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RESEARCH PAPER

Ozonation of Procion Blue Reactive Dye and its Kinetics Study

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ABSTRACT

In advanced oxidation processes, the application of ozonation has been immensely used in recent years for the treatment of effluent water from pharmaceutical, textile and chemical industries. In this study, procian blue, a major and vastly used reactive dye in the textile industry was chosen for ozonation. This work investigated the effect of ozonation for the treatment of synthetic textile effluent water. The change of pH values of dye solutions from 2-12 had moderate effect on dye removal. The degradation rate was faster during the initial period of ozonation and reached highest dye removal around 90 minutes. The highest 87% removal of dye was observed for the case of 60 mg/L dye solution at pH 12. At higher pH, the dye degradation increased as the rate of formation of hydroxyl radical increased with pH. Factors influencing on dye degradation like concentration of dye, time of ozonation, and addition of H_2O_2 with ozone (combined treatment) were also evaluated. The combined treatment (5 g/L of hydrogen peroxide) increased the degradation of dye to 92% as compared to 85% for pure ozonation process of 60 mg/L dye solution of initial pH 10. The procian blue dye degradation followed pseudo-first order kinetics with a value of rate constant 2.48×10^{-2} /min.

Keywords: Textile effluent; Prosian blue dye; Ozonation; Dye degradation; Kinetics

INTRODUCTION

The textile industry is one of the leading industries which consumes synthetic dyes for coloring of fabrics. 30% of the total synthetic dyes used in the textile industry belongs to the group of reactive dyes (Prola et al., 2013; Dotto et al., 2012). Reactive dyes are considered to form covalent bonds with the fibre molecules most effectively and rigidly. In a market survey, the worldwide consumption of reactive dyes was 60,000 tons in 1988 which increased almost three times in 2004 (Ghaly et al., 2014). The average annual world production of indigo dye is 80,000 tons, while the global turnover market for naphthol dye is about 112, 000 tons per annum (Franssen et al., 2010; UNSD, 2013). Dyeing processes and subsequent washing release huge amount of coloured wastewater which causes direct contamination to the aquatic life (Hessel et al., 2007). This wastewater obstructs the light penetration into the water, thus altering the photosynthetic rate of aquatic life (Allegre et al., 2006; Royer et al., 2009; Cardoso et al., 2011). Most of the dyes are carcinogenic in nature, hazardous and change mutagenesis (de Lima et al., 2007; Carneiro et al., 2010; Oplatowska et al., 2011; Palanivelan et al., 2019). The reactive dyes are stable compounds due to the presence of complex aromatic rings. It is difficult to decompose the dyes into its lower molecular fragments using conventional processes and are often non-biodegradable (Wang et al., 2014).

Among the conventional separation processes, filtration, adsorption, ion exchange and coagulation have its limitation to remove the reactive dyes from wastewater. These processes,

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reduce COD but still a considerable amount of residual colour remain in the wastewater. Different adsorbents like clay, synthetic talc, bio-adsorbents from agricultural residues, chitosan, soybean hulls, etc were used to remove the reactive dyes from wastewater (Bahrami et al., 2020; Rahman et al., 2013; Alencar et al., 2012; Gonen & Onalan, 2016; Honorio et al., 2016, Georgin et al., 2018). It showed around 80-90% textile dye removal but needed extreme acidic environment (pH 2-4). Further, these processes are relatively slow, only arrest the dyes on a medium, unable to decompose the pollutants and need regeneration processes.

Electro oxidation and biodegradation of procion blue in textile effluent was studied using fungal strain Phanerochate Chrysosporium. The studied claimed around 92% COD and complete colour removal after the end of the stepwise processes (Selvakumar et al., 2010). In another study of the biosorption and biodegradation, 30% removal of azo-dye was reported using fungi Aspergillus Niger and Aspergillus Terreus after three hours of biosorption. Biodegradation and biosorption treatment needs prolong time and may generate toxic metabolites (Almeida & Corso, 2014). Tony and Mansour (2018) used Fe_2O_3 nanoparticles of various particle size to remove procion blue dye from textile wastewater. The effects of initial dye concentration, nanoparticle concentration, pH and working temperature were investigated which reported maximum 83% dye removal and 88% COD reduction. Melati et al. (2017) studied colour and COD removal of procion red wastewater by photo catalytic method of using TiO_2 catalyst under solar irradiation. Complete colour removal was observed using catalyst of 6 g/L and highest 62% COD removal was observed for catalyst of 8 g/L for 12 hours of solar irradiation (Sari et al., 2017).

Advanced oxidation processes (AOPs) have emerged as an effective technique for accelerating the oxidation and mineralization of a wide range of organic contaminants. The hydroxyl radical ($^{\cdot}OH$) is produced by chemical, photochemical, photocatalytic, or electrochemical reactions, reacts non-selectively with most of the unsaturated organic compounds until their total mineralization (Philippopoulos & Nikolaki, 2010). In AOPs, ozonation process releases $^{\cdot}OH$ which reacts with the organic compounds through one of the following mechanisms (El-Ashkar et al., 2021).

$$R + {}^{\cdot}OH \rightarrow ROH \qquad \text{(radical addition)}$$

$$R + {}^{\cdot}OH \rightarrow R + H_2O \qquad \text{(hydrogen abstraction)}$$

$$R_n + {}^{\cdot}OH \rightarrow R_{n-1} + OH^- \qquad (e^- \text{ transfer})$$

Now-a-days, ozonation is effective to decompose dyes of aromatic structure. Under suitable operating conditions, the final products can be low molecular weight oxygenated compounds as aliphatic acids, CO_2 and H_2O (Zaharia et al., 2009) and almost complete mineralization of organics is possible. Ozone and hydrogen peroxide treatment of wastewater was reported by Suryawan et. al. (2019) at varying pH and concentrations of H_2O_2. They observed that for pH > 4, enhanced biodegradability of organic matter. For pH values above 7, smaller concentrations of hydrogen peroxide are sufficient for ozone decomposition, and it yields a high rate of hydroxyl radicals. Ozonation is a faster process due to greater gas-liquid interface area, oxidize the dyes to decompose into smaller molecules. Also, oxidation can be performed in wide range of pH and cost-effective manner (Khuntia et al., 2012). The unreacted ozone self decomposes to oxygen.

In the present study, ozonation of synthetic dye solution of reactive dye procion blue using a commercial microbubble ozone generator is reported. The effect of pH of the reaction medium on ozonation, the reaction time and concentration of dye have been studied in terms of percentage dye degradation. Treatment using hydrogen peroxide with ozone has also been reported and compared with ozonation process. Further, a kinetics model of ozonation of dye solution has been established.

MATERIAL & METHODS

Procion blue (also known as Reactive Blue 4) of molecular formula $C_{23}H_{14}Cl_2N_6O_8S_2$ (1-Amino-4-[3-(4,6-dichlorotriazin-2-ylamino)-4-sulfophenylamino] anthraquinone-2-sulfonic acid) was procured from M/s Sigma-Aldrich, USA. Figure 1 shows the structure of procion blue (Nascimento et al., 2018; Tkachenko et al., 2014). De-ionized (DI) water (M/s Merck Limited, India) was used to prepare all the solutions and reagents. NaOH (>98% assay) and H_2SO_4 (analytical grade) were purchased from Merck, India.

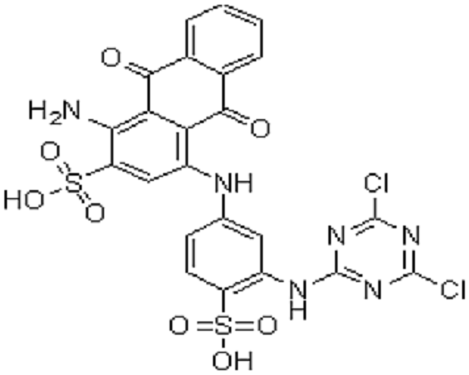


Fig 1: Molecular structure of procion blue dye (Reactive Blue 4)

Overall experimental setup consists of an ozone generator (Faraday, A series), a magnetic stirrer, an acrylic cylindrical vessel of capacity 2 L and tubing to pass ozone gas into the dye solution. Faraday’s A series ozone gas generator (Figure 2) is used for this experimentation. Ozone generator uses high voltage, high frequency corona-discharge technology for ozone production (Udhayakumar et al., 2016). This generator is having the ozone generation capacity of 4 g/h. Feed air flow rate to the generator is 10 – 12 Lpm.

Fig 2: Ozone generator

Figure 3 shows the schematic diagram of experimental setup for ozonation. For batch experiment, 1 L of dye solution of particular concentrations was filled in a cylindrical reactor vessel. According to various experimental conditions, the pH of dye solution was adjusted with the help of NaOH and H_2SO_4. The dye solution was stirred using magnetic stirrer (Remi, India) in order to get effective distribution of ozone gas bubbles throughout the dye solution. The ozone gas generated in the generator was bubbled through dye solution via plastic tubing. The porous ball (microporous diffuser) is attached at the end of pipe which breaks down the ozone gas into smaller size bubbles. Generation of small diameter bubbles increases contact surface area of ozone gas thereby increasing mass transfer from gas phase to liquid phase within the short span of contact time inside the dye solution.

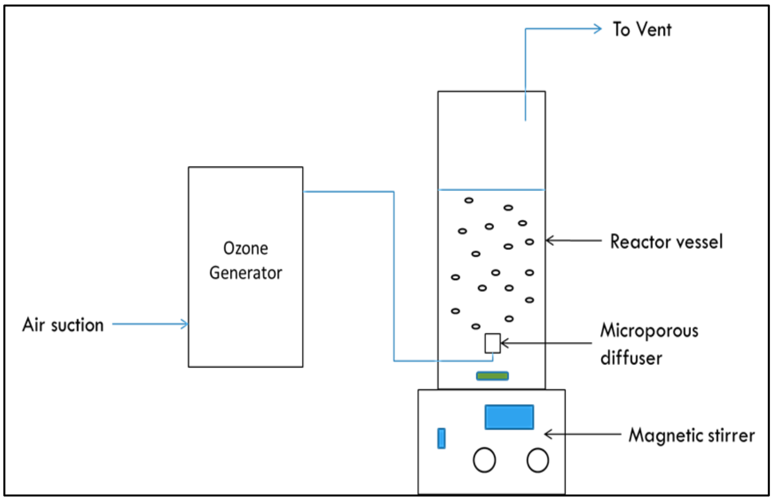


Fig 3: Schematic of ozonation experimental setup

The use of H_2O_2 (oxidation potential 1.80 and 0.87 V at pH 0 and 14, respectively) in combination with ozonation decomposes organic pollutants into harmless compounds. Moreover, H_2O_2 self-decomposes in water and oxygen.

For experimental purpose, 60 ppm procion blue dye solution was prepared, and its initial pH was maintained at 10. hydrogen peroxide concentration was 1, 3 and 5 g/L in the dye solution respectively and then, it was treated with ozonation process using ozone generator.

A fixed amount of procian blue dye was added to 1000 mL DI water (pH 7.2) at room temperature (30-32°C). An acrylic cylindrical vessel of capacity 2 L was used for sample preparation. A magnetic stirrer (Remi, India) was used to dissolve the dye into water with an in-build stirring speed controller knob. The stirring speed was kept at 800 rpm using a magnetic stirrer bar of 40 mm length and 8 mm O.D. (M/s. Tarsons India). The ozonation time, dye concentration and pH of solution were independently varied over certain range as shown in Table SS1 (in supplementary sheet). During ozonation 5 mL sample was withdrawn at each 10 min interval for UV-Visible spectroscopy analysis. Experiments were done in triplicate.

The sample preparation for ozone + H_2O_2 treatment is as follows. 1 L DM water (pH 7.2) was taken in a cylindrical vessel and added with 60 mg Procion blue dye (water soluble). pH of dye solution was observed to be 6.3. pH of the dye solution was taken to 10 by adding suitable amount of NaOH solution. This dye solution was treated separately with 1, 3 and 5 g/L of hydrogen peroxide (H_2O_2), respectively. Ozone gas was bubbled through dye solution along with constant magnetic stirring at 800 rpm. Samples (5 mL) were collected from the solution after every 10 minutes. This ozonation treatment was applied for 110 minutes. All the samples were analyzed for absorbance using visible spectrophotometer.

Samples of ozonation were collected during experiments after every 10 minutes. These samples were analysed for absorbance using UV visible spectrophotometer (Shimadzu, Japan). The absorbance was measured at 584 nm. A standard calibration curve was obtained for different known concentrations of dye and its corresponding absorbance at 584 nm. The pH was maintained using a pH meter (Hanna, India).

RESULTS AND DISCUSSION

Figure 4 shows the variation of pH in procion blue solutions with ozonation time. The initial dye concentration of the dye solutions was kept 70 mg/L, 60 mg/L, 40 mg/L and 20 mg/L respectively. The initial pH values of 4, 6, 8, 10 and 12 decreased with ozonation time until stable pH values were reached. The initial pH was adjusted using acid or base solutions. The decrease in pH values is the clear indication of formation of organic and inorganic anions as an effect of ozonation. The formation of acidic by-products is very rapid during the initial phase of the treatment for pH 4 to 12 due to the higher ozone consumption and alkalinity of the solutions. The formation of hydroxyl radical (˙OH) is favoured at basic pH which attacks the dye molecules non-selectively to mineralization. At lower initial pH value of 2, there was no significant change of pH. ˙OH could be consumed by scavenging effect of the H$^+$ at pH below 4 which would limit the ozone degradation rate. At lower pH, ozone can sustain its molecular form which selectively attacks the dye molecules and less oxidant than the hydroxyl radicals (Alvares et al., 2011; Soares et al., 2006).

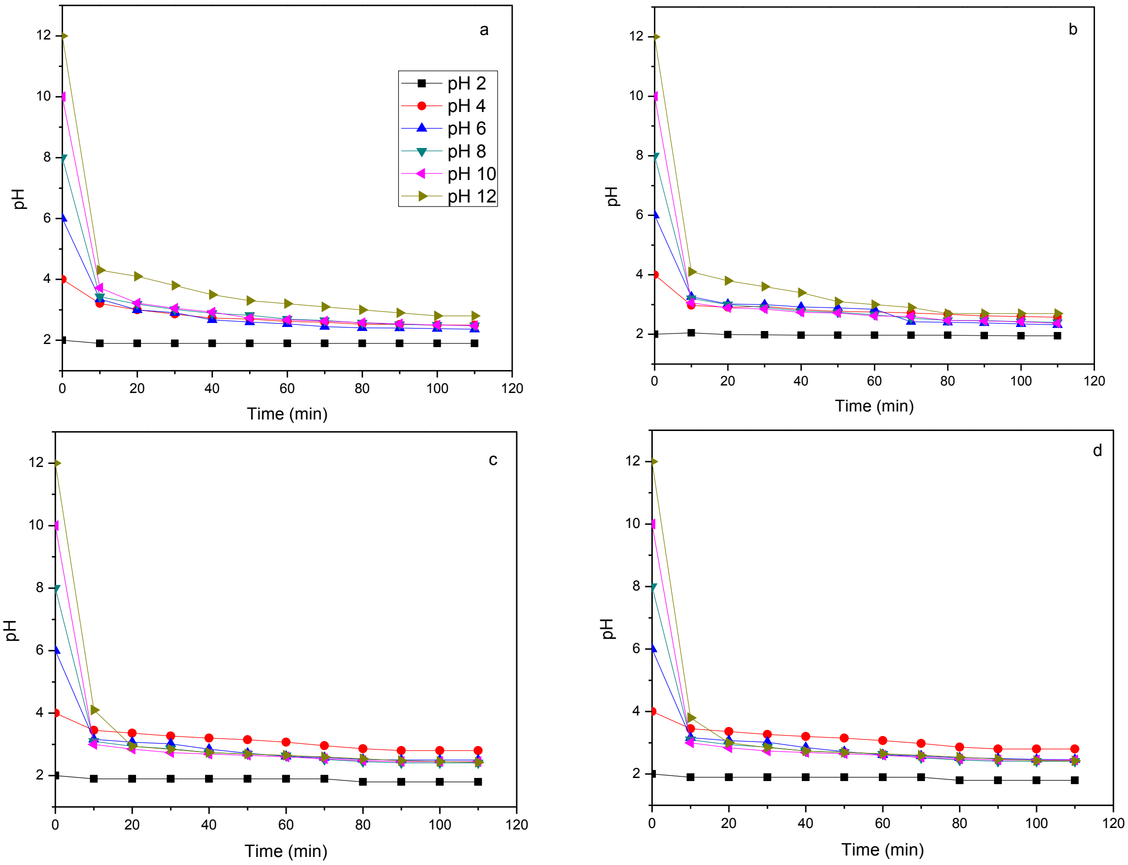


Fig 4: Variation in pH with ozonation time for initial dye concentration of (a) 70 mg/L, (b) 60mg/L, (c) 40 mg/L and (d) 20 mg/L.

The percent dye removal with ozonation time at different pH is presented in Figure 5. The dynamic dye removal followed a similar trend at various pH. Each plot of the Figure 5 has two parts. The dye removal efficiency gradually increased up to around 90 minutes irrespective of their initial pH values where it reached its maximum values and after that no significant changes were observed in % dye removal. For an example, for ozonation time of 90 minute and initial dye concentration of 60 ppm, the % dye removal was 75.33, 77.17, 79.33, 83.17, 85.0 and 87.33 for pH 2, 4, 6, 8, 10 and 12, respectively. It also conveyed that the dye solutions at higher initial pH values removed dye concentration more efficiently due to the fact of enhanced formation of $^{\cdot}$OH at high pH. There was 11-17% increase in % dye removal for the variation of initial pH value from 2 to 12. Figure 6 shows the colour removal of procion blue dye solution (70 ppm, pH 12) by ozonation at different time interval.

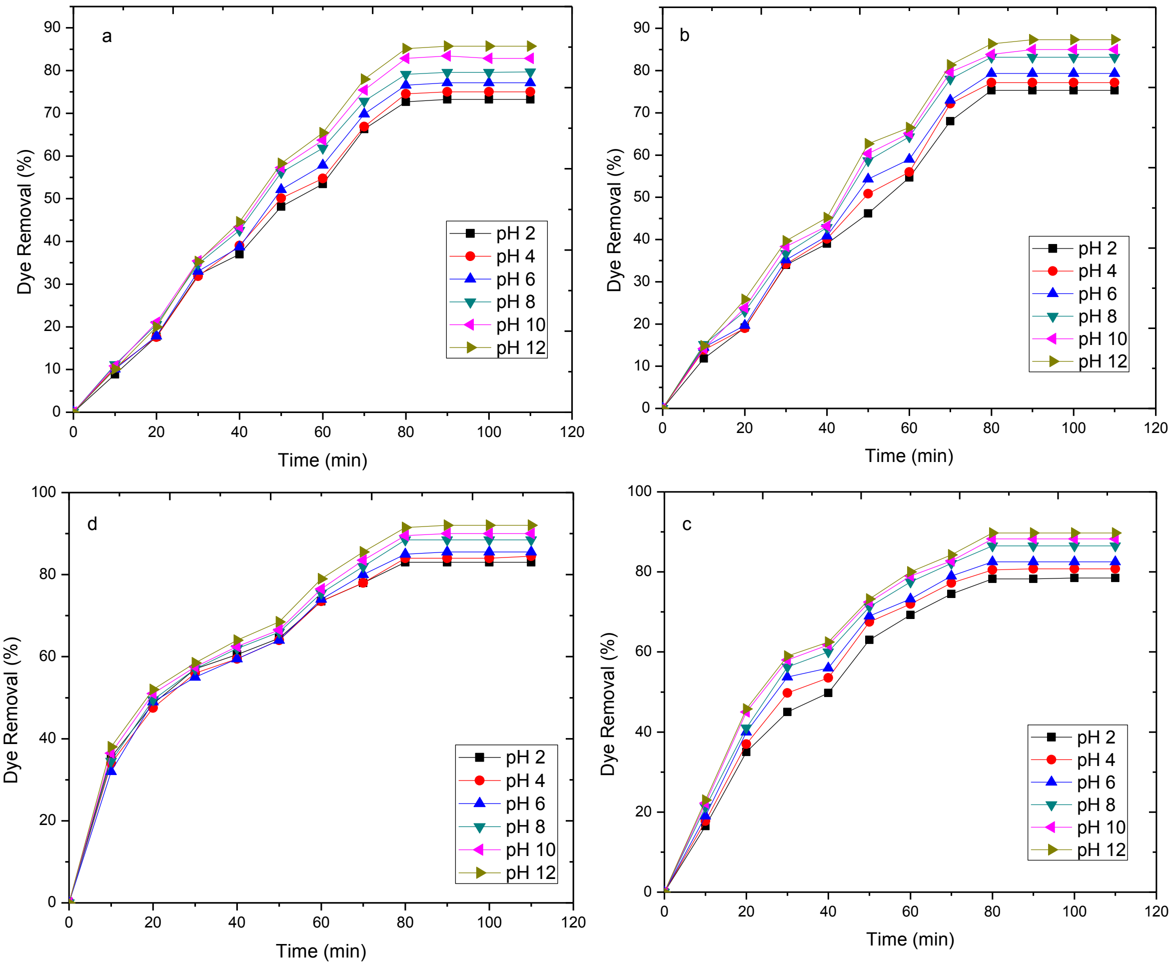


Fig 5: Removal of dye (%) with ozonation time at different pH for initial dye concentration of (a) 70 mg/L, (b) 60 mg/L, (c) 40 mg/L and (d) 20 mg/L

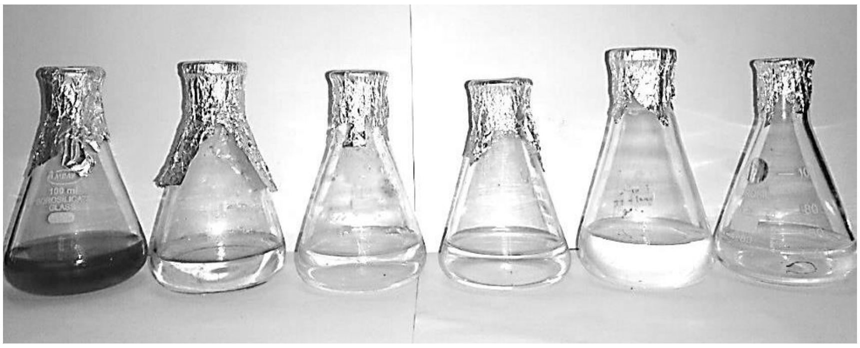


Fig 6: Colour removal of procion blue dye solution (70 ppm, pH 12) by ozonation at different time interval

Figure 7 shows that % dye removal decreases as the initial dye concentration increases within a certain period of ozone treatment. Around 9% reduction of dye removal was observed for 70 mg/L compared with 20 mg/L for the initial pH of dye solution at 4. Similarly, 7% of reduction of dye removal efficiency was noted for the same concentration range at pH 10. The longer ozonation time is necessary for higher dye concentration solutions to achieve certain amount of dye removal. The result can be corroborated with the ozonation treatment for the other azo dyes (Hassani et al., 2018; Sharma et al., 2013).

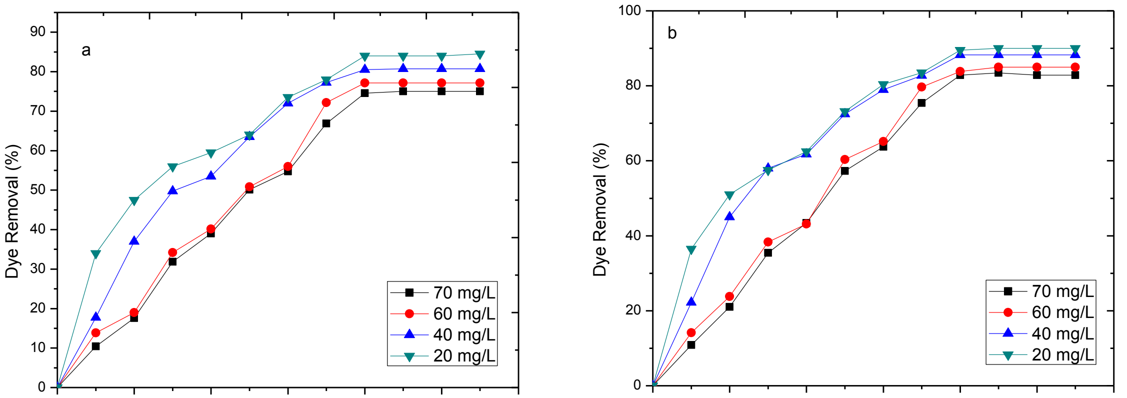
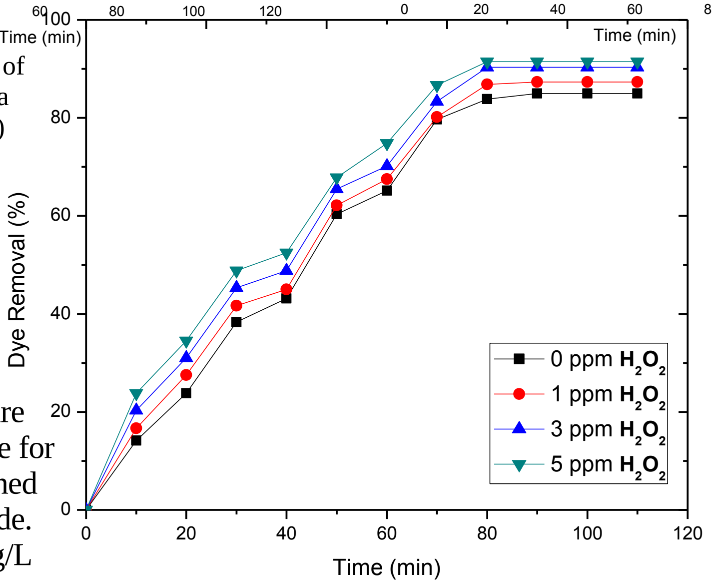


Fig 7: Colour removal of procion blue dye with ozonation time as a function of initial dye concentration at (a) pH 4 and (b) pH 10



The combined treatment of ozone and hydrogen peroxide was performed for procion blue dye degradation. The concentration of dye solutions was maintained at 60 mg/L with initial pH value of 10. Figure 8 compares the dye removal with time for the single ozonation and combined treatments of ozone and peroxide. The peroxide dose was 1, 3 and 5 g/L H_2O_2. On analysis of the Figure 8, it reveals that combined treatments of ozone and peroxide overperforms the single ozonation. It is possible due to the enhanced formation of $^{\cdot}$OH in the initial period of the combined treatment. The higher concentration of $^{\cdot}$OH reacted at higher rate with aromatic and unsaturated organic molecules for mineralization. 6.5% enhanced removal of dye was observed for combined treatment (for 5 g/L H_2O_2) compared to single ozonation. It was also noted that slight increase of dye removal for higher dose of peroxide in the dye solution.

Fig 8: Effect of combined treatment of ozone and H_2O_2 at different peroxide doses on dye removal with time. Conditions: dye concentration of 60 ppm and pH 10

Ozonation of wastewater appeared to be pseudo-first order reaction with respect to the dye concentration as the ozone concentration in wastewater was constant. In a semi-batch reactor, ozone was supplied at constant rate or concentration and the dye degradation rate can be expressed as,

$$\text{Rate} = -\frac{d[dye]}{dt} = k\,[\text{dye}]$$

where [dye] represents the procion blue concentration in wastewater at time t; k (min^{-1}) represents the observed pseudo-first-order rate constant of dye degradation during ozonation.

Figure 9 shows the plot of $-\ln(C/C_0)$ vs t for the synthetic dye solution of concentration 40 mg/L at initial pH 8 which yields a straight line. The high linearity of the fitted straight line in Figure 9 ($R^2 = 0.996$) agreed with that the procion blue degradation followed the pseudo-first order kinetics during ozonation. The value of degradation rate constant was estimated as 2.48×10^{-2} /min. The result is also defensible by the study of remazol black B dye degradation (De Souza et al., 2010).

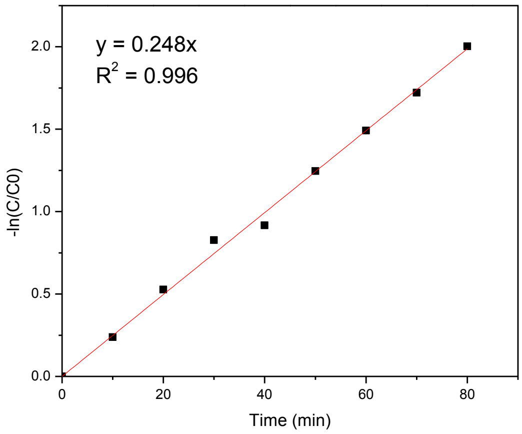


Fig 9: Pseudo-first order reaction kinetics of procion blue degradation by ozonation; concentration of 40 mg/L dye solution, pH 8, temperature at 32°C

CONCLUSION

Ozonation was found to be an effective process for the procion blue dye degradation. The maximum dye degradation was observed about 92% for 20 mg/L dye solution of initial pH value of 12. A moderate effect of pH values was noticed for dye removal by ozonation. Rate of dye degradation increased at higher pH values. Around 12 % changes in dye removal were reported while varying pH from 2 to 12 for 60 mg/L synthetic dye solution. The pH values decreased rapidly during the initial stages of ozonation which indicate the formation of anionic by-products because of oxidation by ozone.

The degradation of dye decreased with the increase of dye concentration from 20-70 mg/L in synthetic solution. Combined treatment of ozone and H_2O_2 leads to an enhanced color removal as compared to single ozonation. The percent removal of dye solutions was 87.3, 90.3 and 91.5, respectively, with the addition of 1, 2 and 5 g/L H_2O_2, respectively for dye concentration 60 mg/L and pH 10 solutions. Removal of dye increased with the increase of H_2O_2 concentration from 1 to 5 g/L into the dye solution. The enhanced formation of hydroxyl radicals attributed to this. Procion blue dye degradation followed the pseudo-first order kinetics during the ozonation with the value of rate constant 2.48×10-2 per min.

NOMENCLATURE

C	Concentration of dye at time t
C_0	Initial concentration of dye
t	Time
k	Rate constant

ABBREVIATIONS

AOP	Advanced oxidation process
COD	Chemical oxygen demand

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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FIGURE CAPTION

Figure No.	Description
Figure 1	Molecular structure of procion blue dye (Reactive Blue 4)
Figure 2	Ozone generator
Figure 3	Schematic of ozonation experimental setup
Figure 4	Variation in pH with ozonation time for initial dye concentration of (a) 70 mg/L, (b) 60mg/L, (c) 40 mg/L and (d) 20 mg/L.
Figure 5	Removal of dye (%) with ozonation time at different pH for initial dye concentration of (a) 70 mg/L, (b) 60 mg/L, (c) 40 mg/L and (d) 20 mg/L
Figure 6	Colour removal of procion blue dye solution (70 ppm, pH 12) by ozonation at different time interval
Figure 7	Colour removal of procion blue dye with ozonation time as a function of initial dye concentration at (a) pH 4 and (b) pH 10
Figure 8	Effect of combined treatment of ozone and H_2O_2 at different peroxide doses on dye removal with time. Conditions: dye concentration of 60 ppm and pH 10
Figure 9	Pseudo-first order reaction kinetics of procion blue degradation by ozonation; concentration of 40 mg/L dye solution, pH 8, temperature at 32°C