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Heat activated persulfate oxidation of Reactive Black 5

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ABSTRACT

Sulfate radical based advanced oxidation processes gained great attention for the removal of refractory organic pollutants from wastewaters. In this study, heat and solar activated persulfate were tested for the removal of Reactive Black 5 from water matrices. Experiments were carried out under 1/30, 1/50, 1/100, 1/500 and 1/1,000 dye/potassium persulfate ratio at room temperature, 40°C and 60°C. Experiments that were conducted at 1/500 and 1/1,000 molar ratios and 60°C resulted in ≥99% color removal after reasonable reaction time (5–10 min). 99% of mineralization was observed after 90 min of treatment. Outdoor oxidation runs were conducted in July at the main campus of the European University of Lefke and resulted in complete de-colorization after 30 min at 1/1,000 molar ratio while 70% de-colorization observed when molar ratio was adjusted to 1/100. An increase of temperature from 25°C to 40°C was observed during the 90 min of reaction time without any additional heating.

Keywords: Sulfate radicals; Reactive Black 5 removal; Heat-activated persulfate; Advanced oxidation processes

1. Introduction

Dealing with recalcitrant water pollutants has always been a problematic issue, particularly, elimination of the dye molecules from textile wastewaters. Today, more than 10.000 types of dyes are being produced in the world. The most important types can be listed as azo, anthraquinone, phthalocyanine and triarylmethane [1]. Azo dyes comprise more than half of the total produced amount of dyes [2]. Moussavi and Mahmoudi [1] reported this number as 70% azo and 15% anthraquinone types of dyes. About 1%–20% of the total produced amount of dyes are lost during the dyeing process and discharged to the environment through textile effluents [3] which possess a threat to human health and are known to be toxic and carcinogenic. Dyes can be treated with physical and physicochemical methods such as coagulation/floatation, adsorption, ultrafiltration, precipitation, etc. Although these methods are effective for the removal of dye molecules, they are not destructive methods. They concentrate and transfer problematic molecules from one phase to another [3–5]. Conventional secondary treatment methods are also ineffective to decompose dye molecules because of their toxic and low biodegradable nature. Oxidation and advanced oxidation processes (AOPs) are therefore considered as an alternative for the treatment of such wastewaters since it is possible to oxidize and remove organic molecules through oxidation and even more effectively through advanced oxidation techniques [6,7].

Conventional AOPs rely on hydroxyl radical ($OH^{\bullet}$) formation which is the most powerful radical that attacks unselectively and causes the elimination of the pollutants. During the last decade, sulfate radical ($SO_4^{\bullet-}$) based AOPs gained great attention as an alternative for hydroxyl radical based AOPs [8]. Sulfate radicals' oxidation potential is comparable to hydroxyl radicals' oxidation potential. Sulfate

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radicals have a greater half-life than hydroxyl radicals which enables them to have higher contact time with the targeted molecule and increases mass transfer possibility through mediums. Sulfate radicals were also reported to react with organic molecules more selectively than the hydroxyl radicals [9]. Sulfate radical based AOPs rely on activation of persulfate (PS) or peroxymonosulfate by processes such as; UV radiation, heat addition or contacting with transition metals [6,8].

In literature, activation of persulfate (PS) by UV, solar and visible light irradiation process found promising for water decontamination and disinfection. 91.8% propranolol (20 μM) was removed after 30 min by the application of UV/PS (PS concentration: 0.4 mM) and the reaction rate constant was found as 0.0817 min^{-1} [10]. In another study, UV/PS (PS concentration: 2 mM) process caused 100% removal of cyclohexanoic acid (0.39 mM) within 30 min and the reaction rate constant was calculated as 0.17 min^{-1} [11]. Complete elimination of dichloroacetonitrile (2 μM) by UV/PS (PS concentration: 1 mM) treatment was achieved after 20 min [12]. In the UV-C/PS system, near complete degradation of sulfadiazine (99.8%) was observed within 10 min under 50 mg L^{-1} of PS concentration [13]. The removal percent of propylparaben (200 μg L^{-1}) after 30 min of UV-A/PS (PS concentration: 500 mg L^{-1}) exposure was 100% and the reaction rate constant was found as 0.039 min^{-1} [14]. Solar/PS (PS concentration: 0.5 mM) process was tested for disinfection purposes and resulted in the efficient removal of two model fecal indicators [15]. Water disinfection was achieved after 120 min by visible light/PS (PS concentration: 2 mM) process [16].

Various hydroxyl radical based AOPs have been studied recently [17–22] for the investigation of Reactive Black 5 (RB 5) removal from water. However, there is a lack of information concerning sulfate radicals' efficiency for the removal of RB 5. In this study, heat-activated PS was used to observe; reaction kinetics between the dye and sulfate radicals, dye removal and mineralization efficiencies under different reaction conditions. Our study also included a pair of preliminary test run for solar activated PS. The examined parameters include PS dosage and reaction temperature. Dye removal was monitored with an ultraviolet-visible spectrophotometer (UV-vis) while mineralization and reaction by-products monitored with total organic carbon (TOC) analyzer and gas chromatography-mass spectrometer (GC-MS). RB 5 contains an azo bond (N=N) which is mainly responsible for the color of the molecule as well as benzene and naphthalene aromatic rings [23]. Possible degradation products after the radical attack were also monitored and discussed.

2. Materials and methods

2.1. Materials

Potassium persulfate (ACS reagent ≥ 99%) and Reactive Black 5 (dye content 50%) were purchased from Isomer Laboratory and Medical Supplies Ltd., North Cyprus and supplied from Sigma Aldrich, USA. Potassium hydrogen phthalate (Reag. Ph Eur) and acetonitrile (gradient grade for liquid chromatography) were supplied from Merck Millipore, Germany and obtained from Tin Mühendislik, Turkey. Distilled water was produced from Sartorius 61316 system and purchased from Sartonet, Turkey. C18 SPE cartridges were supplied from Cayman chemical company, USA and purchased from Energon Ltd., Cyprus.

2.2. Oxidation reactions

The initial concentration of aqueous dye solutions was adjusted to 50 mg L^{-1}. Reactions were conducted in a beaker that was placed in a water bath and stirred continuously. Prior to the experiments, the temperature of the water bath was adjusted to the desired temperature values and the reaction started after the addition of potassium persulfate. Reactions were conducted under ambient pH conditions (pH 5) and pH was not adjusted during the experiments. The solution pH decreased to 3 ± 0.1 at the end of the experiments due to the by-product formation. Aliquots were collected at predetermined time intervals, cooled down immediately and analyzed. Parameters that were studied are dye/potassium persulfate molar ratio and temperature. Molar ratios examined were 1/30 1/50, 1/100, 1/500 and 1/1,000 and reaction temperatures were between room temperature (25°C) and 70°C. In addition, a preliminary experiment was conducted to reveal the activation effect of solar radiation on the generation of sulfate radicals.

2.3. Analytical methods

RB 5 concentrations were analyzed by a UV-visible spectrophotometer at 590 nm (Rayleigh UV 1601). Mineralization was observed with TOC measurements (Shimadzu, Kyoto, Japan, V_{CPN}-TOC analyzer via non-purgeable organic carbon method). No quenching agent was required prior to TOC and UV analyzes since the samples were cooled down immediately. No significant changes in color or TOC content was observed after sampling at ambient temperature. Samples for selected runs were also analyzed by GC-MS (Shimadzu, Kyoto, Japan) for the estimation of oxidation by-products. Prior to analysis, solid-phase extraction was performed and the procedure was as follows: Finisterre C18 cartridges were conditioned by 5 mL acetonitrile and 5 mL distilled water after that 50 mL sample were filtered by a vacuum pump and finally samples were collected in 5 mL acetonitrile. GC-MS temperature program was adjusted following EPA Method 8270 [24] recommendation (initial oven temperature 100°C was increased to 260°C at a 5°C min^{-1} rate. Injection temperature and interface temperatures were 260°C and ion source temperature was kept at 250°C). Teknokroma TRB-5MS (5% dimethyl-95% diphenyl polysiloxane) column having 30 m × 0.25 mm × 0.25 μm dimension was used for chromatographic separation. Helium was selected as the carrier gas at a flow rate of 1 mL min^{-1}. WILEY 7 library (USA) was used for the identification of by-products.

3. Results and discussions

Experiments were conducted with different persulfate dosages at room temperature, 40°C and 60°C. Results showed that the de-colorization rate and efficiency significantly increased with increased persulfate dosage and temperature. Organic carbon removal which shows total oxidation efficiency [7] was also monitored and removal efficiency over 99% was recorded for experiments conducted at 60°C with molar ratios of 1/500 and 1/1,000. No significant color and TOC removal were observed in the runs conducted at room temperature.

3.1. Effect of potassium persulfate dosage

Significant dye removal was recorded for the runs conducted at 40°C and 60°C. However, de-colorization and mineralization were not observed when experiments were carried out at room temperature. Figures showing dye removal at 40°C and 60°C under various potassium persulfate dosages are given in Fig. 1. TOC removals are also reported in Fig. 2.

It can be observed from Figs. 1 and 2 that the increased persulfate dosage resulted in increased decolorization rate, de-colorization efficiency and TOC removal for the studied dosages. This result is expected since the reaction rate is directly proportional to the reactant concentration. Results also indicate that the studied dosages did not have any inhibiting effect on oxidation of dye solutions. It is also reported in the literature that increased sulfate dosage had a positive effect on the oxidation rate and efficiency of targeted pollutants [25–28].

TOC removal was observed in the runs conducted with dye/potassium persulfate molar ratios of 1/500 and 1/1,000. TOC removal of 10% and 25% were observed for the mentioned sulfate dosages at 40°C while almost complete mineralization was achieved in the runs conducted at 60°C.

Our findings also suggested that the sulfate radicals needed to be activated by heat to be able to observe decolorization within the reaction time provided. Similar results were also reported in the literature for heat-activated persulfate oxidation [29]. Oxidation at room temperature did not have any effect on mineralization even for the periods that can be expressed in days. Only slight de-colorization was observed at the highest potassium persulfate dosage (1/1,000; dye/potassium persulfate molar ratio).

3.2. Effect of temperature

An increase in temperature favored reaction rate for both sulfate-dye oxidation and the oxidation of by-products. It is reported in the literature that decomposition of persulfate molecules which result in the formation of sulfate radicals are favored at higher temperatures [26,30–33]. In literature, heat-activated persulfate oxidation reactions commonly expressed with pseudo-first-order reaction kinetics

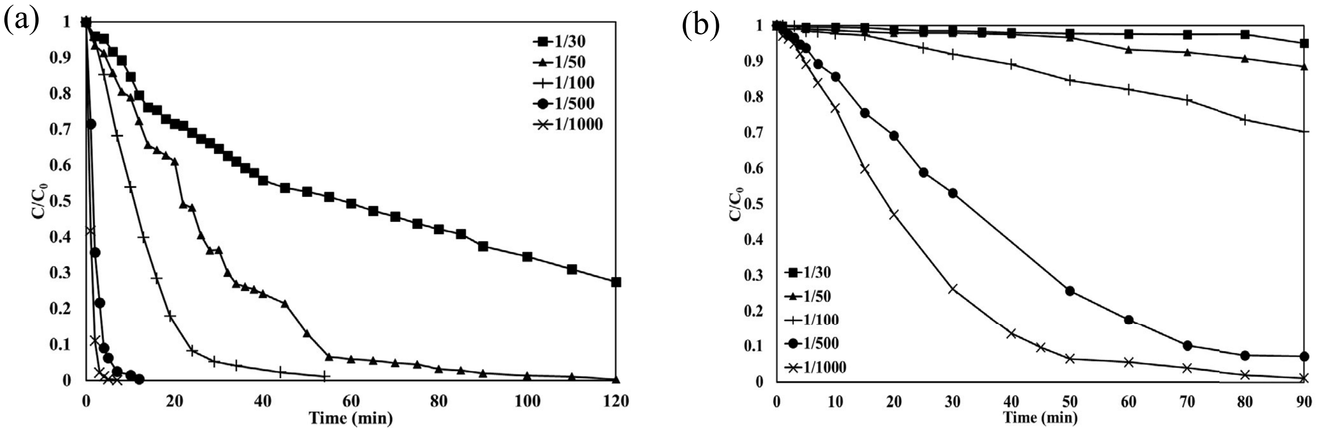


Fig. 1. Dye removal at different potassium persulfate dosages. (a) 60°C and (b) 40°C, initial pH = 5, initial dye concentration = 50 mg L^{-1} potassium persulfate dosages were reported in terms of molar ratio; dye/potassium persulfate.

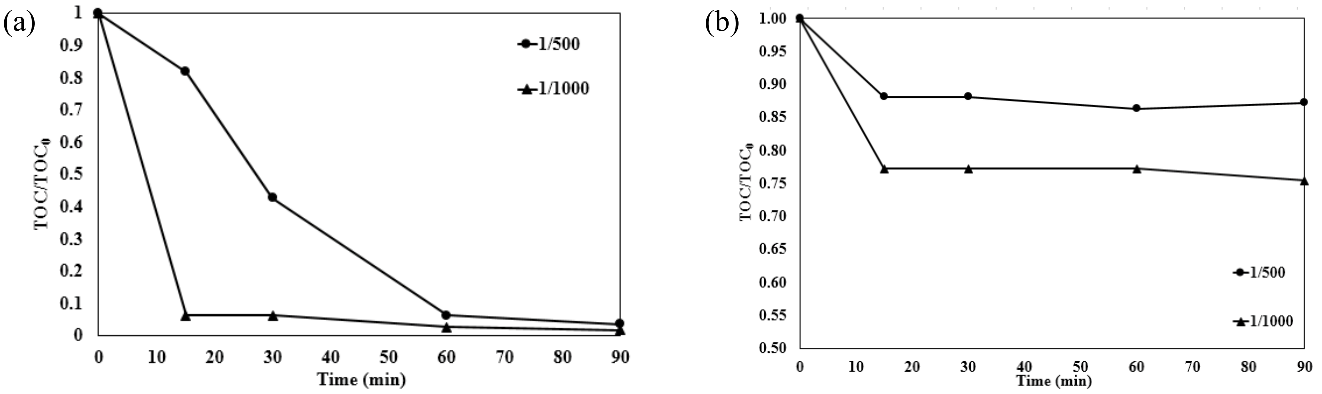


Fig. 2. TOC removal at various potassium persulfate dosages. (a) 60°C and (b) 40°C, initial pH = 5, initial dye concentration = 50 mg L^{-1}.

[25–28,30–35], the model equation for a batch reactor can be given as below:

$$\frac{dC_{\text{dye}}}{dt} = k_{\text{obs}} \times C_{\text{dye}} \tag{1}$$

where k_{obs} is observed reaction rate constant for the pseudo-first-order reaction that is used to define de-colorization kinetics of dye solution. The pseudo-first-order reaction rate constant can be obtained from the plot of $\ln(C_{\text{dye}}/C_{\text{dye},0})$ vs. time through linear regression.

The difference in de-colorization rates obtained in the runs conducted at different temperatures is presented in Fig. 3 with $\ln(C/C_0)$ vs. time plots. It can be seen from the figures that linear regression fits well with the experimental data. De-colorization data obtained in this study also suggested a pseudo-first-order reaction kinetics for de-colorization of RB 5 with heat-activated persulfate oxidation.

Fig. 3 also clearly demonstrates the increase in pseudo-first-order reaction rate constants as temperature increases from 40°C to 70°C. Similar analyses were conducted for all of the runs in this study which showed that heat-activated persulfate oxidation of RB 5 followed pseudo-first-order reaction kinetics for the given reaction conditions. Temperature dependence of the observed reaction rate constant was also investigated by using the Arrhenius equation. Arrhenius equation can be given as;

$$k_{\text{obs}} = Ae^{\frac{-E_a}{RT}} \tag{2}$$

where A is a pre-exponential factor, E_a is apparent activation energy, T is temperature (K), R is universal gas constant (8.314 J mol^{-1} K^{-1}). Eq. (2) can be linearized and plotted to estimate the apparent activation energy of the reaction using Eq. (3):

$$\ln(k_{\text{obs}}) = \ln A - \frac{E_a}{RT} \tag{3}$$

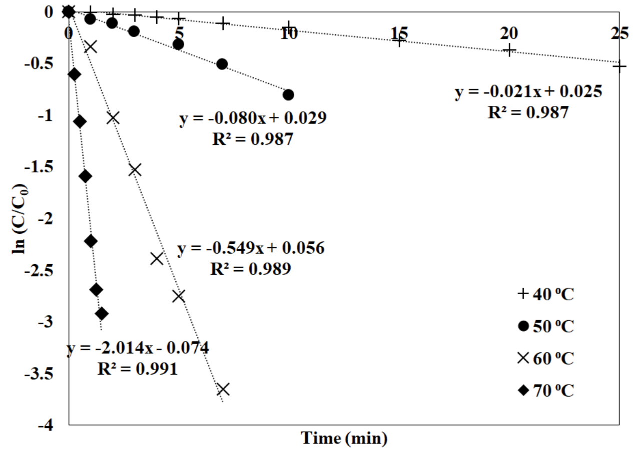


Fig. 3. $\ln(C/C_0)$ vs. time. Dye/potassium persulfate = 1/500, initial pH = 5, initial dye concentration = 50 mg L^{-1}, k_{obs} can be reported with a mean standard deviation of ±0.01.

Fig. 4 represents the plot of ln k_{obs} vs. $1/T$. The apparent activation energy was calculated as 141 kJ mol^{-1} which is in good agreement with the values reported in the literature [26]. The values which were obtained in several other studies are [26]; 141, 108, 144, and 141 kJ mol^{-1} for oxidation of atrazine, trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, respectively.

3.3. Oxidation by-products

Treated samples at 60°C and 1/100, 1/500, and 1/1,000 dye/potassium persulfate molar ratios were extracted and injected to GC-MS to identify the oxidation by-products. The GC-MS method used can only reveal the semi-volatile organic molecules in the mixture. Therefore no peak was observed when the initial RB 5 solution was injected. Mixtures that were treated with 1/100 dye/potassium persulfate ratio showed no significant peaks in GC-MS chromatogram which can be explained by the TOC analyses where no mineralization was observed. From Fig. 2a it can be observed that almost complete mineralization was obtained for the run conducted with 1/1,000 molar ratio and GC-MS chromatograms also support this finding by not showing any significant peaks that can be attributed with by-product formation. On the other hand, some by-products were observed in the samples extracted from the run conducted with a 1/500 molar ratio. The fragmentation pattern of the observed peaks was found similar to 1-Hexacosene and 1-Naphthalenecarboxylic acid by using NIST approved WILEY 7 library (USA) (Table 1). According to the literature, after the cleavage of the N=N azo bond releases benzene, naphthalene, quinone types of aromatic compounds to the mixture [36,37]. Further cleavage of the by-products and RB 5 is the reason for the formation of aliphatic by-products [23] as presented in Fig. 5.

3.4. Solar assisted persulfate oxidation

This study suggests an energy demand for the activation of sulfate radicals. This may result in a major problem for industrial applications of this suggested advanced oxidation method (heat-activated persulfate). The energy requirement

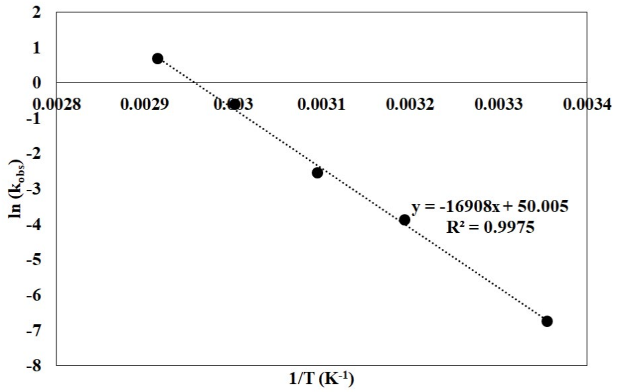
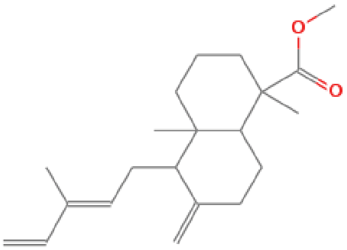


Fig. 4. lnk_{obs} vs. $1/T$ plot for calculation of E_a. Dye/potassium persulfate = 1/500, initial pH= 5, initial dye concentration = 50 mg L^{-1}, T = 25°C–70°C.

Table 1
Observed degradation products (1/500 dye/potassium persulfate molar ratio at 60°C)

Similarity percent %	By-product
84	*Name*: 1-Hexacosene *Molecular formula*: $C_{26}H_{52}$ *Molecular weight*: 365 g mol^{-1} *m/z*: 57.05 (100), 97.05 (93), 43.05 (87.99) 
63	*Name*: 1-Naphthalenecarboxylic acid, decahydro-1,4a-dimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl)-, methyl ester, [1S-[1.alpha.,4a.alpha.,5.alpha.(Z),8a.beta.]]- *Molecular formula*: $C_{21}H_{32}O_2$ *Molecular weight*: 316 g mol^{-1} *m/z*: 73.00 (100), 147.05 (67.05), 221.05 (61.40) 

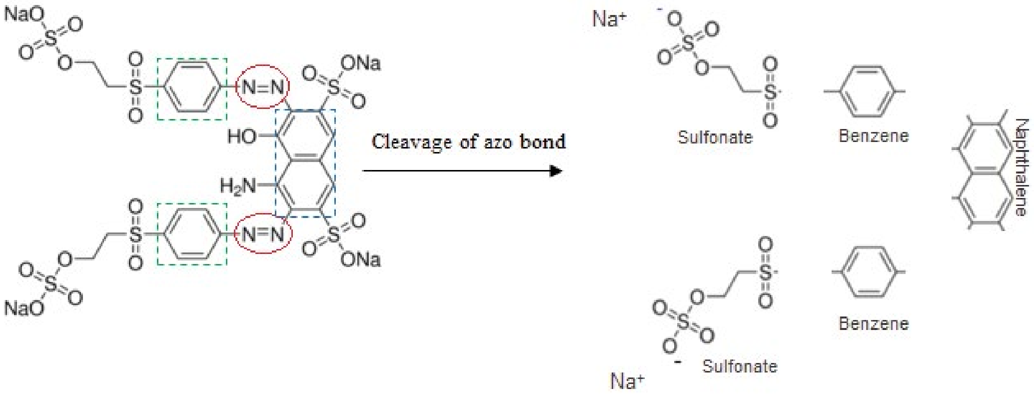


Fig. 5. Proposed degradation pathway for RB 5.

of the method discussed in this study can be supplied from solar energy combined with the activation effect of UV radiation that will be received from the sun. Outdoor oxidation runs without external heating experimented as preliminary trials for a possible future study based on solar activated persulfate oxidation study. Batch oxidation using potassium persulfate under sunlight was conducted by using potassium persulfate with ratios of 1/100 and 1/1,000. Experiments were carried out in July at the main campus of the European University of Lefke which is located at Lefke, Northern Cyprus. The runs in which molar ratio was adjusted to 1/1,000, complete decolorization was achieved after 30 min of reaction time while de-colorization over 70% was observed in the run conducted with a molar ratio of 1/100 after 90 min of total reaction time. A temperature increase from 25°C to 40°C was observed during the 90 min of reaction time without any additional heating. Fig. 6 shows dye removal percentages obtained after solar oxidation experiments. It is worth to note that no de-colorization was observed for the control run which was conducted without the addition of potassium persulfate.

4. Conclusions

Complete oxidation of RB 5 solutions was achieved in the runs conducted with the dye/potassium persulfate ratio of 1/500 and 1/1,000 at 60°C with a reaction time of 90 min. Room temperature experiments only resulted in 36% dye removal with a molar ratio of 1/1,000 after 180 min. Solar oxidation experiments also proved that there is a promising potential of solar activated persulfate oxidation in Northern Cyprus for wastewater treatment.

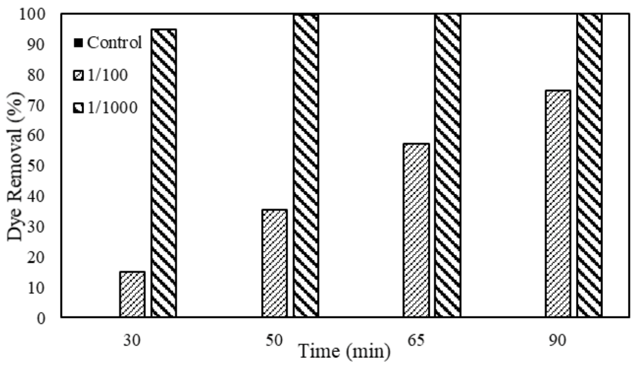


Fig. 6. Dye removal observed after solar assisted persulfate oxidation. Initial pH = 5, initial dye concentration = 50 mg L^{-1}, initial temperature = 25°C, and final temperature = 40°C.

The maximum duration for the experiments was kept as 180 min and less for some experiments. Duration of the experiments can be increased in future studies to achieve increased de-colorization and mineralization with lower dosages of potassium persulfate as consumption of high persulfate might cause accumulation of sulfate ions in the medium that can be classified as a pollutant in high concentrations. A future study focusing on solar activated persulfate should also be conducted with a better-designed reactor in order to use the solar irradiation at an optimum level.

References

[1] G. Moussavi, M. Mahmoudi, Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles, J. Hazard. Mater., 168 (2009) 806–812.

[2] H. Zangeneh, A.A.L. Zinatizadeh, M. Habibi, M. Akia, M. Hasnain Isa, Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: a comparative review, J. Ind. Eng. Chem., 26 (2015) 1–36.

[3] 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, J. Photochem. Photobiol., A, 345 (2017) 80–91.

[4] C.H. Weng, K.L. Tsai, Ultrasound and heat enhanced persulfate oxidation activated with Fe0 aggregate for the decolorization of C.I. Direct Red 23, Ultrason. Sonochem., 29 (2016) 11–18.

[5] Y. Ma, F. Chen, Q. Yang, Y. Zhong, X. Shu, F. Yao, T. Xie, X. Li, D. Wang, G. Zeng, Sulfate radical induced degradation of Methyl Violet azo dye with CuFe layered doubled hydroxide as heterogeneous photoactivator of persulfate, J. Environ. Manage., 227 (2018) 406–414.

[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 (2014) 86–92.

[7] S. Pirgalioğlu, T.A. Özbelge, Comparison of non-catalytic and catalytic ozonation processes of three different aqueous single dye solutions with respect to powder copper sulfide catalyst, Appl. Catal., A, 363 (2009) 157–163.

[8] H.-Y. Shu, S.-W. Huang, M.-K. Tsai, Comparative study of acid blue 113 wastewater degradation and mineralization by UV/persulfate and UV/oxone processes, Desal. Wat. Treat., 57 (2016) 29517–29530.

[9] P. Hu, M. Long, Cobalt-catalyzed sulfate radical-based advanced oxidation: a review on heterogeneous catalysts and applications, Appl. Catal., B, 181 (2016) 103–117.

[10] T. Chen, J. Ma, Q. Zhang, Z. Xie, Y. Zeng, R. Li, H. Liu, Y. Liu, W. Lv, G. Liu, Degradation of propranolol by UV-activated persulfate oxidation: reaction kinetics, mechanisms, reactive sites, transformation pathways and Gaussian calculation, Sci. Total Environ., 690 (2019) 878–890.

[11] Z. Fang, P. Chelme-Ayala, Q. Shi, C. Xu, M. Gamal El-din, Degradation of naphthenic acid model compounds in aqueous solution by UV activated persulfate: influencing factors, kinetics and reaction mechanisms, Chemosphere, 211 (2018) 271–277.

[12] S. Hou, L. Ling, C. Shang, Y. Guan, J. Fang, Degradation kinetics and pathways of haloacetonitriles by the UV/persulfate process, Chem. Eng. J., 320 (2017) 478–484.

[13] M.S.P. Yadav, N. Neghi, M. Kumar, G.K. Varghese, Photocatalytic-oxidation and photo-persulfate-oxidation of sulfadiazine in a laboratory-scale reactor: analysis of catalyst support, oxidant dosage, removal-rate and degradation pathway, J. Environ. Manage., 222 (2018) 164–173.

[14] A. Ioannidi, Z. Frontistis, D. Mantzavinos, Destruction of propyl paraben by persulfate activated with UV-A light emitting diodes, J. Environ. Chem. Eng., 6 (2018) 2992–2997.

[15] L.C. Ferreira, M. Castro-Alférez, S. Nahim-Granados, M.I. Polo-López, M.S. Lucas, G. Li Puma, P. Fernández-Ibáñez, Inactivation of water pathogens with solar photo-activated persulfate oxidation, Chem. Eng. J., 381 (2019), https://doi.org/10.1016/j.cej.2019.122275.

[16] W. Wang, H. Wang, G. Li, T. An, H. Zhao, P.K. Wong, Catalyst-free activation of persulfate by visible light for water disinfection: efficiency and mechanisms, Water Res., 157 (2019) 106–118.

[17] D. Jager, D. Kupka, M. Vaclavikova, L. Ivanicova, G. Gallios, Degradation of Reactive Black 5 by electrochemical oxidation, Chemosphere, 190 (2018) 405–416.

[18] R. Kamaludin, A.S. Mohamad Puad, M.H.D. Othman, S.H.S.A. Kadir, Z. Harun, Incorporation of N-doped TiO_2 into dual layer hollow fiber (DLHF) membrane for visible light-driven photocatalytic removal of reactive black 5, Polym. Test., 78 (2019) 105939.

[19] F. Iranpour, H. Pourzamani, N. Mengelizadeh, P. Bahrami, H. Mohammadi, Application of response surface methodology for optimization of reactive black 5 removal by three dimensional electro-Fenton process, J. Environ. Chem. Eng., 6 (2018) 3418–3435.

[20] B. Palas, G. Ersöz, S. Atalay, Catalytic wet air oxidation of Reactive Black 5 in the presence of $LaNiO_3$ perovskite catalyst as a green process for azo dye removal, Chemosphere, 209 (2018) 823–830.

[21] P.V. Ferreira de Sousa, Y. de Moraes Guimarães, G.C. Pinto, A. Fernando de Oliveira, A. Alberto da Silva, R.P. Lopes, Study of Cu NPs reactivity for compounds with different chemical structures: black reactive dye 5, picric acid and 2,4-D herbicide, Chemosphere, 235 (2019) 749–756.

[22] M.P. Rao, V.K. Ponnusamy, J.J. Wu, A.M. Asiri, S. Anandan, Hierarchical CuO microstructures synthesis for visible light driven photocatalytic degradation of Reactive Black-5 dye, J. Environ. Chem. Eng., 6 (2018) 6059–6068.

[23] H.S. Saroyan, A. Arampatzidou, D. Voutsa, N.K. Lazaridis, E.A. Deliyanni, Activated carbon supported MnO_2 for catalytic degradation of reactive black 5, Colloids Surf., A, 566 (2019) 166–175.

[24] U.S. EPA, Method 8270E (SW-846): Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Washington, DC, 2014.

[25] S.A. Kordkandi, M. Forouzesh, Application of full factorial design for methylene blue dye removal using heat-activated persulfate oxidation, J. Taiwan Inst. Chem. Eng., 45 (2014) 2597–2604.

[26] Y. Ji, C. Dong, D. Kong, J. Lu, Q. Zhou, Heat-activated persulfate oxidation of atrazine: implications for remediation of groundwater contaminated by herbicides, Chem. Eng. J., 263 (2015) 45–54.

[27] Y. Chen, P. Deng, P. Xie, R. Shang, Z. Wang, S. Wang, Heat-activated persulfate oxidation of methyl- and ethyl-parabens: effect, kinetics, and mechanism, Chemosphere, 168 (2017) 1628–1636.

[28] J. Ma, H. Li, L. Chi, H. Chen, C. Chen, Changes in activation energy and kinetics of heat-activated persulfate oxidation of phenol in response to changes in pH and temperature, Chemosphere, 189 (2017) 86–93.

[29] Z. Frontistis, E.M. Mestres, I. Konstantinou, D. Mantzavinos, Removal of cibacron black commercial dye with heat- or iron-activated persulfate: statistical evaluation of key operating parameters on decolorization and degradation by-products, Desal. Wat. Treat., 57 (2016) 2616–2625.

[30] Y. Fan, Y. Ji, D. Kong, J. Lu, Q. Zhou, Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process, J. Hazard. Mater., 300 (2015) 39–47.

[31] N.N. Patil, S.R. Shukla, Degradation of Reactive Yellow 145 dye by persulfate using microwave and conventional heating, J. Water Process Eng., 7 (2015) 314–327.

[32] S. Aliouche, K. Djebbar, T. Sehili, Removal of an azo dye (Alizarin yellow) in homogeneous medium using direct photolysis, acetone/UV, H_2O_2/UV, /UV, H_2O_2//UV, and /heat, Desal. Wat. Treat., 57 (2016) 18182–18193.

[33] S. Yang, P. Wang, X. Yang, L. Shan, W. Zhang, X. Shao, R. Niu, Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide, J. Hazard. Mater., 179 (2010) 552–558.

[34] N. Potakis, Z. Frontistis, M. Antonopoulou, I. Konstantinou, D. Mantzavinos, Oxidation of bisphenol A in water by heat-activated persulfate, J. Environ. Manage., 195 (2017) 125–132.

[35] M. Zhang, X. Chen, H. Zhou, M. Murugananthan, Y. Zhang, Degradation of *p*-nitrophenol by heat and metal ions co-activated persulfate, Chem. Eng. J., 264 (2015) 39–47.

[36] V.M. Vasconcelos, F.L. Ribeiro, F.L. Migliorini, S.A. Alves, J.R. Steter, M.R. Baldan, N.G. Ferreira, M.R.V. Lanza, Electrochemical removal of Reactive Black 5 azo dye using non-commercial boron-doped diamond film anodes, Electrochim. Acta, 178 (2015) 484–493.

[37] R.D. Kale, P.B. Kane, Decolourization by PVP stabilized Fe-Ni nanoparticles of Reactive Black 5 dye, J. Environ. Chem. Eng., 6 (2018) 5961–5969.