Oxidation of reactive black 5 solutions with sulfate radicals activated by iron

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Abstract

Textile Effluents are problematic effluents which cannot be treated with conventional biochemical treatment methods. One of the most promising methods for treatment of non-biodegradable wastewaters is advanced oxidation. In this study, effect of sulfate radical based advanced oxidation methods were investigated for treatment of an azo dye; Reactive Black 5 (RB-5). Sulfate radicals were activated with the addition of Iron(II) and Iron (III) Sulfate to the reaction medium. Effect of pH and persulfate dosage on RB-5 removal were also investigated. It was observed that runs which were conducted with Iron (II) ions yielded better results both in terms of RB-5 removal and reaction rate. It was recorded that RB-5 removal and removal rate both improved with increased persulfate dosage while optimum initial pH was found to be unadjusted pH which was measured as 3. RB-5 removal over 99% was observed in the run conducted at pH 3 with a persulfate dosage of 4 mM and FeSO$_4$ (Fe(II)) dosage of 1 mM.

1. Introduction

Textile effluent containing dyes are known to be toxic and non-biodegradable. With the stability of the modern dyes, the use of conventional biological treatment methods for industrial wastewater is proved to be ineffective [1]. Due to the fact that conventional biochemical treatment methods do not effectively treat the textile effluents, physical and chemical methods can be considered as alternative treatment methods. Advanced oxidation is a chemical treatment method relying on generation of hydroxyl or sulfate radicals and oxidation of targeted pollutants with these radicals. [2-4] sulfate radicals are obtained by activation of persulfate anion (PS) thermally or chemically such as transition metal ions [5]. Iron (II) and Iron (III) ions are amongst these transition metals. Metal activation takes place as shown in equation 1 [6]

$$S_2O_8^{2-} + Me^{n+} → SO_4^{-} + Me^{(n+1)+} + SO_4^{2-}$$  \hspace{1cm} (1)

When Fe$^{3+}$ is used as activator reactions below take place equation 2 shows sulfate radical formation. While equation 3 shows undesired radical consumption. [6]

$$S_2O_8^{2-} + Fe^{2+} → SO_4^{-} + Fe^{3+} + SO_4^{2-}$$  \hspace{1cm} (2)

$$SO_4^{-} + Fe^{2+} → Fe^{3+} + SO_4^{2-}$$  \hspace{1cm} (3)

On the other hand, reaction mechanism for Fe$^{3+}$ can be given as below [7]:

$$S_2O_8^{2-} + Fe^{3+} → SO_4^{-} + Fe^{2+} + SO_4^{2-}$$  \hspace{1cm} (4)

It is also reported that Fe$^{3+}$ ions can react with reaction intermediates to produce Fe$^{2+}$ and activation of PS is carried out with Fe$^{2+}$ ions in some cases resulting a decrease in decolorization rate with the runs conducted with Fe$^{3+}$ [6].
Reaction equations show that increase in iron concentration favors sulfate radical formation while over a certain iron concentration sulfate radical scavenging occurs. [6] On the other hand increase in PS concentration is expected to increase sulfate radical formation leading to increased oxidation rate of the targeted pollutant.

Advanced oxidation of an azo dye; Reactive black 5 (RB-5) with sulfate radical activated by Fe\(^{2+}\) and Fe\(^{3+}\) was studied. Oxidation of RB-5 with various advanced oxidation methods were studied [8-10] although there is limited information about oxidation of RB-5 with sulfate radicals activated by iron ions. Effect of activator, PS dosage and pH of the medium was observed on decolorization of RB 5. Reaction kinetics were also investigated.

2. Experimental

2.1 Materials
Potassium persulfate (ACS reagent ≥99%), Reactive Black 5 (Dye content 50%), sodium hydroxide, sulfuric acid, ferric and ferrous sulfate were purchased from Sigma-Aldrich.

2.2 Analytical
RB5 Concentration was measured by using Rayleigh UV 1601, UV-visible spectrophotometer at 590 nm. pH of the reaction medium was monitored by WTW multi 3430 multimeter. Iron concentration was measured by Raleigh WFX-130B atomic absorption spectrophotometer (AAS).

2.3 Decolorization experiments
Oxidation reactions were conducted in a 250 mL batch reactor for 90 minutes samples were taken with certain intervals and analyzed immediately with UV-Vis spectrophotometer. Iron concentrations throughout reaction period and after precipitation was monitored by using AAS. Initial dye concentration was selected as 50 mg.L\(^{-1}\) (0.05 mM), Iron (II) and Iron (III) concentration was selected as 1mM. Parameters that were investigated were; Activator type (Fe\(^{2+}\) and Fe\(^{3+}\)), PS concentration and solution pH. PS concentrations were selected as: 0.5, 1, 2, 4 mM and medium pH was adjusted to be 3, 4, 7 and 10. This procedure was followed in presence of both Fe\(^{2+}\) and Fe\(^{3+}\). Selected concentrations correspond to molar ratios of; \(10-20-40-80\) in terms of Dye/PS/Iron.

3. Results and discussions
Experiments without pH adjustment (pH = 3) were conducted in order to investigate effect of PS dosage and activator type on decolorization rate. The rest of the experiments which were conducted to observe effect of pH on decolorization rate were conducted with the selected PS dosage in the first set of experiments.

3.1 Effect of activator on decolorization rate
Decolorization rate of RB-5 was observed to be higher when Fe\(^{2+}\) was used as the activator for all PS dosages. Figure 1 represents the decolorization of RB-5 in sulfate radical oxidation experiments activated by Fe\(^{2+}\) and Fe\(^{3+}\). Having higher decolorization rates with presence of Fe\(^{3+}\) was expected since oxidation mechanism with Fe\(^{3+}\) involves production of Fe\(^{2+}\) followed by activation of PS with Fe\(^{2+}\) ions [6]. It is also worth to note that after a reaction period total decolorization values were observed to be similar. Comparison of RB-5 decolorization that were conducted at different PS dosages are presented in Figure 2. It was observed in this study that increase in PS dosage increased both decolorization rate and RB-5 removal. Increase in reaction rate with increasing PS dosage was expected since sulfate radical generation rate is dependent on PS concentration. It can also be reported that increasing PS concentration did not have any inhibiting effect on oxidation reaction for the studied PS concentration range. It is also worth to note that almost 100% dye removal was observed with the runs conducted with 4mM PS and Fe\(^{2+}\) as activator (30 minutes of reaction time). On the other hand, 96% dye removal was observed at the end of 90 minutes of reaction time for the runs conducted with presence of Fe\(^{3+}\) and 4mM PS.
3.2 Effect of pH on decolorization rate
Effect of medium pH was also investigated by adjusting pH of dye solution through addition of 0.1 M NaOH solution. Reactions were started by addition of the required amount of PS. It is well known that addition of OH\(^-\) ions will result iron hydroxide formation which is insoluble in water. Increasing pH didn’t just affect the reaction mechanism it also affected the dissolved iron amount in the medium which decreased the amount of the activator. Results obtained from the pH adjustment experiments are given in Figure 3.

It can be observed from the figure 3 that increasing pH of the medium decreased both RB-5 decolorization rate and dye removal. no significant color removal was observed in the run conducted with presence of Fe\(^{3+}\) ions at pH = 10. This can be explained by precipitation of iron ions as Fe(OH)\(_3\).
Figure 3. Effect of pH on decolorization of RB-5. PS Concentration: 4 mM, Fe Concentration: 0.1 mM, Dye Concentration: 0.05 mM. Activator: Fe^{2+} and Fe^{3+}

4. Conclusions
Iron (II) sulfate addition was found to be more effective than iron (III) sulfate for activation of sulfate radicals. Iron activated sulfate radical oxidation was found to be most effective at acidic conditions. Increase in decolorization rate and RB-5 removal was observed with the increase of PS concentration. TOC removal and byproduct formation should also be investigated in order to understand reaction mechanism better.

References
[1] Ghaly AE, Anathashankar R. Alhattdom, Ramakrishinan, “Production, Characterization and Treatment of textile effluents: A Critical Review”, Journal of Chemistry and Engineering Process 182. (2014)
[2] Yang Shiying, Wang Ping, Yang Xin, Wei Gang, Zhang Wenyi, Shan Liang, “A novel advanced oxidation process to degrade organic pollutants in wastewater: Microwave activated persulfate oxidation” Journal on Environmental Science 21, 1175-1180 (2009)
[3] P. Hu, M. Long, “Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications”, Applied Catal. Built Environment”, 181, 103–117(2016).
[4] S. Bekkouche, S. Merouani, O. Hamdaoui, M. Bouhelassa,” Efficient photocatalytic degradation of Safranin O by integrating solar-UV/TiO_2/persulfate treatment: Implication of sulfate radical in the oxidation process and effect of various water matrix components” Journal of Photochemistry. 345, 80-90 (2017)
[5] Xiang-Rong Xu, Xiang-Zhong Li, “Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion”, Separation and Purification Technology 72 105–111 (2010)
[6] S. Rodriguez, L. Vasquez, D. Costa, A. Romero, A. Santos “Oxidation of Orange G by persulfate activated by Fe(II), Fe(III) and zero valent iron (ZVI)”, Chemosphere 101 86–92 (2014)
[7] Tunlawit Satapanajaru, Maneekarn Yoo-iam, Pinnaree Bongprom, Patthra Pengthamkeerati, “Decolorization of Reactive Black 5 by persulfate oxidation activated by ferrous ion and its optimization”, Desalination and Water Treatment, 56, (2015)
[8] Ming Chang, Yang-hsin Shih, “Synthesis and application of magnetic iron oxide nanoparticles on the removal of Reactive Black 5: Reaction mechanism, temperature and pH effects”, Journal of Environmental Management 224, 235-242 (2018)
[9] Saltuk Pirgalıoğlu Tülay A. Özbeltge “Comparison of non-catalytic and catalytic ozonation processes of three different aqueous single dye solutions with respect to powder copper sulfide catalyst”, Applied Catalysis A: General, 363, 157-163, (2009)

[10] Mustapha Mohammed Bello, Abdul Aziz Abdul Raman, Anam Asghar, “Activated carbon as carrier in fluidized bed reactor for Fenton oxidation of recalcitrant dye: Oxidation-adsorption synergy and surface interaction”, Journal of Water Process Engineering 33, (2020)