

Solar expedited photodegradation of orange-g using H₂O₂

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Decolourisation and degradation of azo dye Orange G was carried out by using the solar-assisted photodegradation process using H₂O₂ and the effect of various parameters on decolourisation and degradation were analysed. Dye solutions of concentration 100 mg/L treated with 30% H₂O₂ were taken in 250 ml conical flasks and they were exposed to sunlight in the lux intensity range of 60,000 to 90,000 lux to study its decolourisation and degradation. Effect of various parameters on decolourisation and degradation of dye like the effect of initial pH, the effect of initial H₂O₂ concentration, the effect of initial dye concentration, the effect of additives like chloride and dihydrogen phosphate of concentration 1 M, the effect of solar light intensity, the effect of temperature were studied as kinetic studies. Optimum pH was found to be 11 and optimum H₂O₂ concentration was found to be 250 mM to achieve 100 % decolourisation of the dye within the shortest time duration of 1.5 hours. Kinetic studies done on the effect of pH and the effect of H₂O₂ concentration also provided evidence for that. Effect of chloride ion has lead to enhancement in the rate of decolourisation whereas addition of dihydrogen phosphate ion inhibits the rate of decolourisation. An increase in solar light intensity has lead to increase in the rate of decolourisation. An increase in temperature has lead to increase in the rate of decolourisation. UV spectrum was taken for the dye and degraded dye to study the extent of degradation of the dye. COD and TOC removal were also studied to know about the mineralisation of the dye.

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1. Introduction

Water is an essential need for the survival of humankind and other living beings. But the availability of safe drinking water for human consumption around the world is less than 1%. According to World Health Organization (WHO), it has become a very big challenge to get potable drinking water without the presence of various pollutants as there is an increasing demand for it because of the enormous increase in world population and increasing technological needs [1].

Water has become polluted by the discharge of industrial effluents that contain hazardous contaminants into water bodies like rivers, streams etc., It produces a negative impact on the environment. Dyes constitute the top rank among the most notorious organic pollutants as they are used as a part of textile, leather, paints, plastics, food, cosmetics, paper, pharmaceutical and dye

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manufacturing [2-5]. They are synthetic, water-soluble, and dispersible organic compounds that are copious sources of coloured organics [4].

There are various types of dyes of which synthetic dyes are those organic compounds that are poly-aromatic that give permanent colour to materials like fabrics. Among the synthetic dyes, azo dyes are the organic compounds that are characterised by the presence of one or more azo groups (-N=N-) bound to aromatic rings associated with auxochromes (-OH, -SO₃) etc., [4, 6]. They are the largest and most important class of synthetic organic dyes. It has been estimated that around 60-70% of all the dyes used in common are azo dyes because of their chemical stability and versatility [5, 6].

The textile industry is the most extensive consumer of water for the dyeing process and they become the most substantial polluter among the various industries. It uses more than 8000 chemicals in various processes of textile manufacturing [4]. Nowadays there was an increase in demand for textile products so that it leads to an increase in the use of synthetic azo dyes. According to an estimate, 7, 00,000 tons of dyes are produced annually and 60-70% of the dyes of total production are used by textile industries. Around 10–15% of the dyes that are not fixed during the dyeing process are discharged as effluents into water bodies like rivers, streams etc., [5].

Because of the presence of some non-biodegradable pollutants like heavy metals like arsenic, zinc, copper, nickel, mercury, cadmium, lead, chromium etc., those are used as additives in the dyeing process, the effluent become toxic as they affect both aquatic life and human beings. They are carcinogenic, mutagenic and cause allergic dermatitis, skin irritation, cancer and gene mutations [3, 5]. Now, the problem is to be addressed that they cannot be degraded by conventional treatment processes [1].

The treatment processes are broadly classified into three categories as Chemical, Physical and Biological methods [5, 6]. Each method has its own advantages and disadvantages. In the physical adsorption technique, the problem is only the occurrence of phase transfer and there is a need of separating the purified effluents and regeneration of adsorbent is also difficult. In case of chemical treatment processes likes coagulation and photoFenton reaction processes high sludge formation occurs. In case of Ozonation, there are some operational difficulties because of the half-life of ozone. In biological methods, the cost is high & the retention time is so long [5]. All of them produces toxic by-products also as they cannot completely degrade the substances present in effluents [1, 5].

Therefore there is a need for the development of destructive processes to treat the effluents and it arose by significant interests currently [6]. There is also an urge for a well-defined technology to cope with the global scarcity of potable drinking water [1].

Advanced Oxidation Process (AOPs) provide an alternative way as they degrade the dyes and other organics in industrial effluents [4]. It is an innovative technique for water treatment as it generates hydroxyl radicals that are powerful oxidising agents that mineralize refractory organic compounds, kills water pathogens, and degrade disinfection by-products [1]. Hydroxyl radical ($\bullet\text{OH}$), is the second strongest oxidant ($E^\circ = 2.87 \text{ V}$) after fluoride ($E^\circ = 3.06 \text{ V}$). They can rapidly and non-selectively react with a wide range of organic pollutants through the mechanism of hydrogen abstraction, electrophilic addition and/or electron transfer to convert them to simpler molecules like CO₂, H₂O and organic ions etc., [3].

AOP techniques involve the use of ultraviolet light in the presence of H₂O₂, TiO₂, O₃ and Fenton's reagent. Among all the processes, UV/ H₂O₂ has the advantage of no sludge formation and carrying out under ambient conditions and the oxygen formed in this process is useful for an aerobic biological decay process [5]. Usage of solar light instead of UV light also has several advantages as it is cheaper and it is abundant in tropical countries like India.

The aim of present work is to study the decolourisation of an anionic azo dye Orange G using AOP Solar/ H₂O₂. Orange G has a wide range of applications like pigmentation of paper, leather, and timber; colouring wools and silks; in preparation of printing inks; as pH indicators, in food and textile applications; etc., It is available in the form of Orange crystalline powder that contains two groups SO₃Na, which are soluble in water. It is usually present in aqueous solutions as a sodium salt, in two tautomeric forms. Organic solvents favour the azo form, whereas the hydrogen form predominates in aqueous solutions [2, 5].

2. Materials and methods

Orange G dye was obtained from Research Lab Fine Chem industries private limited and used as such without further purification.

2.1. Experimental procedure

Orange G dye solution of 100 mg/L concentration was prepared using demineralised water taken in 250 ml conical flasks treated with 30 ml of 30% H_2O_2 which is of concentration 264 mM and they were exposed to solar light in the average lux intensity range of 60,000 to 90,000 lux. A Lux meter of model UA 1010B was used to measure the lux intensity. Digital Spectrophotometer of model Shimadzu 1800 was used to measure the change in absorbance values at certain intervals to evidence the decolourisation.

Effect of initial pH on decolourisation of Orange G was studied by treating it with HCl, Citrate buffer, NaOH, Glycine buffer, Phosphate buffer etc., each of which is of 0.1 M concentration. Dye solution in its own pH was also examined. All the studies were carried out in dye solution of concentration 100 mg/L treated with 30 ml of 30% H_2O_2 which is of concentration 264 mM. pH ranges from 3,5,6,7,9 and 10. pH was measured using a digital pH meter of model AI-102. After studying the effect of pH in acidic, basic and neutral conditions, pH in basic condition was further optimised by treating the dye solution with different volumes and different concentrations of NaOH in the range 8-12 as basic pH was suitable for decolourisation in short time duration.

The effect of initial H_2O_2 concentration on decolourisation of Orange G was studied by treating it with different H_2O_2 concentrations ranging from 50 mM to 500 mM and its optimum condition is found out.

The effect of initial dye concentration on decolourisation of Orange G was studied by treating it with different dye concentrations ranging from 50 mg/L to 500 mg/L, optimum dye concentration is found out.

The effect of additives like chloride and dihydrogen phosphate ion on decolourisation of Orange G was studied by treating it with them of concentration 1 M concentration.

The effect of solar light intensities on decolourisation of Orange G was studied by treating it with different solar light intensities with the dye solution concentration of 100 mg/L.

The effect of temperature on decolourisation of Orange G was studied by treating it with different temperatures and optimum temperature is found out.

2.2. Mineralisation

TOC of Orange G dye and degraded Orange G dye in optimised conditions was measured using the TOC_Liquid method. Similarly, COD of Orange G dye and degraded Orange G dye in optimised conditions was measured by the Acid digestion method. UV-visible spectrum of Orange G dye and degraded Orange G dye was taken by UV 1700 series spectrometer for analysing the extent of degradation of Orange G dye.

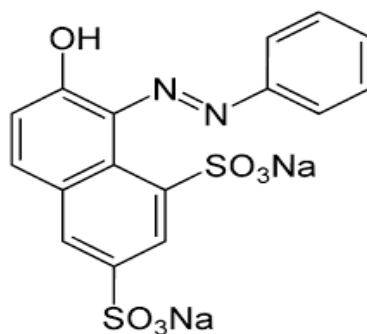


Fig. 1. Structure of Orange G.

2.3. Characteristics of Orange G

Molecular formula: $C_{16}H_{10}N_2Na_2O_7S_2$

Molecular weight: 452.36

λ max= 478 nm.

IUPAC name: disodium salt of 7-hydroxy-8-[(E)-phenyldiazenyl]naphthalene-1,3-disulfonic acid.

Generic name: Acid orange 10

Type: Anionic Azo dye

2.4. Literature survey on the degradation of Orange G by various methods

Table 1. Literature survey on the degradation of Orange G.

S.No	Method	Optimized conditions	% of decolourisation	% of mineralization (COD/TOC removal)	Reference
1	C_{60} /MCM-41 Photocatalysts	Sample= $3C_{60}$ /MCM-41, C_{60} Wt%= 3, SSA_{BET} (m^2g^{-1})=831, SA (micromol g^{-1})=36.5 SSA_{BET} = Specific surface area SA= Specific adsorption	74.9% in 135 minutes	--	John Kyriakopoulos, Eleana Kordouli, Kyriakos Bourikas, Christos Kordulis, Alexis Lycourghiotis, Decolorization of Orange-G Aqueous Solutions over C_{60} /MCM-41 Photocatalysts, 9(2019), 1-12.
2	Fenton	pH=4, [Dye]= 1.11×10^{-4} M, $[Fe^{2+}]$ = 3.5×10^{-5} M, $[H_2O_2]$ = 1×10^{-2} M, Temp= 20^0 C	94.6% in 60 minutes	--	Sheng-Peng Sun, Cheng-Jie Li, Jian-Hui Sun, Shao-Hui Shi, Mao-Hong Fan, Qi Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study, Journal of Hazardous Materials 161 (2009), 1052-1057.

S.No	Method	Optimized conditions	% of decolourisation	% of mineralization (COD/TOC removal)	Reference
3	Persulfate/Fe ²⁺	pH=3, [persulfate]= 4mM, [Fe ²⁺]= 4mM, [Dye]= 0.1mM	99% in 30 minutes	TOC removal= 96% in 24 hours	Xiang-RongXu, Xiang-Zhong Li, Degradation of azo dye Orange G in aqueous solutions by persulphate with ferrous ion, Separation and purification Technology, 72(2010), 105-111.
4	Solar photocatalytic degradation by Zinc Oxide	pH=3.5, [ZnO]= 0.1 g, [Dye]= 5 ppm,	100% in 20 minutes	--	Muhammad Nasri Abdul Rahman, Nur Aisyah Hamzah, Wan Farahiyah Wan Kamarudin, Zildawarni Irwan, Mohd Rabani Yaafar, Noor Erni Fazlina Mohd Akhir, Solar Photocatalytic Degradation of Orange G Dye Based on Zinc Oxide, 7(11)(2017), 72-78.
5	Photocatalytic degradation using TiO ₂ /Fe ₃ O ₄ nanocomposites	(TiO ₂) _{0.2} (Fe ₃ O ₄) _{0.8} nanocomposite [Dye]= 50 mg/L with 29.50 nm	60% in 120 min		B.Mercyrani, R.Hernandez-Maya, M.Solis-Lopez, Christeena Th-Th, S.Velumani, Photocatalytic degradation of Orange G using TiO ₂ / Fe ₃ O ₄ nanocomposites,(2018), 1-9.
6	UV/H ₂ O ₂	pH=3, [Dye]= 50 ppm, [H ₂ O ₂]= 0.5%, two 15W UV tubes+ one 125 W UV tubes	99.9% in 90 minutes		Neetu DIVYA, Ajay BANSAL, Asim K.JANA, Degradation of acidic Orange G dye using UV-H ₂ O ₂ in batch photoreactor, 3(1)(2009), 54-62.

3. Results and discussion

3.1. Characterization of Orange G

3.1.1. UV-Visible Spectrometric analysis

UV-Visible spectrum of Orange G consists of three main peaks at 273.5 nm, 328 nm and 477 nm (Figure 2). Peaks at 273.5 and 328 nm are assigned to its aromatic rings like benzene and naphthalene and the peak at 477 nm is assigned to the azo group. After treatment by Solar/H₂O₂ peaks (Figure 3) at 273.5 nm and 477 nm almost disappeared showing that the chromophore and the conjugated system were completely destroyed. On the other hand, the peak at 328 nm declined slowly. It indicates that certain aromatic rings were still present.

Similar results were obtained in the case of Xiang- Rong Xu et al in the case of degradation of the same Orange G dye by persulfate with ferrous ion [6].

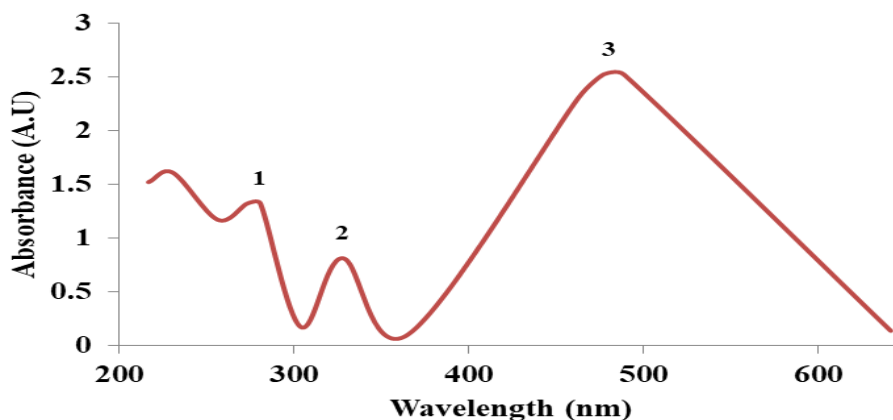


Fig. 2. UV-Visible spectrum of Orange G dye.

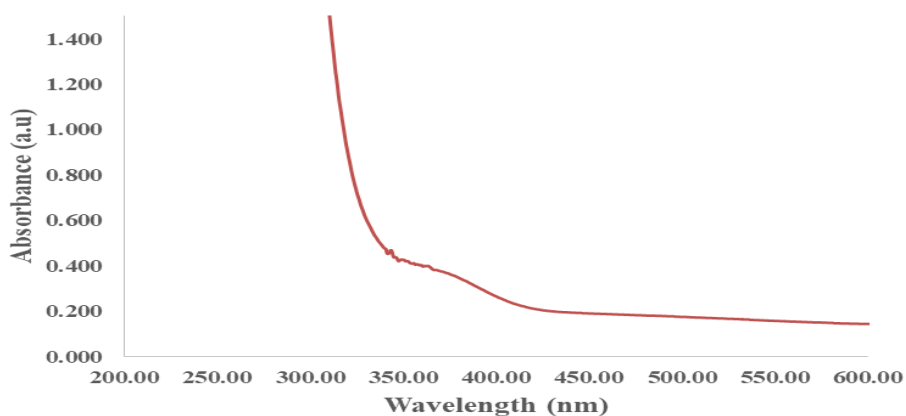


Fig. 3. UV-Visible spectrum of degraded Orange G dye.

3.2. Effect of various parameters on decolourisation of Orange-G

3.2.1. Effect of initial pH

Table 2 showed decolourisation of Orange-G of concentration 100 mg/L in different pH range was studied by treating it with HCl of 0.1 M concentration in pH 3, citrate buffer of 0.1 M concentration in pH 5, phosphate buffer of 0.1 M concentration in pH 7, glycine buffer of 0.1 M concentration in pH 9 and NaOH of 0.1 M concentration in pH 10 with the initial H₂O₂ concentration of 264 mM. Its decolourisation in its own pH 6 was also studied. From figure 4, it was observed that the percentage of decolourisation in acidic pH 3 was only 8.05%. When pH was increased to 5, decolourisation was decreased to 1.15%. When pH was further increased to 6,

decolourisation was increased to 4.3%. In neutral pH 7, decolourisation was increased to 5.68%. In basic pH 9, decolourisation was increased to 93.26%. On further increasing pH to 10, decolourisation was 100%.

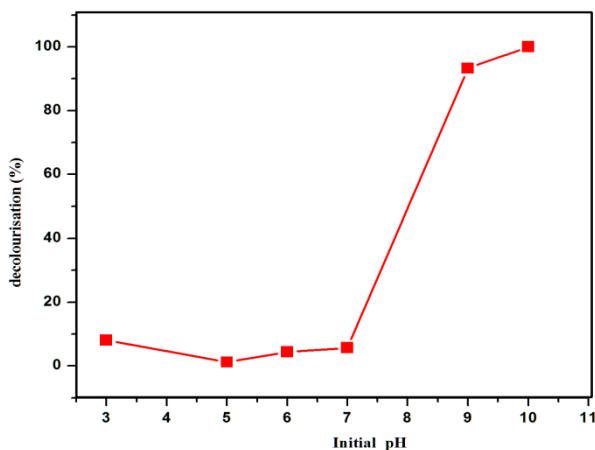


Fig. 4. Effect of initial pH: Reaction conditions: Orange G dye solution of concentration 100 mg/L with H_2O_2 concentration of 264 mM in different pH ranges from 3 to 10.

Table 2. Effect of initial pH.

pH	% of decolourisation in 5 hours	$k(Hr^{-1})$
3	8.05	0.0270
5	1.15	0.0023
6	4.3	0.0088
7	5.68	0.0141
9	93.26	0.5395
1.0	100	1.3736

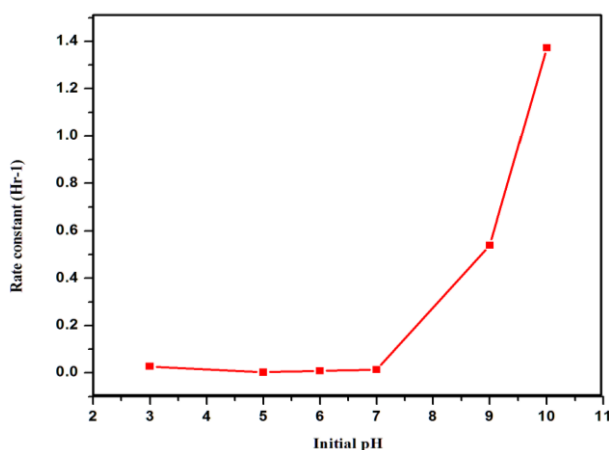


Fig. 5. Kinetic studies on effect of initial pH: Reaction conditions: Orange G dye solution of concentration 100 mg/L with H_2O_2 concentration of 264 mM in different pH ranges from 3 to 10.

Kinetic studies on the effect of initial pH on the decolourisation and degradation of Orange G can be done by varying the pH and study its decolourisation in a certain period of time

like one hour by decrease in its colour. The order of the reaction is found to be pseudo-first order with respect to dye concentration, viz,

$$\ln [A_t] - \ln[A_0] = -kt \quad (1)$$

where k = first order rate constant

t = irradiation time

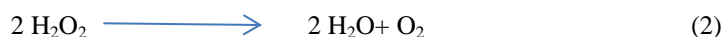
A_0 = initial absorbance value before the start of the decolourisation reaction

A_t = absorbance value at time t after the start of the decolourisation reaction [7].

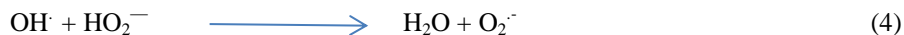
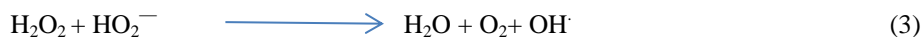
Figure 5 showed the kinetic studies on the effect of initial pH have also provided evidence for the maximum percentage of decolourisation of orange G dye in basic pH of 9 and 10. The rate constants calculated for the decolourisation reaction in the corresponding pH of 9 and 10 was found to be maximum. Hence it was concluded that maximum decolourisation was observed in basic pH of 9 and 10. So it was necessary to optimise the basic pH from the range 8 to 12.

Decolourisation of Orange G was lower in acidic pH of 2, 3 and 6 and neutral pH of 7 was because of the following reasons:

In this pH 7 H_2O_2 dissociated into water and oxygen other than forming hydroxyl radical. Hence there is a decrease in the concentration of hydroxyl radicals to attack and degrade the dye [8,9].



At pH 3 there was an increase in the concentration of hydroperoxy anions which are formed from H_2O_2 . Hydroperoxy anion, which is a conjugate base of H_2O_2 reduced the concentration of H_2O_2 by convert it into water, oxygen. The hydroperoxy anion also reacts with the hydroxyl radical and converts them into radical anions. Hence there is a decrease in the availability of hydroxyl radicals to attack the dye molecules and degrade them according to the following equations [9].



In acidic pH 2 obtained by addition of HCl to the dye solution, concentration of conjugate base of HCl, Cl^- increases. They react with hydroxyl radicals lead to the formation of inorganic radical ions according to the following equation.



These radical ions show a much lower reactivity than hydroxyl radicals. It leads to the decrease in the rate of decolourisation reaction [8,10].

3.2.2. Effect of initial basic pH

Table 3 indicated on further optimising the pH for decolourisation of azo dye Orange G of concentration 100 mg/L in basic condition, it was treated with different concentrations of NaOH to get pH from 8 to 12 with the H_2O_2 concentration of 264 mM. From figure 6, it was observed that decolourisation was increased from 4.6% to 100 % on increasing pH from 8 to 11 and it was decreased to 93.33% on further increasing pH from 11 to 12. Hence it was concluded that the optimised pH for decolourisation of azo dye Orange-G was 11.

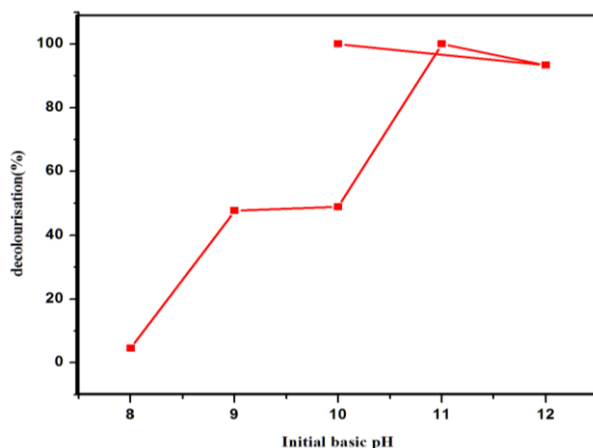


Fig. 6. Effect of initial basic pH: Reaction conditions: Orange G dye solution of concentration 100 mg/L with H_2O_2 concentration of 264 mM in different basic pH ranges from 8 to 12.

Table 3. Effect of initial basic pH.

pH	% of decolourisation in 1.5 hours	$k(Hr^{-1})$
8	4.6	0.0314
9	47.64	0.4319
10	48.84	0.4469
11	100	4.2194
12	93.33	1.8057

Kinetic studies on the effect of initial basic pH on the decolourisation and degradation of Orange G can be done by varying the pH by adding NaOH of different concentrations to get different pH values in the basic range from 8 to 12 and study its decolourisation every 30 minutes by decrease in its colour. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equ I).

Kinetic studies done on the effect of basic pH on decolourisation of Orange G also proved that the maximum decolourisation occurred in basic pH of 11 (figure 7). The rate constant calculated for the corresponding pH 11 for decolourisation reaction was the maximum. Tanja Kurbus et al. have reported similar results in the treatment of vinyl sulphone dyes by UV/ H_2O_2 as all of them had their decolourisation in basic pH of 12. A. Riga et al. have reported in the case of degradation of Procion H-excl dyes by UV/ H_2O_2 where the degradation of dyes took place effectively in basic pH of 12 and above. Abbas Rezaee et al. have also reported the same result in reactive blue 19 by UV/ H_2O_2 , which has its effective degradation in basic pH of 11 [11-13].

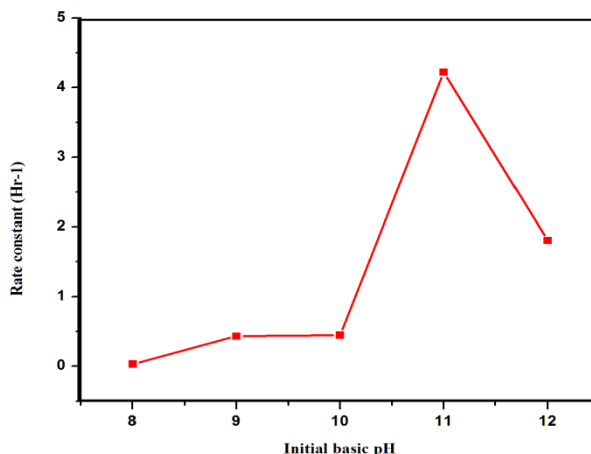


Fig. 7. Kinetic studies on the effect of basic pH: Reaction conditions: Orange G dye solution of concentration 100 mg/L with H_2O_2 concentration of 264 mM in different basic pH ranges from 8 to 12.

In basic medium, there is an increase in the concentration of formation of conjugate base of H_2O_2 , HO_2^- . HO_2^- absorbs solar radiation more intensely than hydrogen peroxide which leads to an increase in the concentration of hydroxyl radicals. Hence there is more availability of hydroxyl radicals to attack and degrade the dye molecules [8].



3.2.3. Effect of initial H_2O_2 concentration

Table 4 revealed the effect of initial H_2O_2 concentration on decolourisation of Orange-G of concentration 100 mg/L was studied by treating dye solution with different concentrations of H_2O_2 ranging from 50 mM to 500 mM in its optimum pH 11. From figure 8, it was found that 100% decolourisation was achieved in the shortest time duration of 1.5 hours in the H_2O_2 concentration of 250 mM.

Table 4. Effect of initial H_2O_2 concentration.

H_2O_2 concentration	% of decolourisation in 1.5 hours	$k(Hr^{-1})$
50 mM	84.27	1.2333
100 mM	96.43	2.2219
150 mM	97.65	2.5001
200 mM	97.62	2.4922
250 mM	100	4.4977
300 mM	98.82	2.9623
350 mM	97.62	2.4922
400 mM	96.47	2.2298
450 mM	97.62	2.4922
500 mM	96.43	2.2219

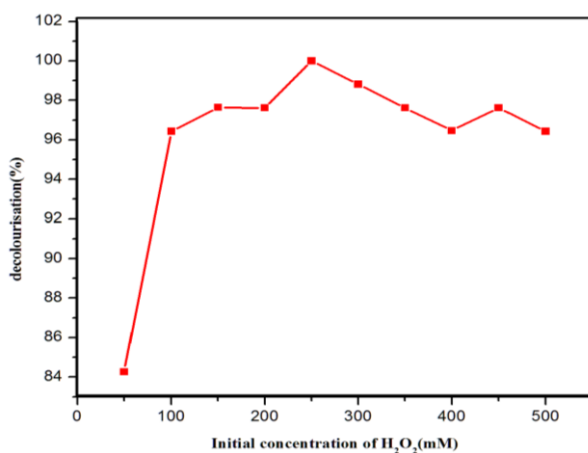


Fig. 8. Effect of initial H₂O₂ concentration: Reaction conditions: Orange G dye solution of concentration 100 mg/L with different H₂O₂ concentration ranges from 50 mM to 500 mM in optimised pH 11.

Figure 9 showed the kinetic studies on the effect of initial H₂O₂ concentration on degradation of Orange G can be done by varying the H₂O₂ concentration from 50 mM to 500 mM. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equ I).

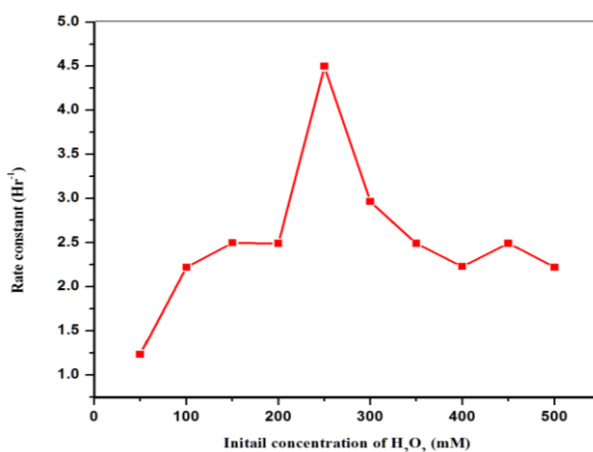


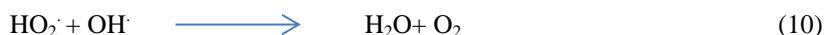
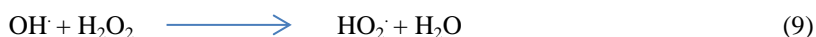
Fig. 9. Kinetic studies on the effect of initial H₂O₂ concentration: Reaction conditions: Orange G dye solution of concentration 100 mg/L with different H₂O₂ concentration ranges from 50 mM to 500 mM in optimised pH 11.

Rate constant calculated based on kinetic studies also provided as an evidence for the maximum decolourisation of Orange G in 250 mM H₂O₂ concentration. Hence it was concluded that 250 mM was the optimum concentration of H₂O₂.

Lower rate of decolourisation of Orange G dye below and above the optimised concentration of 250 mM was attributed to the following reasons:

H₂O₂ produces hydroxyl radicals by photolysis reaction in presence of sunlight. The produced radicals react with an excess H₂O₂ to form oxygen and water. They produced a negative effect on the decolourisation of Orange G as their concentration dominates the concentration of hydroxyl radicals. It therefore, leads to lower availability of hydroxyl radicals and so the attack of hydroxyl radicals on dye molecules to degrade the dye becomes lesser in probability. Therefore higher concentration of H₂O₂ lowers the decolourisation rate. [8, 14-17].

Similarly in the lower concentration of H_2O_2 , production of hydroxyl radicals was lower and so there was a very lower concentration of hydroxyl radicals to react with an excess concentration of dye molecules to degrade them according to the following equations [8,14-17].



Similar results have been reported by A.Riga et al. in the case of Procion H-ex1 dyes which were treated by $TiO_2/UV/H_2O_2$, Xuanmo Liu in the case of Reactive Black 5 dye treated by Fenton and Fenton-like system, Reza Marandi et al. in the case of Reactive Black B dye treated by UV/H_2O_2 /biosorbent system, Hang Xu et al. in case of Reactive Red SBE treated by Fenton process, Azam Aleboyeh et al. in case of Acid Blue 74 treated by UV/H_2O_2 process, Fatima H.AlHamedi et al. in case of Rhodamine B treated by UV/H_2O_2 process, Silvia Gabriela Schrank et al. in case of Vat Green 01 dye treated by UV/H_2O_2 process, Raja et al. in case of Reactive Red-180 by solar/ H_2O_2 process, Raja et al in case of Congo Red by Solar/ H_2O_2 process etc.,[7,8,10,12,14,16-19].

3.2.4. Effect of initial dye concentration

Table 5 showed the effect of initial dye concentration on decolourisation of Orange-G was studied by treating different concentrations of dye solution ranging from 50 mg/L to 500 mg/L. The optimised dye concentration is 50 mM (Figure 10). It was observed that the percentage of decolourisation decreases with an increase in dye concentration.

Table 5. Effect of initial dye concentration.

Dye concentration	% of decolourisation in 1 hour	k(Hr ⁻¹)
50 mg/L	100	6.2549
100 mg/L	98.75	4.3828
200 mg/L	97.14	3.5559
300 mg/L	92.11	2.5394
400 mg/L	89.92	2.2946
500 mg/L	85.6	1.9382

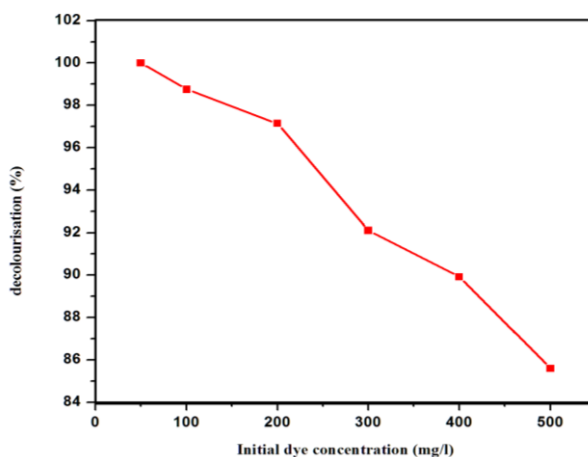


Fig. 10. Effect of initial Dye concentration: Reaction conditions: Orange G dye solution of different concentrations ranging from 50 mg/L to 500mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11.

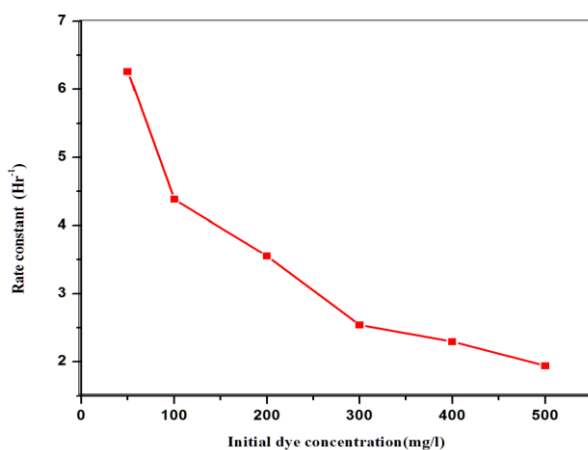


Fig. 11. Kinetic studies on the effect of initial Dye concentration: Reaction conditions: Orange G dye solution of different concentrations ranging from 50 mg/L to 500mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11.

Kinetic studies on the effect of initial dye concentration on decolourisation and degradation of Orange G can be done by varying the dye concentration from 50 mg/L to 500 mg/L. Figure 11 showed the decolourisation of orange G decreases its colour within a short interval of time period ten minutes. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equation I)

Rate constant calculated based on kinetic studies also provided as an evidence for the maximum decolourisation of Orange G in 50 mg/L dye concentration. The rate of decolourisation of Orange G dye decreases with the increase in dye concentration. It may be due to the following reasons:

Increase in dye concentration induced a rise in internal absorbance and the dye solution becomes more and more impermeable to solar radiation. But in the reaction mixture H_2O_2 can be irradiated only to a certain fraction and it leads to a reduction in the formation of hydroxyl radicals. Therefore, there was a lack in the concentration of hydroxyl radicals to react with an excess of dye molecules on increase in the concentration of dye solution to degrade them. Also,

there was an increase in the concentration of intermediate compounds which are highly reactive free radicals and there was a competition between dye molecules and intermediate compounds to react with hydroxyl radicals as the reaction between intermediate compounds and hydroxyl radicals dominated. It leads to a lesser rate of decolourisation in the higher concentration of dye solution. [9, 14, 16, 20]

Similar results have been reported by M.Muruganandham et al in the case of Reactive Yellow 14 treated by UV/H₂O₂, Xuanmo Li et al in the case of Reactive Black 5 treated by Fenton and Fenton like system, Hideyuki Katsumata et al in the case of Reactive Yellow 86 treated by the solar-assisted photo-Fenton process, Montaser Y. Ghaly et al in the case of Maxoline Navy 2 RM 200% basic dye treated by solar/TiO₂ process, Amrit Pal Toor et al in the case of Direct Yellow 12 dye treated by UV/TiO₂ process, Hang Xu et al in the case of Reactive Black B dye treated by UV/ H₂O₂/biosorbent system, B.Neppolian et al in case of Reactive Yellow 17, Reactive Red 2, Reactive Blue 4 treated by UV/TiO₂ process, Hang Xu et al in case of Reactive Red SBE treated by Fenton process, Azam Aleboye et al in case of Acid Blue 74 treated by UV/H₂O₂, Fatima.H.Alhamedi et al in case of Rhodamine B treated by UV/H₂O₂, Raja et al in case of Decolourisation of Reactive Red 180 dye by solar/H₂O₂, Raja et al in case of Decolourisation of Congo Red dye by solar/H₂O₂ etc.,[7-9, 15-22].

3.2.5. Effect of additives

Radical scavengers act as antioxidants by donating electron and inactivate the hydroxyl radical thereby affect the degradation of organic compounds like dyes. The common sources of inorganic anions which act as radical scavengers are chloride, carbonate and bicarbonate present in textile wastewater. Various chemical pollutants like wetting agents, dyes, softening agents, oils, wax and other additives which are used throughout the dyeing processes are generated as wastes and they act as the origin for the above radical scavengers.

Table 6 exhibited the effect of additives like chloride and dihydrogen phosphate of concentration of 1M in decolourisation of Orange-G was studied by treating them with dye solution of concentration 100 mg/L in the optimised pH 11 and optimised H₂O₂ concentration of 250 mM. From figure 12, it was observed that the chloride ion has an enhancement effect on decolourisation. The decolourisation of dye was achieved 93.33% within 45 minutes. Surprisingly, 100% decolourisation was achieved by adding chloride ion of 1 M concentration. While addition of dihydrogen phosphate ion of 1 M concentration has produced an inhibitory effect on decolourisation of the dye. Only 3.61% decolourisation was observed on adding dihydrogen phosphate ion with the dye solution in the same time duration of 45 minutes.

Figure 13 revealed the kinetic studies on the effect of additives on degradation of Orange G can be done by adding chloride ion and dihydrogen phosphate ion of 1 M concentration. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equation I)

Table 6. Effect of additives.

Additives	% of decolourisation in 45 minutes	k(Hr ⁻¹)
Dye	93.33	3.7465
Dye+ Cl ⁻	100	8.9475
Dye +H ₂ PO ₄ ⁻	3.61	0.0491

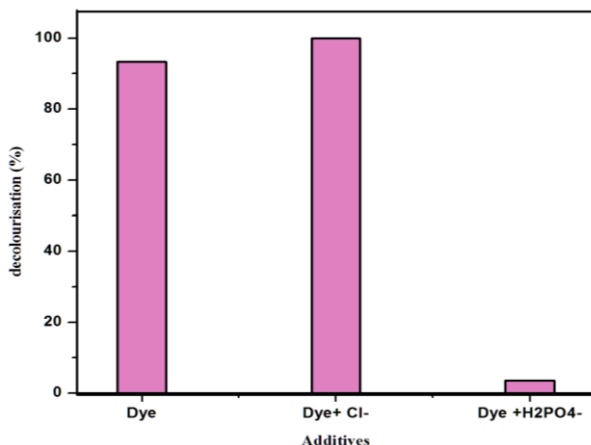


Fig. 12. Effect of additives on decolourisation of Orange G: Reaction conditions:

- (i) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11;
- (ii) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 with Chloride ion of 1 M concentration;
- (iii) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 with dihydrogen phosphate ion of 1 M concentration.

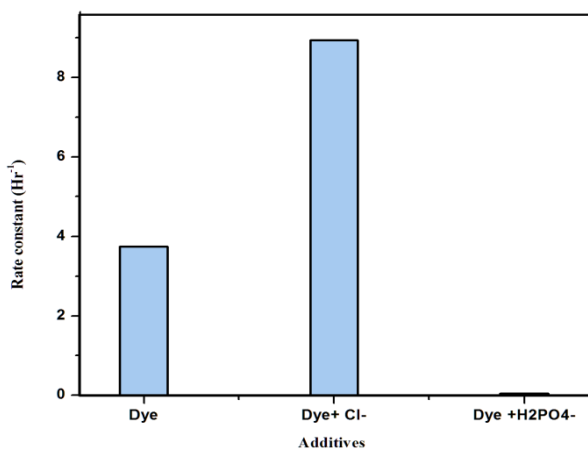


Fig. 13. Kinetic studies on effect of additives on decolourisation of Orange G: Reaction conditions:

- (i) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11;
- (ii) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 with Chloride ion of 1 M concentration;
- (iii) Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 with dihydrogen phosphate ion of 1 M concentration.

Rate constants calculated based on kinetic studies also proved that there is a decrease in decolourisation in Orange G on adding dihydrogen phosphate ion of 1M concentration and increase in decolourisation in Orange G on adding chloride ion of 1M concentration.

There was inhibition in photodegradation of dye when the concentration of chloride ion in the form of NaCl in the dye solution was lower as of 0.001 M, 0.01 M and 0.1 M (0.058 g/lit , 0.58 g/lit , 5.8 g/lit). When the concentration exceeds above 58 g/lit i.e. of more than that of 1M, photodegradation of the dye increases with an increase in NaCl concentration. So that, it had been

observed that there was an increase in degradation of dye with the presence of NaCl which is of 1M concentration. Similar results were observed by Jiangang Qu et al in the case of Reactive Black 5 dye degraded by UV/H₂O₂ which also had its increase in photodegradation which contains NaCl as an additive in the concentration of 1 M [23]. It was due to the following reason:

In low concentrations, Cl⁻ ion acts as scavengers whereas in high concentrations like 50 g/L and above, there is a constant formation of reactive chlorine species which have enough activity to attack and decompose the dye molecules [23].

However, there was inhibition on adding dihydrogen phosphate ion which is in the form of sodium dihydrogen phosphate which is of 1M concentration in the dye solution. The inhibition effect is because of the following reasons:

The dihydrogen phosphate ion acts as the scavenger for hydroxyl radicals which react with them to form inorganic radical ions which show lower reactivity than hydroxyl radicals and they do not take part in dye decolourisation. There was also a competition between dye and inorganic radical anions on reaction with the hydroxyl radicals.



Similar results were observed in case of Miljina D Radovic et al. in case of decolourisation of Reactive Blue 19 dye degraded by UV/H₂O₂ which also had its decrease in photodegradation which contains NaH₂PO₄ as an additive in the concentration of 1 M.[24]

3.2.6. Effect of solar light intensity

Table 7 confirmed the effect of solar light intensity on decolourisation of Orange-G of concentration 100 mg/L was studied by comparing the percentage of decolourisation in different solar light intensities with the optimised concentration of H₂O₂ of 250 mM with the optimum pH 11. It was found that increase in solar light intensity has lead to increase in the decolourisation percentage of the dye (figure 14).

Table 7. Effect of solar light intensity.

Solar light intensity(Lux)	% of decolourisation of Orange-G	k(Hr ⁻¹)
33500-36200	83.52	2.405
45700-46000	92.85	3.519
62000-62700	93.33	3.746
64400-65800	95	3.995

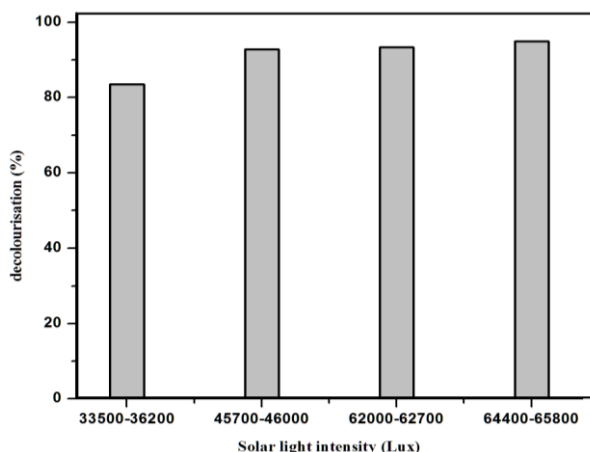


Fig. 14. Effect of solar light intensity on decolourisation of Orange G: Reaction conditions: Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 exposed to different solar light intensities.

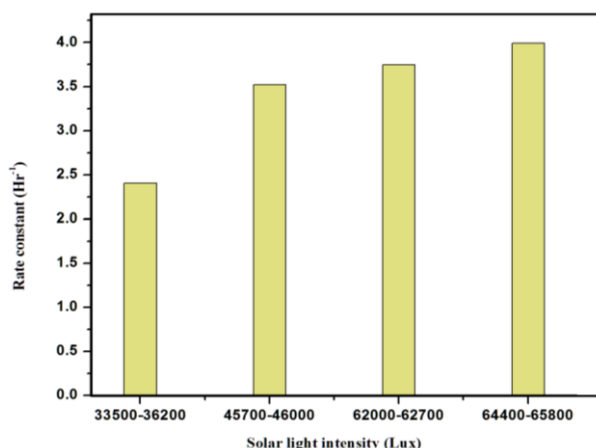


Fig. 15. Kinetic studies on the effect of solar light intensity on decolourisation of Orange G: Reaction conditions: Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 exposed to different solar light intensities.

Figure 15 showed the kinetic studies on the effect of solar light intensity on degradation of Orange G can be done by varied solar light intensities. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equation I)

Rate constants calculated based on kinetic studies also proved that increase in solar light intensity leads to an increase in decolourisation. Similar results were observed by M. Muruganandham et al in the case of decolourisation of Reactive Yellow 14 treated by solar/ H_2O_2 method [9]

The increase in decolourisation of dye is because of an increase in the production of hydroxyl radicals. Light intensity determines the amount of photons absorbed by the H_2O_2 molecules. With the increase in the solar power H_2O_2 molecules absorb more photons which also produce more hydroxyl radicals. In solar/ H_2O_2 process, the photolysis of H_2O_2 depends on the incident solar light intensity directly. As the intensity of solar light is low the photolysis of H_2O_2 is limited and the generation of hydroxyl radicals to degrade the dye is also limited. The solar power tested lied in the linear range and hence all the photons generated were effectively used to generate hydroxyl radicals [9].

3.2.7. Effect of temperature

Table 8 demonstrated the effect of temperature on decolourisation of Orange-G was studied by comparing the percentage of decolourisation of the dye of concentration 100 mg/L in different temperatures with the optimised concentration of H_2O_2 of 250 mM with the optimum pH 11. From figure 16, it was found that the increase in temperature has lead to an increase in the decolourisation percentage of Orange-G.

Table 8. Effect of temperature.

Temperature ($^{\circ}\text{C}$)	% of decolourisation of Orange-G	$k(\text{Hr}^{-1})$
39	83.52	2.405
42	92.85	3.519
45	93.33	3.746
46	95	3.995

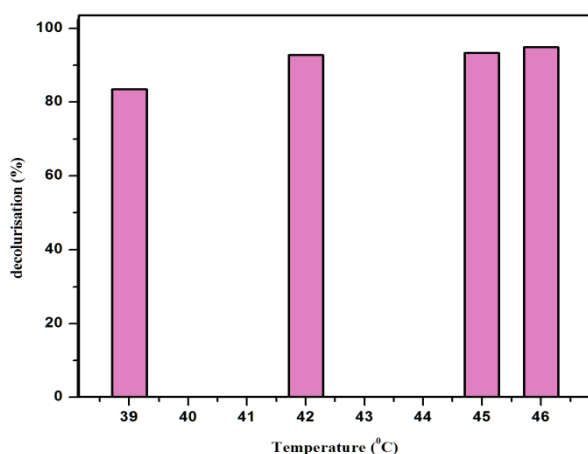


Fig. 16. Effect of temperature on decolourisation of Orange G: Reaction conditions: Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 exposed to different temperatures.

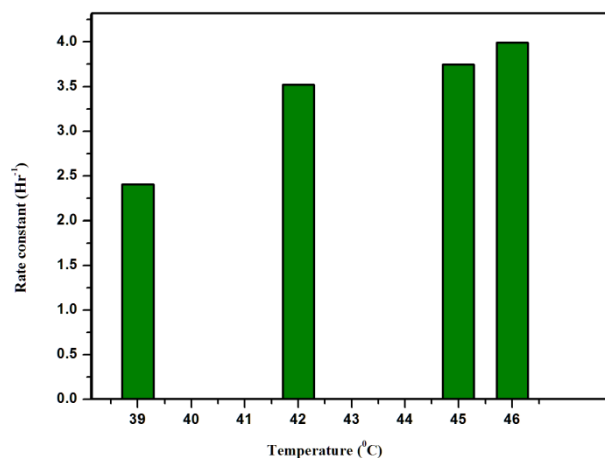


Fig. 17. Kinetic studies on the effect of temperature on decolourisation of Orange G: Reaction conditions: Orange G dye solution of concentration 100 mg/L with optimised H_2O_2 concentration of 250 mM in optimised pH 11 exposed to different temperatures.

Figure 17 showed the kinetic studies on the effect of temperature on degradation of Orange G can be done by varying temperatures in high and low heat radiations. The order of the reaction is found to be pseudo-first order with respect to dye concentration (using equation I)

Rate constants calculated based on kinetic studies also proved that the increase in temperature leads to increase in decolourisation.

It can be explained on the basis that the degradation reaction accelerated by rise in temperature which leads to an increase in the generation of hydroxyl radicals. Therefore it enhances the degradation of the dye. This phenomenon can be explained as on increasing temperature up to certain extent (i.e) up to 50°C dissociation of H₂O₂ increases in solar-assisted photodegradation process which leads to the generation of hydroxyl radicals. But above 50°C, actually dye degradation decreases because of the decrease in the concentration of DO and spontaneous decomposition of hydrogen peroxide into water and oxygen.

Similar results were observed by Meric et al in the case of decolourisation of Remazol Red dye treated by Fenton process and Pare et al in the case of degradation of Neutral Red by Visible light/ZnO in which 45°C was found at the optimum temperature, in case of decolourisation of Reactive Red 120 dye treated by UV/ H₂O₂ by Mansoorian et al and in case of decolourisation of Reactive Blue 19 and Reactive Red 198 treated by Fenton and revised Fenton methods by Rishi Ananth Shankar et al [25-28].

3.2.8. COD removal

The values of COD depend on the initial concentration of dye, its chemical structure and time taken for decolourisation. Table 9 pointed out the COD value of Orange G dye before degradation was 40 mg/L and it was reduced to 12 mg/L after degradation. Hence the COD removal was 70% and it was observed that oxidation was done in an effective way (figure 18) [11].

Table 10 pointed out the TOC value of Orange G dye before degradation was 0.1544 ppm and after degradation, it was reduced to 0.1414 ppm. % of TOC removal rate was found to be 8.41 (figure 19). Hence it was observed that some new organic compounds were formed during mineralisation which was unidentified as they were no longer coloured but they needed more time for degradation [11].

It is known that complete mineralization of a dye does not mean that it is completely decomposed into smaller and simpler molecules like CO₂, H₂O, etc.; there may be a presence of some longer-lived reaction intermediates in the degraded and mineralized product. The obtained results were found to be satisfactory and mineralization done by solar/H₂O₂ occurred effectively. Thus, it was concluded that solar light was more effective in generating hydroxyl radicals by the photolysis process of H₂O₂. It also activated the bonds of organic molecules to degrade further [11].

Table 9. COD removal.

COD of Orange G before degradation	COD of Orange G after degradation	% of COD removal
40.00 ppm	12.00 ppm	28.00 ppm(70%)

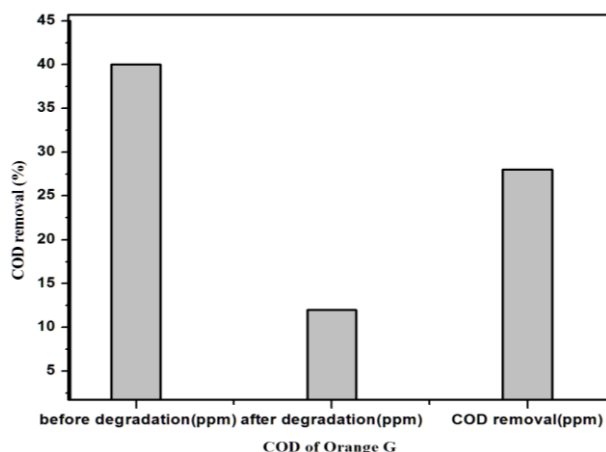


Fig. 18. COD removal of Orange G dye.

3.2.9. TOC removal

Table 10. TOC removal.

TOC of Orange G before degradation	TOC of Orange G after degradation	% of TOC removal
0.1544 ppm	0.1414 ppm	0.0130 ppm(8.41%)

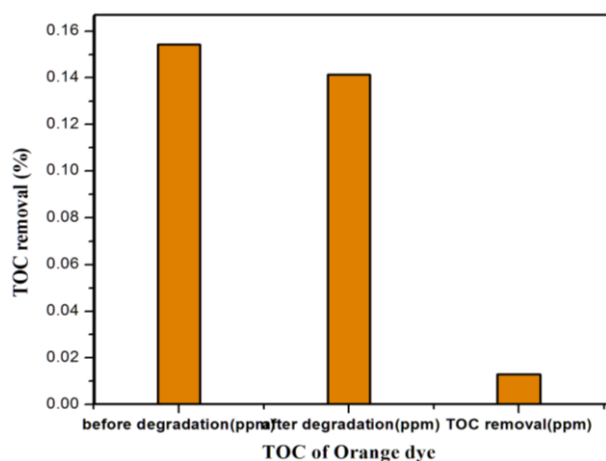


Fig. 19. TOC removal of Orange G dye.

3.3. Pictorial representation

The picture provides an evidence for 100% decolourisation of azo dye Orange G. The optimum conditions were pH=11, H₂O₂ concentration of 250 mM with the dye concentration of 100 mg/L.

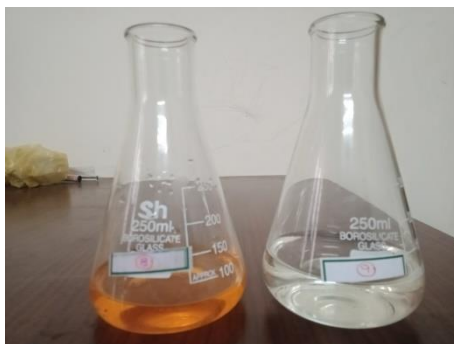


Fig. 20. Pictorial representation of degradation of Orange G dye.

4. Mechanism

The mechanism of orange G dye degradation was shown in Fig.21. Under sunlight irradiation dye molecules get excited and transfer electron from valence band to the conduction band. Electron in the conduction band can reduce molecular oxygen and produce the super oxide radical. These superoxide radical ions react with the dye and subsequently transfer the organic pollutants into less toxic material. The electron in valence band reacts with H_2O_2 molecules produce hydroxyl radicals which are highly reactive. These radicals react with the dye and consequently transfer the organic pollutants into less toxic material.

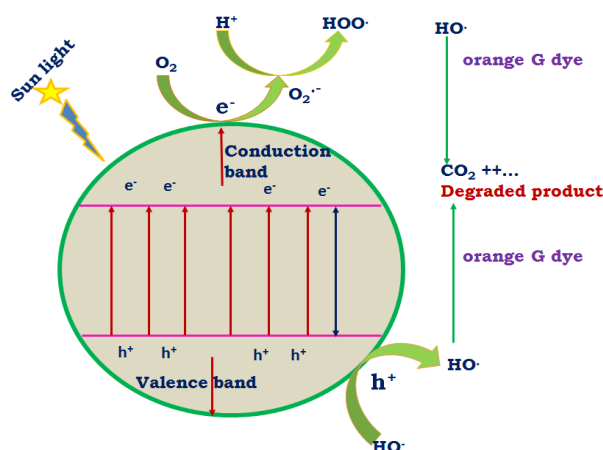


Fig. 21. Mechanism of Orange G dye degradation.

5. Conclusion

The solar-expedited photodegradation process using H_2O_2 , also known as solar/ H_2O_2 , was an effective method for complete decolourisation of Orange G dye within the shortest period of 1.5 Hours with the optimum conditions of $\text{pH}=11$, H_2O_2 concentration of 250 mM with the dye concentration of 100 mg/L. UV-Visible spectrometric analysis and Pictorial representation were also provided as a piece of evidence for complete decolourisation of dye. COD removal done by this method was also found to be 70% and TOC removal was found to be 8.41%. Among the literature surveys done on the degradation of Orange G dye by various methods, it also proved that it was one of the efficient methods as better results were obtained by this. This method has various advantages also that it does not form any sludge as formed by Fenton and Photo-Fenton method. It does not form any suspension that has to be filtered after treatment as formed using TiO_2 and ZnO photocatalysts. It is not so harmful as ozone, which is toxic and not so costlier as it does not use

UV light irradiation in combination with H₂O₂. Hence we can conclude that it is an efficient method for the degradation of Azo dyes like Orange G.

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