solani*, *Int. J. Green Herb. Chem.*, **2**, 31 (2013).
5. N. Puvaneswari, J. Muthukrishnan and P. Gunasekaran, Toxicity and assessment and microbial degradation, *Indian J. Exp. Bio.*, **44**, 618 (2006).
6. P. Nigam, G. Armour, I. M. Banat, D. Singh and R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, *Bioresour. Technol.*, **72**, 219 (2000).

7. D. Suteu, C. Zaharia, D. Bilba, A. Muresan, R. Muresan and A. Popescu, Decolorization of wastewaters from the textile industry, *Industria Textila.*, **60**, 254 (2009).
8. C. Zaharia, D. Suteu, A. Muresan, R. Muresan and A. Popescu, Textile wastewater treatment by homogenous oxidation with hydrogen peroxide. *Environ. Eng. Manag. J.*, **8**, 1359 (2009).
9. R. Slimani, I. El Ouahabi, F. Abidi, M. El Haddad, A. Regti, M. R. Laamari, and S. Lazar, Calcined eggshells as a new biosorbent to remove basic dye from aqueous solutions: Thermodynamics, kinetics, isotherms and error analysis, *J. Taiwan Inst. Chem. E.*, **45**, 1578 (2014).
10. M. Fayazi, D. Afzali, M. A. Taher, A. Mostafavi and V. K. Gupta, Removal of Safranin dye from aqueous solution using magnetic mesoporous clay: Optimization study, *J. Mol. Liq.*, **212**, 675 (2015).
11. M. Fayazi, M. G. Motlagh and M.A.Taher, The adsorption of basic dye (AlizarinredS) from aqueous solution onto activated carbon/ γ -Fe₂O₃ nano-composite: Kinetic and equilibrium studies, *Mater. Sci. Semicond. Process.*, **40**, 35 (2015).
12. F. Deniz and S. Karaman, Removal of Basic Red 46 dye from aqueous solution by pine tree leaves, *Chem. Eng. J.*, **170**, 67 (2011).
13. C. J. Ogugbue and T. Sawidis, Bioremediation and detoxification of synthetic waste water containing triarylmethane dyes by *Aeromonas hydrophila* isolated from industrial effluent, *Biotechnol. Res. Int.*, **11**, 11 (2011).
14. M. Tekbas, H. C. Yatmaz and N. Bektas, Heterogeneous photo-Fenton oxidation of reactive azo dye solutions using iron exchanged zeolite as a catalyst, *Micropor. Mesopor. Mat.*, **115**, 594 (2008).
15. M. Fayazi, M. A. Taher, D. Afzali, A. Mostafavi, Enhanced Fenton-like degradation of methylene blue by magnetically activated carbon/hydrogen peroxide with hydroxylamine as Fenton enhancer, *J. Mol. Liq.*, **216**, 781 (2016).
16. A. S. Stasinakis, Use of selected advanced oxidation processes (AOPs) for wastewater treatment, *Global NEST Journal.*, **10**, 376 (2008).
17. I. A. Arslan, A. B. Isil and W. B. Detlef, Advanced oxidation of a reactive dyebath effluent: comparison of O₃, H₂O₂/UV-C and TiO₂/UV-A processes, *Water Res.*, **36**, 1143 (2002).
18. H. Selcuk, Decolorization and detoxification of textile wastewater by ozonation and coagulation process, *Dyes Pigments.*, **64**, 217 (2005).
19. I. A. Arslan and A. I. Balcioglu, Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes; a case study with hydrolyzed Reactive Black 5, *J. Photoch. Photobio.*, **141**, 247 (2001).
20. D. Sargunamani, M. Muthukumar and N. Selvakumar, Statistical analysis of the effect of aromatic, azo and sulphonic acid groups on decolorization of acid dye effluents using advanced oxidation processes, *Dyes pigments.*, **65**, 151 (2005).
21. S. M. Lucas and A. J. Peres, Decolorisation of azo dye Reactive Black 5 by Fenton and Photo-Fenton oxidation, *Dyes pigments.* **71**, 235 (2006).
22. C. L. Hsueh, Y. H. Huang, C. C. Wang and C. Y. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, *Chemosphere.*, **58**, 1409 (2005).
23. A. Aleboyeh, H. Aleboyeh and Y. Moussa, Critical effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange. *Dyes Pigments.*, **57**, 67 (2005).
24. U. Bali, E. Catalkaya and F. Swngul, Photodegradation of Reactive Black 5, Direct Red 28 and Direct Yellow 12 Using UV, UV/H₂O₂ and UV/ H₂O₂/Fe⁺²: a comparative study, *J. Hazard. Mater.*, **114**, 159 (2004).