Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Decolourization of Reactive Dye by Catalytic Ozonation based Advanced Oxidation Process in the Presence of Nano Gypsum

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Synthetic dye wastewater released into water bodies from industrial units such as textile manufacturing, dyeing and printing etc causes a negative environmental impact. Dye pollution poses significant environmental and health concerns. There are many methods available to treat dye wastewater such as adsorption, ion exchange, membrane process, coagulation and flocculation etc., still Advanced Oxidation Process is considered to be the best vowing to its broad applicability, complete mineralization, low sludge generation, decomposition of intermediates, non-selective reactivity etc,. In present study Catalytic Ozonation, an Advanced Oxidation Process was used to decolourise C. I. Reactive Blue - 5, a persistence dye using a nanocatalyst named nano gypsum. Nano gypsum was prepared and characterized using TEM and XRD studies. The average particle size of nano gypsum was found to be 25nm. The effect of various parameters such as catalytic dosage, contact time, ozone flow rate, solution pH and initial concentration on the removal of dye were studied. The maxiumum dye colour removal of 96.7% was achieved in presence of ozone and nano gypsum catalyst at dosage of 1.5 g/L, pH of 8, contact time of 30 min and flow rate of 3 L/min.

Keywords: Dye Colour Removal, Advanced Oxidation Process, Catalytic Ozonation, Nano Gypsum.

1. Introduction

The contamination of water has turned into a worldwide environmental issue. Worldwide, water resources are regularly found to include organic molecules, including pesticides, dyes, and medicinal chemicals, all of which have been shown to have the potential to be hazardous to human health and environment (Zang et al. 2021). Synthetic aromatic organic molecules called dyes are used extensively in the food processing, paper and printing, drug, cosmetic, apparel, and leather sectors to color a wide range of materials. The chromophore group affects the dye's color. Typically, it has a complex structure and a relatively biotoxic substrate (Sunita et al. 2021). Based on their kind and properties, dyes can be categorized. Within dye structures are molecules known as auxochromes and chromophores, which are heterocyclic and aromatic (Taheri et al. 2021).

Dyes from textiles pollute water bodies by raising Biochemical and Chemical Oxygen Demand, lowering photosynthetic activity, inhibiting vegetation growth and entering the food chain, inducing resistance to biological breakdown and accumulation of substances in the body and even potentially causing poisonous effects, gene mutations and even cancer to animals. Thus in order to protect the environment, peoples health and water resources from possible negative impacts, effluents with dyes should be treated properly with much care so as to be less harmful to the environment (Rania et al. 2022).

Dye color can be removed effective through three methods: Chemical, Biological and physical. As far as the physical methods are concerned, moist chamber techniques, membrane filtration techniques, nanofiltration, electrodialysis, reverse osmosis perstraction and adsorption are some of the anti fouling methods. In particular, the disadvantages of membrane filtration methods coined are over shrinkage of the filter due to time, continuity and blockage of the system as well as sludge production. Adsorbents are selective for particular colors throughout the adsorption process, and full adsorbent regeneration is not achievable. Coagulation in conjunction with precipitation, flocculation using Fe[II] / Ca[OH]2, electro flotation, electrokinetic coagulation, traditional oxidation techniques using oxidizing agents (ozone), radiation, etc. are examples of chemical procedures. These chemical methods are often expensive and the disposal of accumulated concentrated sludge is another problem. Biological methods include artificial wetlands, trickling filters, oxidation ponds, and so forth. Nonetheless, they are only suitable for certain dyes while biological means have disadvantages such as long retention time and sludge separation technologies (Sivarajasekar et al. 2015) (Mona et al. 2022). Advanced Oxidation Processes (AOP) has attracted interest during the last few decades because of generation of extremely Reactive Oxygen Species (ROS) such as hydroxyl radicals. These radicals are considered desirable for many applications owing to the fact it is more oxidizing than ozone (2.1 eV) at (2.8 eV) (Santosh et al. 2018; Jyothi et al. 2015).

To break down pollutants and transform them into less hazardous byproducts like CO2 and H2O, AOP primarily rely on the formation of radicals, such as hydroxyl radicals (OH-), superoxide radicals (O2-) and singlet oxygen (1O2). They have all contributed to their popularity in efficient processing of waste and other waste materials because of their high performance over a wide range of pH values at which AOP can operate, their cheap and eco-friendly nature and ability to mineralize efficiently (Mona et al. 2022; Farzan et al. 2022).

Advanced Oxidation Processes (AOP) like ozonation are essential due to their oxidative skills and continue to be appealing since this therapy can be retrofitted into existing wastewater treatment facilities. Ozonation is a commonly used disinfection process for water supply treatment systems. They have the capability to remove organic molecules at the molecular level using disintegration and degradation. Ozone radicals, however, are less potent oxidizing agents when compared with hydroxyl radicals thus presenting a limitation towards achieving maximum degradation of organic pollutants. Ozonation appears to enhance the effectiveness of the ionization process, for instance, better destruction of types of organic contaminants (Pesqueira et al. 2020; D. Seibert et al. 2020).

Due to their effectiveness in removal of organic pollutants, much emphasis has been laid on ozonation and catalytic ozonation amongst Advanced Oxidation Processes. Still, the ozonation process is not without its drawbacks, such as, a brief half-life, limited form stability and solubility, and unceasing ozone production in order to lower the costs per hour and the energy consumption (Didim et al.. 2015). As noted in the above-mentioned aspects, the Ozonation techniques have therefore been combined with other oxidants in order to overcome these restrictions (Jianlong and Chen. 2020). These conditions facilitate and enhance the removal of wastewater contaminants by means of nanomaterials as catalysts. Surface reactions are very important for effective contaminant removal in AOPs, since surface active sites are occupied by different oxidants (O3, H2O2) generating hydroxyl radicals and combined oxidation and hydrolysis reactions take place.

It is worth mentioning that there is an effect wherein it generally enables nanomaterials to cover up to higher concentrations at the active areas in particular when addressing the removal of pollutants which is mostly observed because of the specific large surface area they possess and the dimension of less than or equal to 100 nm. Moreover, some nanomaterials have super-paramagnetic properties with increased active sites in dense surface area that attract particulates, and assist in the destruction of the particulates once hit with the catalysts in catalytic advanced oxidation. There are many different sorts of nanomaterials which have been previously employed as catalysts for such processes, including zeolite, carbon nanotube (CNT), metal and oxide, metal organic framework (MOF). They increase the colour removal efficiency in waste water treatment. (Mangalam et al. 2019; Deshpande et al. 2020; Ikhlaq et al.. 2020).

2. Literature Review

In Advanced Oxidation Process, Catalytic Ozonation is one of the process employed for the complete removal of pollutants in the presence of ozone gas and a catalyst. Many researchers have been investigated the performance of different catalysts in the removal of diverse dyes using catalytic ozonation. These are some papers referred related to catalytic ozonation (an Advanced Oxidation Process). In all the papers, the procedure starts with the preparation of a catalyst for the process to remove a pollutant such as dyes, pharmaceutical wastes, industrial wastes etc., from water. After the preparation of the catalyst or nanocatalyst, characterisation is done using XRD and SEM analysis to know the exact compound (catalyst) prepared. Pollutant (such as dye) of known concentration is prepared in aqueous medium and treated with ozone gas in presence of a catalyst. The pollutant removal studies are made and the

parameters like catalytic dosage, pH, reaction time, flow rate etc., are optimised to get the maximum percentage of dye removal.

Kinetic studies are made in some papers, usually following pseudo first order kinetics. In some papers comparison is made using different Advanced Oxidation Process (or) with different catalysts (or) with and without catalyst etc., The papers referred and the optimised values for different dyes and catalysts in catalytic ozonation are shown in Table-1

In many cases metal oxides, metal composites and nanomaterials were used as catalysts with optimum dosage varying from 0.1g to 3g per Lit; Ozone flow rate varies from 1L/min to 5L/min. Initial dye concentration was used to be 5 to 100mg/L in laboratory setting and its gone up to 760mg/L in case of real time textile effluent. Optimum pH varied from 2 to 12 but for to real time usage it was kept in between 6 to 8. Reaction time is between 10min and 100min. In almost all the papers 100% dye concentration was removed. If nano materials were used as catalysts, small amount of catalyst causes much degradation. In some papers TOC and COD were also removed to great extent. In some papers kinetic studies were performed following pseudo second order model.

In this study the persistant textile dye named C.I. Reactive Blue – 5, treated with ozone in the presence of a nanocatalyst named nano gypsum. The effect of various parameters such as catalytic dosage, Ozone flow rate, solution pH, contact time and temperature on the removal were studied through different sets of non flow batch experiments. Kinetic and thermodynamic studies were also performed.

Table-1: Catalytic Ozonation for Removal of Different Dyes from Wastewater

S No	Dye	Catalyst	Optimum catalytic dosage	Ozone flow rate	Initial dye concentration (mg/L)	pH	Reaction Time (min)	Maximum Percentage Removal	Reference
1	C.I. Methylene Blue	Bismuth oxyiodide (BIOI)	0.1 g/L	1 kg/hr	5	6	10	100	(Sarre et al, 2024)
		N,Pd-TiO2	0.1 g/L	1 kg/hr	5	6	10	100	
2	C.I. Reactive Black 5	Metal oxide composite of Ag-Ce-O, made with co-precipitation method)	0.5g/L	30L/hr	100	10	80	100	(Nikita et al. 2023)
	COD @ RB5 of 100mg/L	--	0.7g/L	60L/hr	--	10	80	88	
3	C.I. Direct Blue-1	ZnSnO3@S-doped g-C3N4 nanocomposite	200mg/L	2.83mL/S	50	2 (Expirimented at 3&5)	15	100%	(Elaheh et al. 2024)
S No	Dye	Catalyst	Optimum catalytic dosage	Ozone flow rate	Initial dye concentration (mg/L)	pH	Reaction Time (min)	Maximum Percentage Removal	Reference

4	Real time textile effluent with azo reactive dyes	...	...	6g/hr	COD 289	9.34	60	COD removal of 90% with final COD at 29 mg/L	(Jameelamma l et al. 2022)
5	C.I. Methylene blue	iron loaded peanut shell ash	0.1g	1mg/min	50	6	15	71% without catalyst & 78% with catalyst	(Amir et al. 2020)
6	Oxalic Acid	porous magnetic-$MnFe_2O_4$/ spherical carbon nano-catalyst	3g/L	100mL/ Min (120rpm stirring speed)	100	3	60	96.59%	(Xiaoguang et al. 2021)
7	C.I. Reactive Black 5	Zeolites modified with $CuMn_2O_4/gC_3N_4$	1mg/L	1 mg/min	30	10	30	97%	(Amir et al. 2021)
8	C.I. Reactive Black 5	Silver–Cobalt Oxide Composite	0.5g/L	30L/hr	100	7	80	100.00%	(Nikita and Jayesh, 2020)
9	C.I. Reactive Black 5 (RB5)	..	..	20L/hr	500	12	18	100%	(Lucyna et al. 2018)
	Textile waste water	..	..	40L/hr	790	11.89	18	100%	
10	Petrochrmi cal waste water	Nanostructured MgO	0.3mg	0.2g/hr	..	9	30	100%	(Leili et al. 2020)
11	Denim Effluents	Ozone-electro coagulation process		5.2g/hr, 0.2915 mA cm^{-2}	Colour 630 pt-Co	7.23	12	64.27%	(García et al. 2013)
12	C.I. Methylene Blue (MB)	Fe/Ce Co-Doped in Attapulgit	0.4 g	250mL/m in	80m	7, (35 degC)	20	90%	(Jianping et al. 2024)
S No	Dye	Catalyst	Optimum catalytic dosage	Ozone flow rate	Initial dye concentra tion (mg/L)	pH	Reactio n Time (min)	Maximum Percentage Removal	Reference
13	C.I. Rhodamine B dye	ZrO2-Pumic-H2O2	0.9g, H2O2-4.46mmol/Lit	8L/min	100	9.31	20	100%	(Reza et al. 2021)
14	C.I. Reactive Black 5 dye	Metal oxide Ag-La-Co based nano composite	1g/L	30L/hr	100	7	80	97%; (TOC removal 92%)	(Nikita et al. 2023)
15	C.I. Sunset yellow dye	Iron Oxide	1g/L	$5g/M^3$	45	7	60	cod-88%, Toc - 83%	(Toro et al. 2020)
16	C.I. Acid blue 9 and Acid Orange 7	WO_3@CoFe-LDH nanocomposite	1 g/L	3 L/hr (Sonocat alytic ozonation)	50	8	100	100%	(Alireza et al. 2020)

17	C.I. Rhodamine B (RhB)	TiO_2/MnO_2 sprayed ceramic membrane	----	2.5 g/cm^3	20	7	40	100%	(Peng et al. 2023)

3. Materials and Methodology

Materials

Instruments utilized include an ozonator, an X-ray diffraction (XRD) device, a Transmission Electron Microscope (TEM), a UV-Vis spectrophotometer, a magnetic stirrer with hotplate and thermometer. Chemicals include Hydrochloric acid, sulfuric acid, potassium iodide, sodium hydroxide pellets, methanol and distilled water of AR-grade were used. C. I. Reactive Blue - 5 dye solution of 50 mg/L dosage was used.

Preparation of Nano Gypsum Catalyst

50 mL of methanol and 50 mg of calcium carbonate were added to a Pyrex glass container, which was then sealed. The container was then filled with 500 mL of 1 M sulfuric acid using a micropipette, and a magnetic stirrer was used to agitate the mixture. At a temperature of 20 °C and one atmosphere, the reaction was allowed to continue for 425 minutes. To obtain nano gypsum (CaSO4.2 H2O), the sample was filtered, cleaned with methanol, and dried at 600° C (Satoru and Naoto, 2018). Equation-1 below depicts the production of nano gypsum, and Figure-1 shows an image of nano gypsum.

5 (Liu et al., 2011)

$$CaCO3 + H2SO4 + 2H2O \rightarrow CaSO4.2\ H2O + CO2 + H2O \quad .....(1)$$

Figure-1: Image Showing Nano Gypsum

Experimental Methodology

The color of C.I. Reactive Blue–5 dye was removed from an aqueous solution using catalytic ozonation experiments (C.I. 61205; molecular weight: 774.15; UV wavelength max: 600 nm). It has the structure depicted in Figure-2 (Liu et al. 2011). Nano gypsum was employed as a catalyst in this reaction. The nano gypsum catalyst was first made via synthesis. Studies using an electron microscope (TEM) and X-ray diffraction (XRD) were conducted to verify the material and its particle size. 50 mg of C. I. Reactive Blue - 5 dye was diluted in 1L of distilled water to form a stock solution with a 50 mg/L concentration, which was then used to

prepare the test solution. It takes 0.1M of HCl at a steady pH. Experiments on catalytic ozonation were conducted in a glass column reactor with a gas inlet and outlet facility seen in Figure 3 to eliminate the color of C.I. Reactive Blue-5 dye in the presence and absence of nano gypsum catalyst.

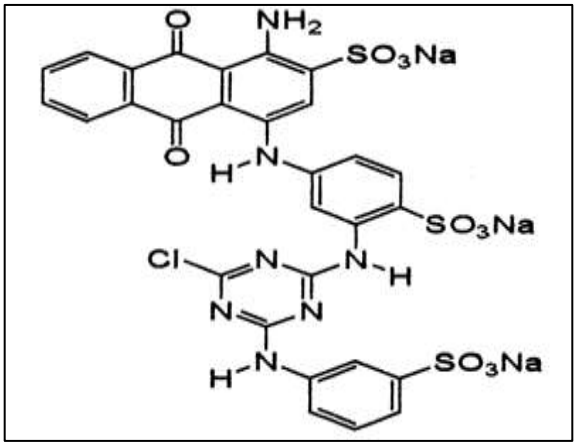

Figure-2: Image showing the structure of C.I. Reactive Blue-5 (Liu et al. 2011).

To create ozone, the ozonator was supplied with atmospheric air. Through the sparger, it was bubbled into a glass column. The studies were conducted with constant magnetic stirring, changing the catalytic dose, pH, and contact time. Samples were removed at various intervals and filtered using ashless 0.45 μm filter paper to eliminate any suspended particles. The KI solution bottles contain the leftover ozone that emerges from the glass column (Dong et al. 2013). Additionally, temperature was adjusted via a magnetic stirrer and a hotplate. Using a UV–visible spectrophotometer, the absorbance of the samples was determined at a wavelength of 600 nm. The decolorization efficiency was determined as percentage colour removal:

Percentage Colour removal = $(C_0 - C_t / C_0) * 100$ .....(2)

Where C_0 and C_t are the dye concentrations at times zero and t respectively.

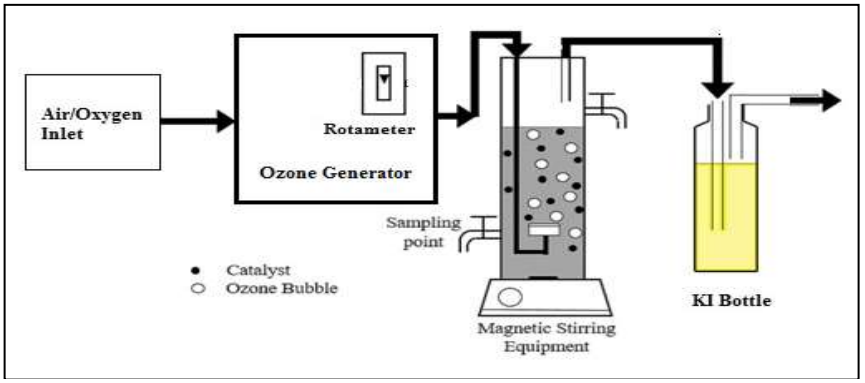

Figure-3: Image Showing Ozonator Setup

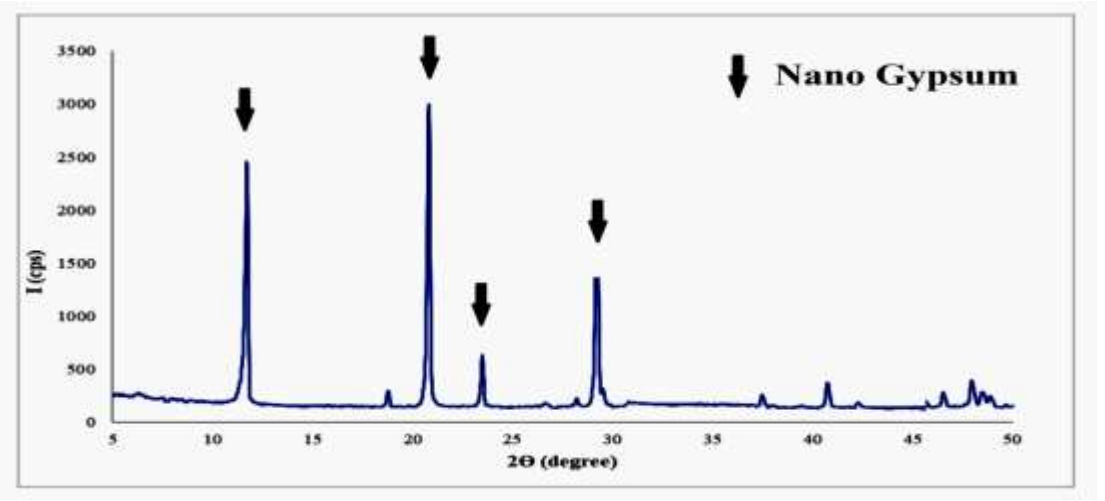

Figure-4: XRD Pattern of Nano Gypsum

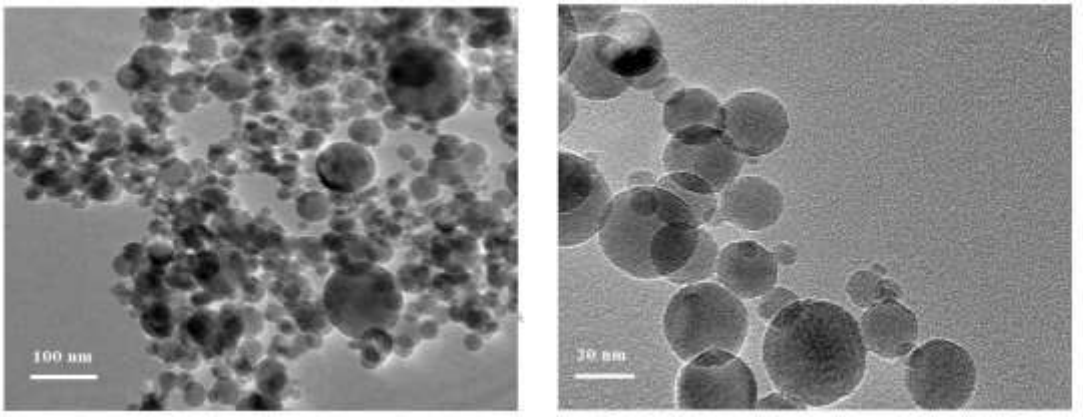

Figure-5: TEM Images of Nano Gypsum

4. Results and Discussion

Characterisation of Nano Gypsum Catalyst using Transmission Electron Microscope (TEM) and X-Ray Diffraction (XRD) Analysis

The synthesized nano gypsum's X-ray diffraction (XRD) patterns are displayed in Figure 4. The Standard International Centre for Diffraction Data (ICDD) was used to examine the crystallographic parameters derived from the created pattern. Peaks at 2-theta values of 11.646 (020), 20.74 (021), 23.40 (040), 31.85 (221), 40.69 (151), 45.41 (170), and 47.71 (080) were produced by the synthetic gypsum. The artificially produced gypsum's peaks matched those found in the ICDD database (Sahadat et al. 2022).

Table-2: The Particle Size Data of Nano Gypsum Extracted from the TEM images

Parameter	Value
Mean (nm)	25
Median (nm)	22.4

Mode(nm)	16.25
Standard Deviation	12.1
Kurtosis	5
Skewness	1.6
Range(nm)	89.4
Minimum(nm)	5.7
Maximum(nm)	96.1
Sum	12778
Count	530

Information about the morphology, size distribution, and size of the nanoparticles is obtained from the TEM. To determine whether agglomeration is present in the system or whether good dispersion has been attained, TEM images can also be utilized. Characterizing nanoparticles can be greatly aided by electron microscopy (Nalwa et al. 2004). Agglomerates of many primary particles are typical nanoparticles. We refer to the agglomerates as secondary particles. They developed when strong chemical connections (hard agglomerates) or weak surface forces (soft agglomerates) like Vanderwal's or capillary forces kept together the initial particles (Jillavenkatesa et al. 2001). To comprehend the particle size and other statistical data indicated in Table 2, TEM pictures are presented in Figure 5. The nano gypsum particle size data as mentioned in Table-2 by counting more than 500 particles producing particle size data of nano gypsum. It is discovered that the particles' mean diameter is 25 nm.

Dye Colour Removal Studies

Effect of Catalyst Dosage

The effect of catalytic dosage on percentage colour removal was investigated by varying catalytic dosage from 0 to 2.5 g/L at pH of 7, contact time (t) of 40 min, ozone flow rate of 3 L/min and initial concentration of 50 mg/L in solution of 1L. From Figure-6, it was observed that in presence of ozone alone, at zero catalytic dosage, the percentage colour removal was 29.4 %. In the presence of ozone and nano gypsum catalyst, maximum percentage colour removal of 96.4 % occurs at the dosage of 1.5 g/L. After the optimum catalytic dosage of 1.5g/L the percentage colour removal is constant.

Catalytic ozonation proved to be more effective than ordinary ozonation when the catalyst was used, improving the removal efficiency. Because there are three possible routes for degradation available with catalytic ozonation systems: Adsorbed ozone on the catalyst surface breaks down into radicals that attack organic pollutants in the liquid phase; Adsorbed organic pollutants on the catalyst surface react with ozone and other reactive species; and Adsorbed both ozone and organic pollutants on the catalyst surface, where surface reactions take place (Wang and Chen, 2020).

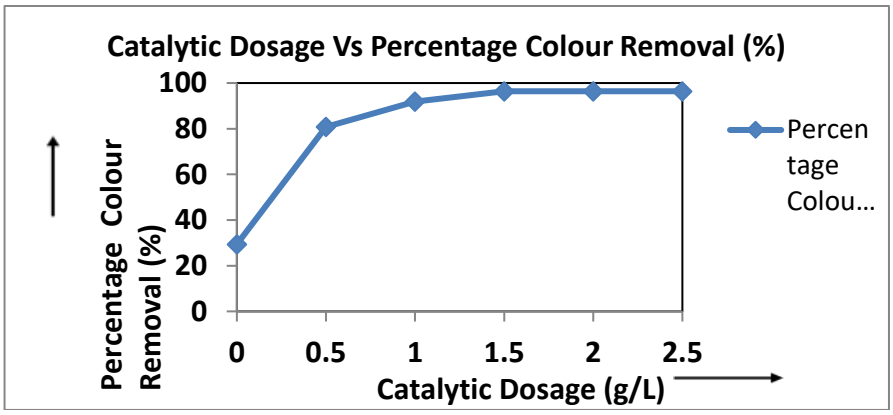

Figure-6: Plot Showing Catalytic Dosage Vs Percentage Colour Removal at pH-7, Contact Time (t)= 40min , Ozone Flow Rate = 3 L/min, Initial Concentration = 50 mg/L, Volume of Solution = 1L

Effect of pH

The effect of pH on the percentage colour removal was investigated by varying pH from 2 to 12 at catalytic dosage of 1.5g/L, reaction time (t) of 40min, ozone flow rate of 3 L/min, initial concentration as 50 mg/L in solution of 1L and results were presented in Figure-7.

From Figure-7 the percentage colour removal of 63.2 % occurred in presence of ozone alone at pH 12. Percentage colour removal of 96.7 % was occurred at pH 8 in presence of ozone and nano gypsum catalyst. At pH 12, the presence of higher OH -- ion concentration leads to the dye colour removal in case of ozone alone. At pH 2 the dye colour removal was less.

Similarly in case of photocatalytic activity of N- TiO2 nanoparticle in degradation of C.I. Reactive Blue-5, the photo degradation using N- TiO2 is maximum at pH 11. At pH 2 the neutral catalyst surface cannot attack sufficient neutral dye molecules and hence its degradation amount quickly decreases (Leili et al. 2021).

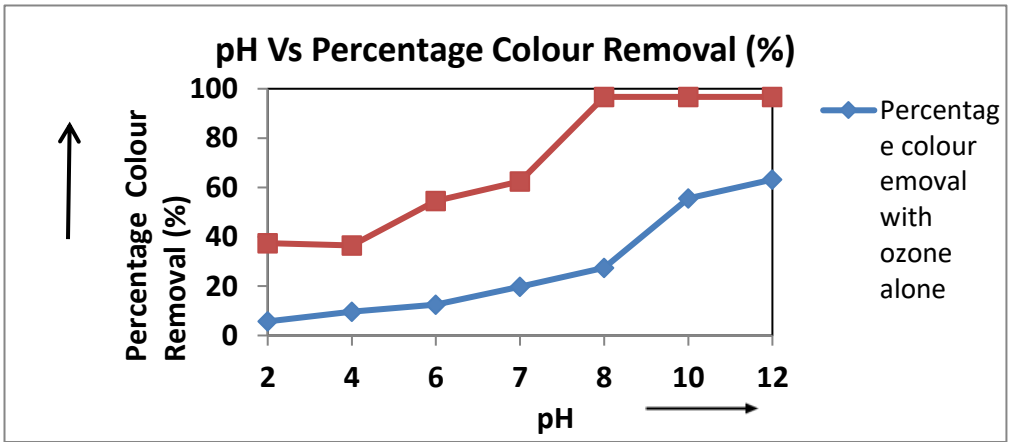

Figure-7: Plot Showing pH Vs Percentage Colour Removal at Catalytic Dosage = 1.5g/L, Reaction Time t= 40min , Ozone Flow Rate = 3 L/min, Initial Concentration = 50 mg/L, Volume of Solution = 1L

Effect of Contact Time

The effect of contact time on the percentage colour removal was investigated by varying contact time from 0 to 40 min in the removal of C.I Reactive Blue-5 dye in the presence of ozone alone and ozone with nano gypsum at catalyst dosage of 1.5 g/L, pH of 8, ozone flow rate of 3 L/min, initial concentration of 50 mg/L in solution of 1L and the results were portrayed in Figure-8. From Figure-8, the percentage colour removal was 28.2% in presence of ozone alone and in the presence of ozone with nano gypsum, the percentage removal was 96.7% at an optimum contact time of 30 min.

Similar findings were reported when ozonation was used in conjunction with zeolites modified using CuMn2O4 / gC3N4 to remove C.I. Reactive Black 5 dye. This method produced a 97 % dye color removal at the ideal contact duration of 30 minutes (Amir et al. 2021). Similarly, 100 % color removal was achieved at the ideal contact period of 30 minutes while treating petrochemical effluent with nano MgO in the catalytic ozonation method (Arjomandi et al. 2019).

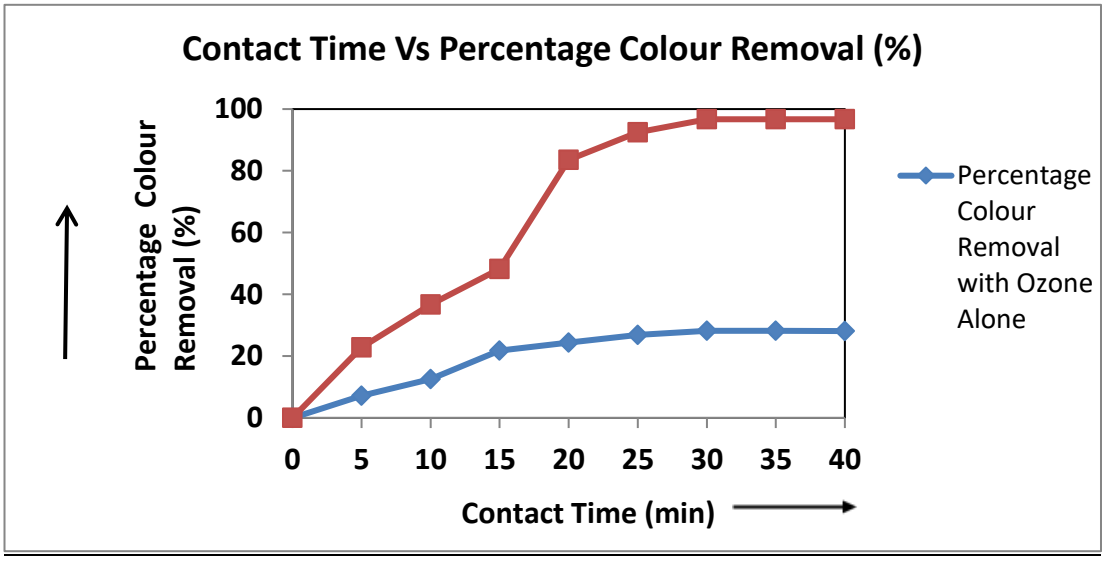

Figure-8: Plot Showing Contact Time Vs Percentage Colour Removal at Catalytic Dosage = 1.5g/L, pH=8, Ozone flow rate = 3 L/min, Initial Concentration = 50 mg/L, Volume of Solution = 1L

Effect of Ozone Flow rate

The effect of ozone flow rate on the percentage colour removal was investigated by varying the flow rate from 0 to 5 L/min at catalyst dosage of 1.5 g/L, contact time of 30 min, pH of 8 , initial concentration of 50 mg/L in 1L solution and the results were portrayed in Figure-9. From Figure-9, the percentage colour removal was 22.16%, in presence of only catalyst at the ozone concentration of zero L/min, maximum percentage colour removal of 96.7% was occurred when the ozone flow rate was 3L/min. Even after the increase in flow rate beyond the optimum flow rate, there is not much effect in the percentage dye colour removal.

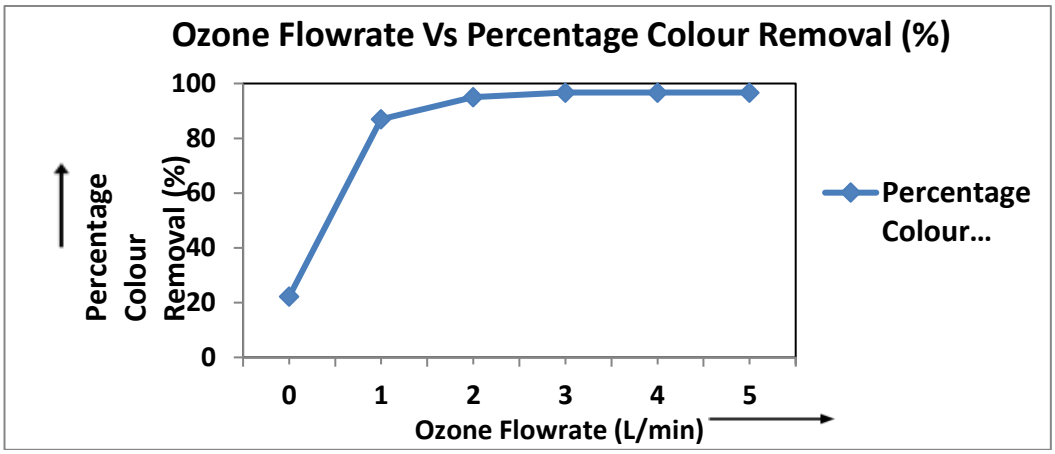

Figure-9: Plot Showing Ozone Flowrate Vs Percentage Colour Removal at Catalytic Dosage = 1.5g/L, pH=8, Contact Time=30 min, Initial Concentration = 50 mg/L, Volume of Solution = 1L

Effect of Temperature

The effect of temperature on the percentage colour removal was experimented by varying the temperature from 303 K to 343K at an optimum catalyst dosage of 1.5g/L, an optimum pH of 8, an optimum contact time of 30 min, ozone flow rate of 3 L/min, initial dye solution concentration of 50 mg/L and volume of solution as 1L and results are indicated in Figure-10. From Figure-10, it was observed that in presence of only ozone the percentage colour removal increased from 22.16% to 37.1%, when temperature is varied from 303 K to 343 K. In presence of ozone and catalyst, the percentage dye colour removal increased from 95% to 96.16 %, when temperature is varied from 303 K to 343 K. Increase in temperature enhances the rate of reaction thereby improving the dye colour removal capacity.

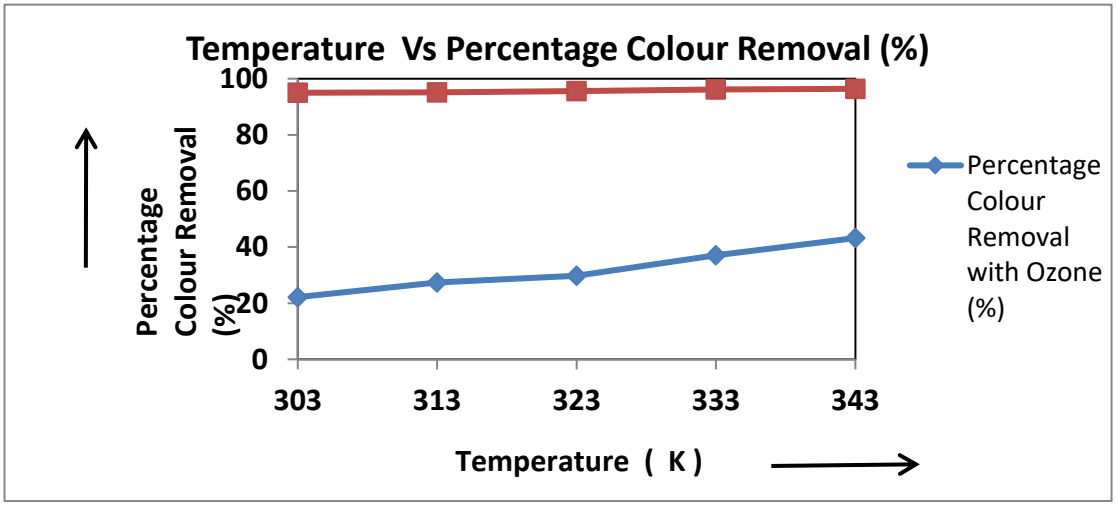

Figure-10: Plot Showing Temperature Vs Percentage Colour Removal at Catalytic Dosage = 1.5g/L, pH=8, Contact Time=30 min, Ozone Flow Rate = 3L/min, Volume of Solution = 1L

Kinetic Studies

Kinetic studies were important in learning more about the reaction mechanism that aids in process efficiency optimisation. The rates of solute and contact time are also provided in these investigations. The most popular kinetic models, out of the several that were available, were (i) pseudo 1st order models and (ii) pseudo 2nd order models. Rate Kinetics and their equations were as shown in Table-3.

Table-3: Rate Kinetics and their Equations (K. Vasanth Kumar, 2006)

Type	Non-linear Form	Linear Form	Plot	Parameters
Pseudo 1st Order	$q = q_e(1 - e^{-K_1 t})$	$\ln(q_e - q) = \ln(q_e) - K_1 t$	$\ln(q_e - q)$ Vs. t	K_1
Pseudo 2nd Order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{1}{q} = \frac{1}{K_2 q_e^2 t} + \frac{1}{q_e}$	$\frac{1}{q}$ Vs. $\frac{1}{t}$	q_e, K_2

Where,

K_1 = Rate of reaction in first order (g / mg min),

K_2 = Rate of reaction in second order (g / mg min).

q = Amount of dye colour removed at any time (mg / g),

q_e = Amount of dye colour removed at equilibrium (mg / g),

t = Contact time (min).

Experimental data was applied to Pseudo 1st Order & Pseudo 2nd Order models and plots were presented in Figure-11 and Figure-12.

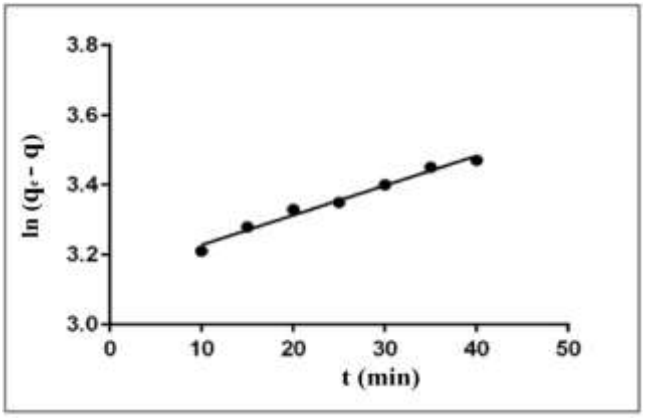

Figure-11: Plot Showing Pseudo 1st Order Model for log⁡〖(q_e-q) Vs. t〗 (min) at Catalytic Dosage = 1.5g/L, pH=8, Contact Time=0 to 40min, Initial Concentration=50mg/L Ozone Flow Rate = 3L/min, Volume of solution = 1L

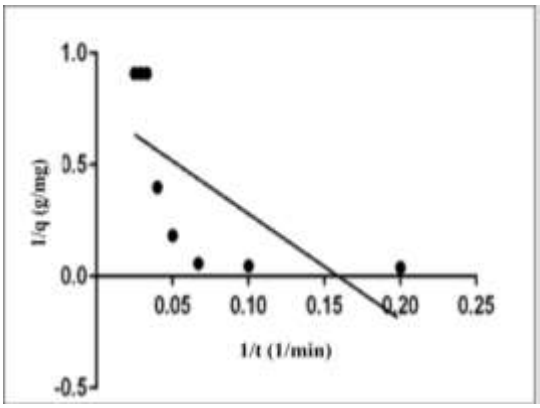

Figure-12: Plot Showing Pseudo 2nd Order Model for 〖1/q〗 〖 (g/mg) Vs. 1/t〗 (1/min) at Catalytic Dosage = 1.5g/L, pH=8, Contact Time=0 to 40min, Initial Concentration=50mg/L Ozone Flow Rate = 3L/min, Volume of Solution = 1L

The values of Pseudo 1st Order and Pseudo 2nd Order model were presented in Table-5.

Table-4: Kinetic Parameters for Pseudo 1st Order and Pseudo 2nd Order Models

Kinetic Models	Parameters	Nano Gypsum Catalyst
Pseudo 1st order kinetic model	q_e, exp (mg / g)	33.33
	q_e, cal (mg / g)	23.173
	K_1 (g / mg. min)	0.019
	R^2	0.9807
Pseudo 2nd order kinetic model	q_e, exp (mg / g)	33.33
	q_e, cal (mg / g)	1.327
	K_2 (g / mg. min)	0.120
	R^2	0.4945

From Table 4, it can be shown that the pseudo first order kinetic model with a regression coefficient (R^2) of 0.9807 is followed in the elimination of C.I. Reactive Blue -5 employing catalytic ozonation in the presence of nanogypsum catalyst. Given that the regression coefficient (R^2) for this process is 0.4945, the pseudo-2nd order kinetic model is not suitable. According to the pseudo first-order model, the difference in saturation concentration and the amount of solid uptake over time determines how quickly solute uptake changes. Similar to this, pseudo first order kinetics is used in O_3/H_2O_2 based color removal investigations of the azo dye C.I. Procion Blue (Tapas and Benedicte. 2020). Kinetic investigations for the O_3/UV dye color removal of C.I. Acid Red-17 followed Pseudo First Order Kinetics (El Nemr et al. 2018; Soumaya et al. 2022).

Thermodynamic Studies

Studies on thermodynamics are very helpful in determining the nature and applicability of the process. To determine the spontaneity, affinity, and heat change of the process, thermodynamic parameters were evaluated, including change in free energy (ΔG_0), change in entropy (ΔS_0), and change in enthalpy (ΔH_0). The following equation describes the

relationship between the "equilibrium constant" (Ka) and the "standard free energy change" (ΔG_0):

$$\Delta G_0 = -RT \ln K_a \qquad (3)$$

Ka, the equilibrium constant was calculated by the following equation,

$$K_a = q_{eq} / C_{eq} \qquad (4)$$

Where q_{eq} was the amount of dye removed and C_{eq} was the equilibrium concentration in the solution. Enthalpy change ΔH_o & entropy change ΔS_o were estimated from the following equation.

$$\ln K_a = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \qquad (5)$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \qquad (6)$$

Linear Vant Hoff plots i.e Ln (q_{eq} / C_{eq}) Vs (1 / T) in presence of ozone and nano gypsum and in presence of ozone alone were shown in Figures 13 and 14. The values of ΔH & ΔS were calculated from the slope & intercept of the linear Vant Hoff plot i.e Ln (q_{eq}/C_{eq}) Vs (1/T) (1/K) were mentioned in Table-5 (Gopal and Elango, 2007) (Meenakshi et al. 2008) (Subramani S.E et al. 2017).

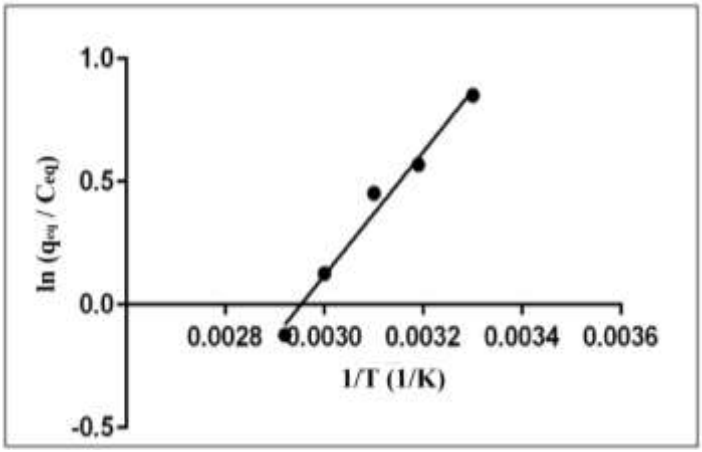

Figure-13: Plot Showing Linear Vant Hoff plot i.e Ln (q_{eq}/C_{eq}) Vs (1/T) (1/K) in Ozonation Alone (in Absence of Catalyst) at pH=8, Contact Time=0 to 40min, Initial Concentration=50mg/L Ozone Flow Rate = 3L/min, Volume of Solution = 1L

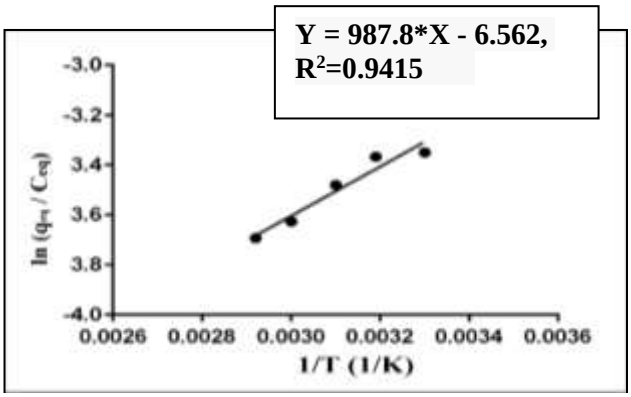

Figure-14: Plot Showing Linear Vant Hoff plot i.e Ln (q_{eq}/C_{eq}) Vs (1/T) in Presence of Ozone and Catalyst at Catalytic Dosage = 1.5g/L, pH=8, Contact Time=0 to 40min, Initial Concentration=50mg/L, Ozone Flow Rate = 3L/min, Volume of Solution = 1L

Table 5: Thermodynamic Parameters for Catalytic Ozonation of C.I. Reactive Blue-5 in Presence of Nano gypsum

	ΔH_0 (KJ / mol)	ΔS_0 (k J / mol K)	ΔG_0 (kJ/mol) = ΔH_0 - T ΔS_0				
			303 K	313 K	323 K	333 K	343K
In presence of ozone alone	-20.87	-0.0618	-2.144	-1.526	-0.986	-0.296	0.347
In presence ozone and catalyst	-8.213	-0.0545	8.3005	8.84	9.39	9.93	10.48

From Table 5, the values of ΔH 0 (Enthalpy) for both cases with ozone alone and ozone with nano gypsum were negative. This indicates the reaction was exothermic initially.

The values of ΔS0 (Entropy) for both cases with ozone alone and ozone with nano gypsum were negative. This lowers the affinity of the ozone for the dye and decreasing randomness at solid solute interface.

In the presence of ozone alone, the values of ΔG0 were negative at temperatures 303 K, 313 K, 323 K and 333 K. At 343 K ΔG 0 value is positive. This indicates the dye colour removal shifts from exothermic to endothermic at 343 K.

The values of ΔG0 were positive in presence of ozone and catalyst. The increasing trend in ΔG0 value when temperature was increased indicating high temperatures favours reaction and positive values indicates the process is non-spontaneous.

5. Conclusions

The following findings are drawn from the experimental data collected in the Catalytic Ozonation of C.I. Reactive Blue-5 dye in the presence of Nano Gypsum as a catalyst.

1. An X-ray Diffraction (XRD) investigation performed on nano-gypsum verifies that gypsum is the catalyst material. Particle mean diameter determined by Transmission Electron Microscope (TEM) examination was 25 nm.

2. At an ideal catalytic dosage of 1.5g/L, the greatest color removal percentage of 96.4% happened in the presence of ozone and nano gypsum.

3. The maximum removal happened at a pH of 8 when ozone and nano gypsum were present.

4. The percentage of dye removed in the presence of ozone alone was 28.2%; at 30 minutes of optimal contact time, the clearance increased to 96.7% in the presence of ozone combined with nano gypsum. A maximum of 96.7% dye elimination was achieved at a 3L/min ozone flow rate.

5. The percentage colour removal increased from 95% to 96.16 % when temperature is varied from 303 K to 333 K in presence of ozone and nano gypsum. Increase in temperature enhances the rate of reaction by improving the dye colour removal capacity.

6. According to kinetic studies, the pseudo first-order kinetic model describes how dye color is removed by catalytic ozonation in the presence of nano gypsum. According to the pseudo first-order model, the amount of solid uptake over time and the difference in saturation concentration determine how quickly solute uptake changes.

7. From thermodynamic studies, the values of ΔH0 (Enthalpy) for both cases with ozone alone and ozone with nano gypsum were negative. This indicates the reaction was exothermic initially. The values of ΔS 0 (Entropy) for both both cases of ozone alone and ozone with nano gypsum were negative. This lowers the affinity of the ozone for the dye and decreasing randomness at solid solute interface. The values of ΔG 0 were positive in presence of ozone and catalyst. The increasing trend in ΔG 0 value when temperature was increased indicating high temperatures favours reaction. In the presence of ozone alone, the values of ΔG 0 were negative at temperatures 303 K, 313 K, 323 K and 333 K. At 343 K, ΔG 0 value is positive. This indicates the dye removal shifts from exothermic to endothermic at 343 K.

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