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Colour Removal From Acid Dye Using UV/Hydrogen Peroxide Based Advanced Oxidation Process In Presence Of Nano Catalysts

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Abstract
Wastes from textile industry contain mainly synthetic dye effluents that cause toxic and persistent effect on human health and ecosystem. There are many methods available to treat the dye wastewater are classified as physical, chemical and biological processes such as adsorption, coagulation, precipitation, ion-exchange etc., Most of these processes have many disadvantages such as high cost, low efficiency, high generation of sludge etc., Advanced Oxidation Process is considered as the best process due to its wide applicability, total mineralization, low sludge generation, decomposition of intermediates, non-selective reactivity etc., In present study, the various methods in Advanced Oxidation Process such as Ultra violet light and Hydrogen peroxide were applied individually or in combinations to treat an acidic azo dye. The effect of various parameters such as contact time, oxidant concentration, solution pH and initial concentration of oxidant on the removal of dye were studied. The maximum dye colour removal greater than 94% was achieved in presence hydrogen peroxiode concentration of 2g/L and nano catalysts such as Al_2O_3, CuO, SiO_2 and Fe_2O_3 at pH of 3. In presence of UV light at pH-3, the performance of nano Al_2O_3, Fe_2O_3 and CuO were greater than 97% in presence of uv light. The performance of nano SiO_2 is low i.e 34.98%. UV/H_2O_2 reduces the contact time from 150 min to 40 min in presence of nano catalysts.

Keywords:*Dye Colour Removal; Advanced Oxidation Process; Ultra Violet Light; Hydrogen Peroxide*.

1. INTRODUCTION

The toxicity and lack of biodegradability of synthetic dyes make them a serious environmental hazard. Due to the substantial use of dyes in various textile industry processes, which results in large amounts of dye wastewater, the textile sector is responsible for about 54% of the dye effluents currently detected in the environment worldwide (Katheresan et al., 2018). The textile industry uses a variety of synthetic dyes, including reactive, basic, disperse, reactive, acidic, and mordant dyes (Natarajan et al., 2018). Azo dyes are chemical molecules with the functional group RN=NR′ (R and R′ are frequently aryls) commonly used to color textiles, leather, and various foods (Parshetti et al., 2010). Numerous azo pigments are carcinogenic, mutagenic, and poisonous; they are discharged in effluents after use and may harm the environment (Benkhayaet al., 2017).Growing concern has been raised about the environmentally friendly handling of synthetic dyes. Numerous recently developed treatments, including microbiological treatment (Wang & Guo, 2020) and physical adsorption (Ahmed et al., 2017), have drawbacks, including low efficiency, high energy consumption, limited application range, incomplete treatment, and secondary pollutant formation (Anjali &Shantikumar, 2019). Advanced oxidation processes (AOPs) have garnered a lot of interest lately because of the reactive oxygen species' (ROS) strong oxidation capacity, which demonstrated exceptional removal efficiency, quick operation, and adaptability for a range of contaminants. By producing highly reactive free radicals, AOPs break down a range of newly discovered contaminants (Anjali &Shantikumar, 2019), resolving issues that conventional techniques are unable to handle (Chambi et al., 2018), highlighting their adaptability and crucial function in environmental remediation (Wang

et al., 2023, Serra et al., 2024).The sustainable technology for treating organic contaminants in a variety of industrial wastewaters, including those from textile, paper and pulp, and pharmaceutical industries, is the Advanced Oxidation Process (AOP) (Manna & Sen, 2022). AOP's primary benefit is its high mineralization efficiency and low secondary pollutant generation (Kumar et al., 2022). For the degradation of environmentally hazardous compounds, AOP has emerged as a unique and exceptional method in recent years (Alderate et al., 2021). AOPs handle many different kinds of pollutants, such as dimethyl phthalate (Kabdash et al.,2010), chlorinated hydrocarbons (Kralik et al., 2010), effluent from the textile sector (Manikandan et al., 2005), drugs (Gu et al., 2020), and pharmaceutically active chemicals (Sui et al., 2013).The in-situ-formed Reactive Oxygen Species (ROS) in AOPs play crucial roles in degrading contaminants, which can be free radicals (e.g., Hydroxyl radical [•OH], Super Oxide radical [$O_2^{\bullet-}$], Sulfate radical [$SO_4^{\bullet-}$]), and/or non-radical species (e.g., Singlet oxygen [$^1O_2$] and Hydrogen Peroxide) (Zin et al., 2023). Catalyst-free activation mechanisms that are induced by light, acoustic, electro, plasma, and heat can aid in the destruction of pollutants assisted by ROS (Wang et al., 2021). Effectiveness and energy consumption, however, limit their practical applicability despite their sufficiency and simplicity. Because of their affordable reaction acceleration and recyclability, heterogeneous catalysts have drawn more attention in an effort to get over these restrictions. However, the choice, characteristics, preparation, and design of catalysts for enhanced pollutant degradation efficiencies determine the effectiveness of heterogeneous AOPs (Zhu et al., 2022).

One of these methods that attracted a lot of interest is homogeneous chemical oxidation using ultraviolet radiation (UV) in the presence of H_2O_2 (Navaro et al., 2017). Under the right circumstances, H_2O_2 is considered an environmentally beneficial oxidizing agent because it eventually turns into environmentally safe water or OH^- ions (Cobanoglu et al., 2022). When exposed to UV light, H_2O_2 has a strong oxidizing potential and can break down organic colors by producing $OH^\bullet$ radicals. Additionally, because no sludge forms, the UV/H_2O_2 process is clean. They attack the target organic molecules, destroying them and causing them to mineralize into water, carbon dioxide, and innocuous inorganic ions (Banal et al., 2023).On the surface of catalyst, interaction between photo-catalyst and UV radiation produce electron hole pairs.. The oxidative potential of the hole (h^+_{vb}) in the catalyst permits the direct oxidation of the dye to reactive intermediates (Eq. 1).

$$h^+_{vb} + \text{dye} \rightarrow \text{dye}^{\cdot+} \rightarrow \text{Oxidation of the dye} \quad (1)$$

$$h^+_{vb} + H_2O \rightarrow H^+ + OH^\cdot \quad (2)$$

$$OH^\cdot + \text{dye} \rightarrow \text{degradation of dye} \quad (3)$$

Hydroxyl radicals are another reactive intermediate that causes the deterioration. It is created either by the hole reacting with OH^- (Eq. 3) or by the breakdown of water (Eq. 2). Organic dyes can mineralize partially or completely as a result of the hydroxyl radical, a very potent and non-selective oxidant (Kansal et al., 2019). According to the theoretical mechanism, as shown in (Eq. 4), H_2O_2 absorbs UV radiation, which causes the H_2O_2 molecule to split into two OH radicals.

$$H_2O_2 + hv \rightarrow 2\ OH^\cdot \quad (4)$$

Following a complex rate-limiting step, these radicals rapidly undergo non-selective reactions with organic compounds in the aqueous solution (Younggunet al., 2024). Researchers have extensively used nanotechnology for wastewater treatment as it offers potential benefits, including low cost, reusuability, high removal and recovery efficiency of the contaminants from the wastewater (Singh & Batra, 2018).

Numerous nanomaterials such as carbon nanotubes, nano-membranes, zeolites, dendrimers, metals and metal oxides (Ag, Fe, Ti, Zn) are supporting the development of more effective treatment pathways for removal of pollutants from wastewater (Albelbasir& Salan, 2019).

2. LITERATURE REVIEW

In Advanced Oxidation Process, UV/H_2O_2 are the process employed for the complete removal of pollutants in the presence of catalyst used separately or in combination. Many researchers have been investigated the performance of different catalysts in the removal of diverse dyes using catalytic UV/H_2O_2. These are some papers referred related to UV/H_2O_2 (Advanced Oxidation Process). Sometimes visible light based photocatalysis is also employed instead of UV light. 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. In some cases catalysts are procured in markets. Pollutant (such as dye) of known concentration is prepared in aqueous medium and treated with UV/H_2O_2 in presence of a catalyst. The pollutant removal studies are made and the parameters like catalytic dosage, pH, reaction time etc., are optimised to get the maximum percentage of dye removal. Kinetic studies are made in some papers, usually following pseudo first order kinetics. The optimised values for different dyes and catalysts with UV/H_2O_2 from recent literature were shown in Table-1.

Table-1: UV/H_2O_2/Catalystbased Advanced Oxidation Process for removal of different dyes

S. No	Advanced Oxidation Processes (AOPs) considered	Dyes used	Nano-catalysts used	Initial Conentration (mg/L)	pH	Contact/ Irradiation time (min) and Oxidant Dosage (mg/L)	Catalyst Dosage (mg/L)	Optimum Percentage Colour removal (%)	Reference
1	Photocatalysis under visible light	Methylene Blue	Co_3O_4/reduced graphene oxide/ biochar	40, 60, 80 and 100	10.4	120 min	100	98% at initial concentration of 40mg/L	(Amritha et al., 2024)
		Malachite Green	Co_3O_4/reduced graphene oxide/ biochar	40, 60, 80 and 100	10.4	120 min	100	96% at initial concentration of 40mg/L	
2	Photocatalysis under uv light	Acid Black-1	CdS/Ag nanocomposite	10	5	50 min	10mg/100ml	95	(Ravikumar et al., 2024)
		Direct Blue -15		10	5	50 min	10mg/100ml	94	
		Reactive Red 120		50	5	120 min	50mg/100ml	93	
3	Photocatalysis under uv light	Safranin dye	ZnO	50	9	120 min	75	94	(Dariush et al., 2023)
4	Photocatalysis under uv light	Chicago Sky Blue 6B	Cu-Co@TiO_2	50	7	60 min	18	98	(Mumriz et al., 2024)
		Acid Yellow 17	CuCo@TiO_2	50	7	60 min	19	97	
S. No	**Advanced Oxidation Processes (AOPs) considered**	**Dyes used**	**Nano-catalysts used**	**Initial Conentration (mg/L)**	**pH**	**Contact/ Irradiation time (min) and Oxidant Dosage (mg/L)**	**Catalyst Dosage (mg/L)**	**Optimum Percentage Colour removal (%)**	**Reference**
5	Photocatalysis under visible light	Direct Orange 122	Zn/TiO_2	10	6	120 min	50	100	(Luiz et al., 2022)

6	UV/H_2O_2/TiO_2	Reactive Red-147	TiO_2	50	3.4	60min, H_2O_2- 0.9 mL	6g/L	92	(Arshad et al., 2020)
7	UV/H_2O_2	Direct red 80	Bentonite/ TiO_2/Ag nano composite	15mL/L	7	120 min	30	77	(Javanbhakt & Mohammadian, 2021)
		methylene blue		15mL/L	7	120 min	30	100	
8	H_2O_2	Methylene blue	Fe_2O_3 nano particles	30	7	30 m mole H_2O_2	2g/L	98	(Shohreh et al., 2023)
		Crystal violet		30	7	30 m moles H_2O_2	2g/L	96	
		Congo red		30	7	30 m moles H_2O_2	2g/L	62	
9	H_2O_2	Methylene Blue	ZnO	50mL	12	35 min	1.5g	99	(Priyanka et al., 2024)

These were some of the recent studies referred in the Advanced Oxidation Process using light and H_2O_2 for the degradation of dyes. This paper deals in detail with advanced oxidation methods like UV light and H_2O_2 for degradation of an azo dye named C.I. Acid Black 194. Various nanomaterials are used as nanocatalysts in advanced oxidation process. The paper explains the efficiency of each method and drawbacks of every method and its advantages are pointed out, the dosage is suggested for better performance, and parameters such pH, time, and type of the AOPs in presence of different nanocatalystswas examined.

3. MATERIALS AND METHODOLOGY

Materials:

Instruments utilized includes UV-Vis spectrophotometer, jar test apparatus, UV reactor of capacity 1L with UV-lamp of 11w that produce 254nm (UV-C) wave length and magnetic stirrer. Chemicals include Hydrogen Peroxiode, Hydrochloric acid, Sulfuric acid, Sodium Hydroxide pellets, Methanol and Distilled water of AR-grade were used. C. I. Acid Black - 194 dye solution of 100 mg/L dosage was used. Nano materials to be used as catalysts such as Al_2O_3, CuO, SiO_2 and Fe_2O_3 were procured from Techinstro, India. Their particle sizes were in between 20 to 50nm.

Experimental Methodology:

The color of C.I. Acid Black- 194 (Chemical Class: azo dye, CAS No.: 61931-02-0; molecular weight: 993.71 g/mole; Molecular Formula:$C_{20}H_{12}N_3NaO_7S$, UV wavelength max: 597 nm) was removed from an aqueous solution using UV/H_2O_2 based AOP's [38]. Its structure depicted in Figure-1. Al_2O_3, CuO, SiO_2 and Fe_2O_3 were employed as nano catalysts in this reaction. 100 mg of C. I. Acid Black-194 dye was diluted in 1L distilled water was used as test solution. It takes 0.1M of HCl at a steady pH. Experiments of UV and UV/H_2O_2 were conducted in a steel column reactor and experiments related to H_2O_2 alone were conducted in jar test apparatus to eliminate the color of C.I. Acid Black-194 dye in the presence and absence of nano catalyst.

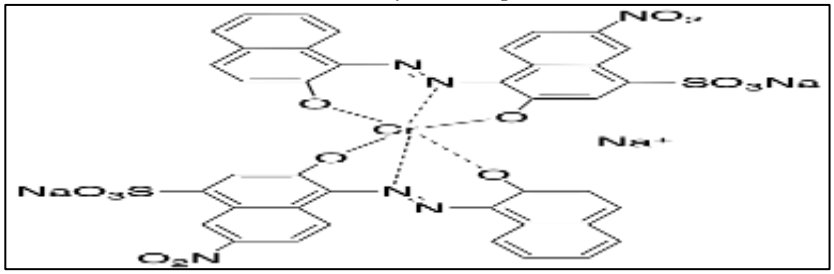

Figure-1: Structure of Acid Black-194 [38]

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. Using a UV–visible spectrophotometer, the absorbance of the samples was determined at a wavelength of 574 nm. The decolorization efficiency was determined as percentage colour removal as given in (Eq.-5) (Francisco et al., 2023):

$$\text{Percentage Colour Removal} = \left(\frac{Co-Ct}{Co}\right) * 100 \qquad (5)$$

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

4. RESULTS AND DISCUSSION

4.1 Dye Colour Removal Studies using H_2O_2

In the colour removal studies of C.I. Acid Black-194 using H_2O_2, the various paramaters such as oxidant dosage, pH, dosage ofcatalystwere needed to be optimized. Initial dye concentration was 100 mg/L and Volume as 300 mL. Experiment is conducted in jar test apparatus with rapid mixing of 2min at 120 rpm, slow mixing at 20 min at 30 rpm, Settlement time was considered as 2 hrs (Thasilu& Karthikeyan, 2016).

4.1.1 Effect of Oxidant Dosage and pH: Dosage of H_2O_2 is increased from 2 to 10 g/L with increment of 2g/L. From Figure-2, the favorable dosage of H_2O_2 to remove CI. Acid Black 194 up to 98.3% is found to be 8g/L. pH is experimented at 3, 7 and 12 at 50% of the favorable dosage. The maximum removal occurred at pH-3 i.e 97.6%. Hence it was considered as favorable pH as shown in Figure-3. From Figure-4, the optimum dosage of H_2O_2 under favourable pH i.e pH-3 was found to be 4mg/L wthere the Percentage dye colour removal was 98.57%.

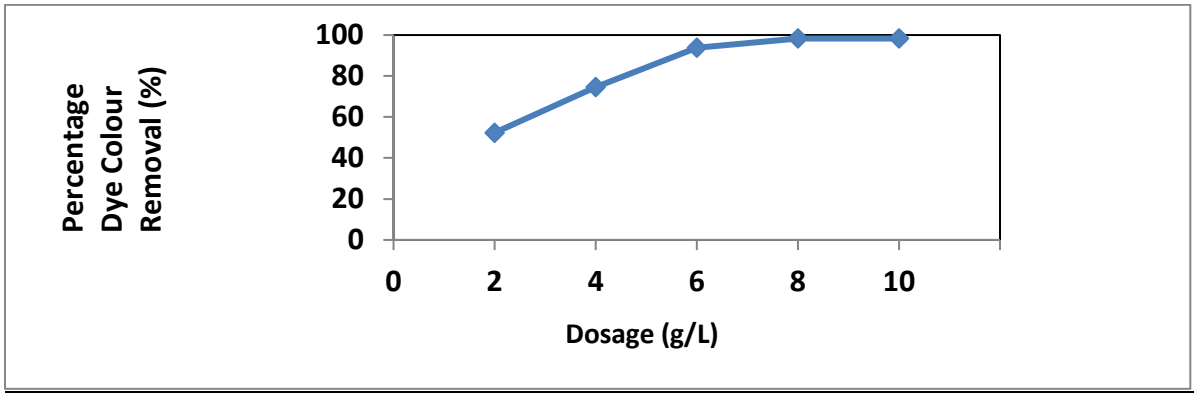

Figure-2: Favorable dosage of H_2O_2

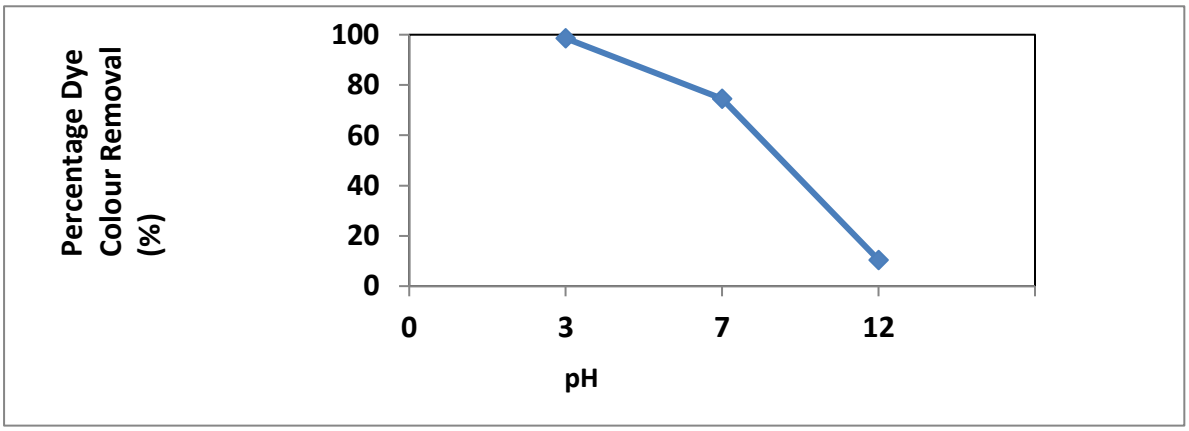

Figure-3: Favorable pH of H_2O_2

International Journal of Environmental Sciences
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Vol. 11 No. 10s, 2025
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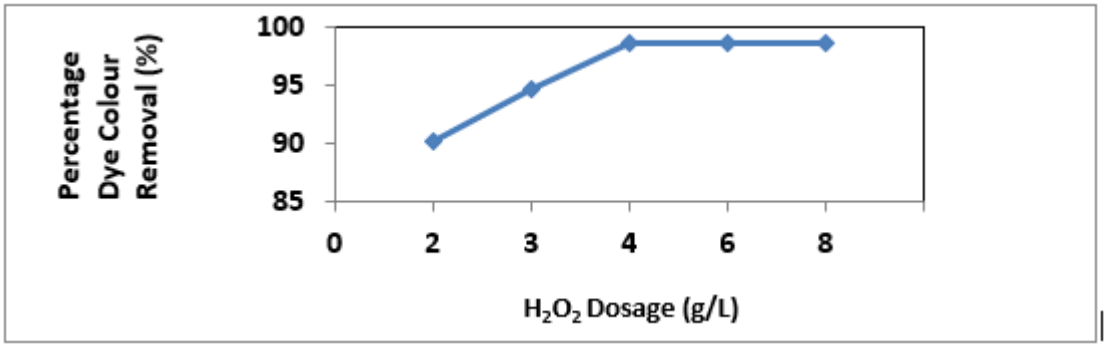

Figure-4: Optimum Dosage of H_2O_2

4.1.2 Effect of Nano Catalysts: At 50% of the optimum dosage of H_2O_2 (i.e 2g/L), the performance of Nano materials Al_2O_3, CuO, SiO_2 and Fe_2O_3 was being studied at pH-3 and initial concentration of 100mg/L. At 0.1g/L dosage of nano Al_2O_3, 97.65% of dye colour was removed, at Nano CuO dosage of 0.15g/L and at favorable H_2O_2 dosage of 0.5g/L, maximum removal of 98.32% occurred. At 0.1g/L dosage of Nano SiO_2& H_2O_2 Dosage of 2g/L, maximum removal was 94.52%. At dosage of Nano $Fe_2O_3$is 0.1g/L at H_2O_2 Dosage of 2g/L. maximum dye colour removal is 98.29% as shown in Figure-5. All the nanomaterials performed well in reducing the dosage of oxidanti.e H_2O_2. So if nano materials are used as catalysts, it enhances the degradation capacity of the oxidant.

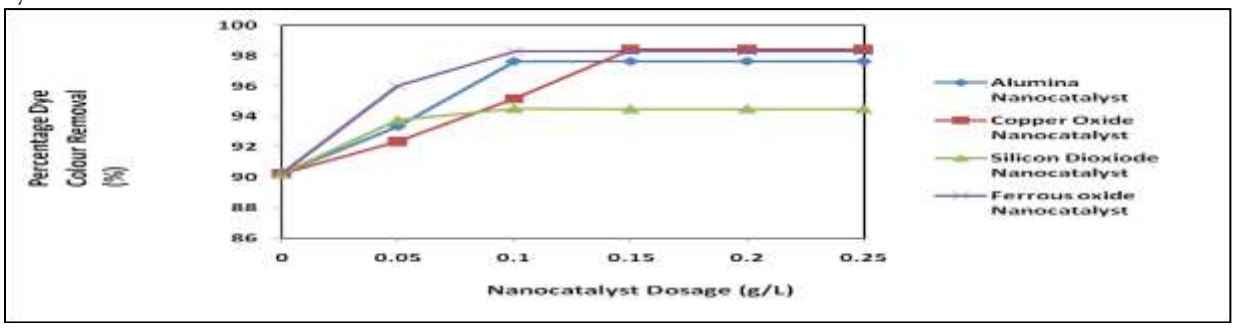

Figure-5: Variation of dosage of nanocatalyst at H_2O_2 Dosage of 2g/L

From Figure -5 maximum removal of 98.3% was achieved in the presence of CuOnanocatalyst and hydrogen peroxide. Nanomaterials catalyzes the breakdown of hydrogen peroxiode which can increase the rate of dye removal by generation of OH^- radicals. Other dyes such as Reactive Red 147 (Arshad et al., 2020), Direct Red 80 (Javanbhakt& Mohammadian, 2021), Methylene Blue [38], Crystal Violet (Priyanka et al., 2024), Acid Red 88 (Francisco et al., 2023), Acid Orange 7 (Giuseppina et al., 2020) etc., were successfully removed with hydrogen peroxiode.

4.2 Dye Colour Removal Studies using UV light

In the colour removal studies of C.I. Acid Black-194 using UV light, the paramaters such as pH, irradiation time are needed to be optimized. Initial dye concentration was considered 100mg/L, Volume is 500mL. Experimentwere conducted in a UV reactor of 1L capacity, magnetic stirring was made to enhance the removal. Irradiation time was considered upto 150 min and concentration was found at every 10 min interval

4.2.1 Effect of pH and Irradiation Time: Irradiation time was considered upto 150min. pH of 3, 7 and 12 were considered for the study in the removal of C.I. Acid Black 194 dye.

From Figure-6, Irradiation time is considered from 0 to 150 min at pH 3, 7 and 12. The dye colour removal at pH 7 and 12 is around 16%. At pH 3, the percentage removal got increased with respect to contact time.. At contact time of 140 min, the colour removal of 27.15% was occurred. Even the dye colour removal is low in case of UV, with the use of nano materials as catalysts, the percentage dye removal can be increased.

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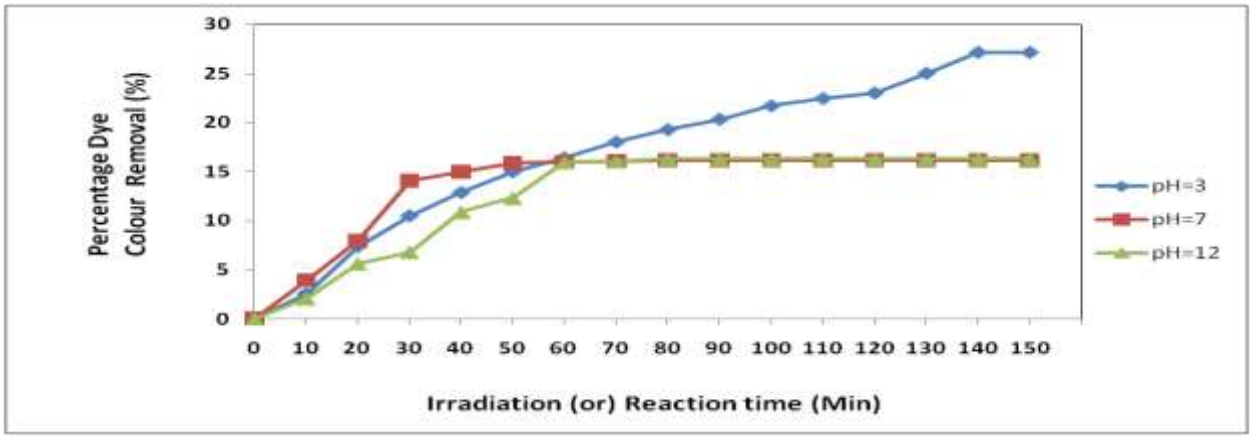

Figure -6: Variation of percentage dye colour removal with respect to pH and irradiation time

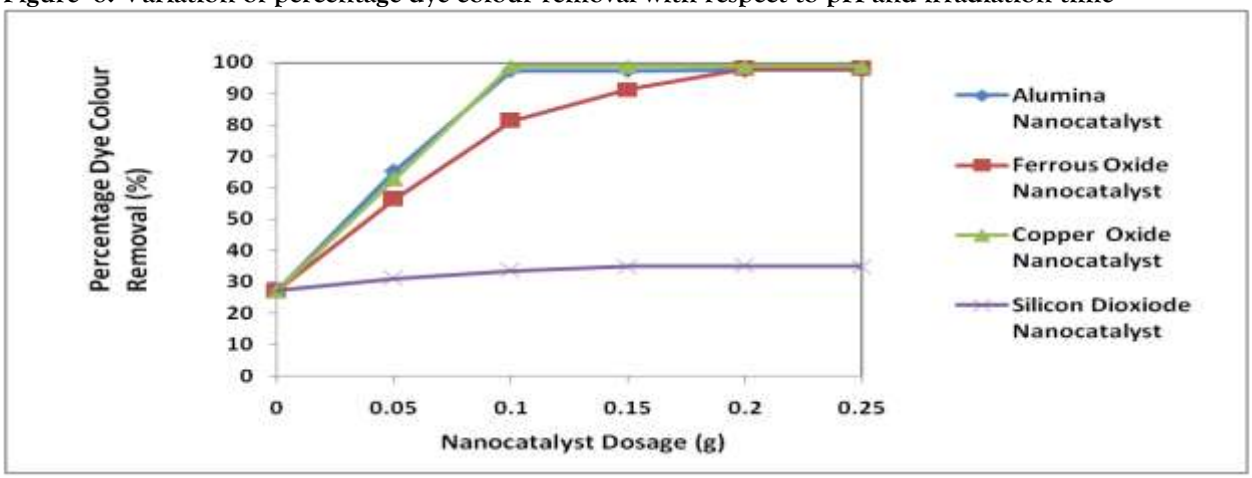

Figure-7: Nanocatalyst dosage and percentage dye colour removal for UV based AOP

4.1.2 Effect of Nano Catalysts: The performance of Nano materials Al_2O_3, CuO, SiO_2 and $Fe_2O_3$is being studied at pH-3 and initial concentration of 100mg/L for the removal of C.I. Acid Black 194 using UV Light. At pH-3, Contact time of 150 min, the dosage of nano materials are varied to find the percentage dye removal as shown in Figure-10. Nano material dosage varied from 0.05, 0.1, 0.15, 0.2 to 0.25 g.

From Figure-7, in case of nano Al_2O_3, at 0.1g dosage gives 97.39 % maximum dye colour removal. In case of nano Fe_2O_3, at 0.2g dosage gives 97.89 % maximum dye colour removal. In case of nano CuO, at 0.1g dosage gives 98.77% maximum dye colour removal. In case of nano SiO_2, at 0.15g dosage gives 34.98% maximum dye colour removal. Except nano SiO_2, other nano materials performed well in removing dye colour.

Certain nanomaterials, particularly metal oxides like titanium dioxide (TiO_2) and zinc oxide (ZnO), are photocatalytic. When exposed to UV light, they absorb photons and generate electron-hole pairs. These electron-hole pairs initiate redox reactions, leading to the formation of highly reactive species, such as hydroxyl radicals (Ravikumar et al., 2024). Dyes like Acid Black-1, Direct Blue -15, Reactive Red -120 (Ravikumar et al., 2024), Safranin dye (Daniush et al., 2023), Chicago Sky Blue 6B, Acid Yellow 17 (Mummiz et al., 2024) etc dyes were removed successfully with UV light in presence of nanocatalysts.

4.3 Dye Colour Removal Studies using UV/H_2O_2

In the colour removal studies of C.I. Acid Black-194 using UV/H_2O_2 light, the paramaters such as pH, irradiation time &H_2O_2 dosage were needed to be optimized. Initial dye concentration is 100mg/L, Volume of sample taken as 500mL. Experiment is conducted in a UV reactor of 1L capacity, magnetic stirring was made to enhance the removal. Irradiation time was considered upto 150 min and concentration was found at every 10 min interval

4.3.1 Effect of H_2O_2 dosage, Irradiation Time and pH: Irradiation time was considered upto 150min. pH of 3, 7 and 12 were considered for the study in the removal of C.I. Acid Black 194 dye colour. Favorable H_2O_2 dosage

as in case of single oxidant as 8g/L (from section-4.1.1), Volume is 500mL, UV irradiation time as in case of single oxidant considered as 150 min, Favorable pH was considered as 3 (from section-4.2.1). Optimum Dosage of H_2O_2 in Presence of UV light is 5g/L and removal was 99.8% as shown in Figure-8.

4.3.2 Effect of Nano Catalysts: The performance of Nano materials Al_2O_3, CuO, SiO_2 and Fe_2O_3 is being studied at pH-3 and initial concentration of 100 mg/L for the removal of C.I. Acid Black 194 using UV Light upto 150min irradiation time. The dosage H_2O_2 is considered as 5 g/L, and nano material dosage was fixed at 0.15 g/L to find the percentage dye removal as shown in Figure-9.

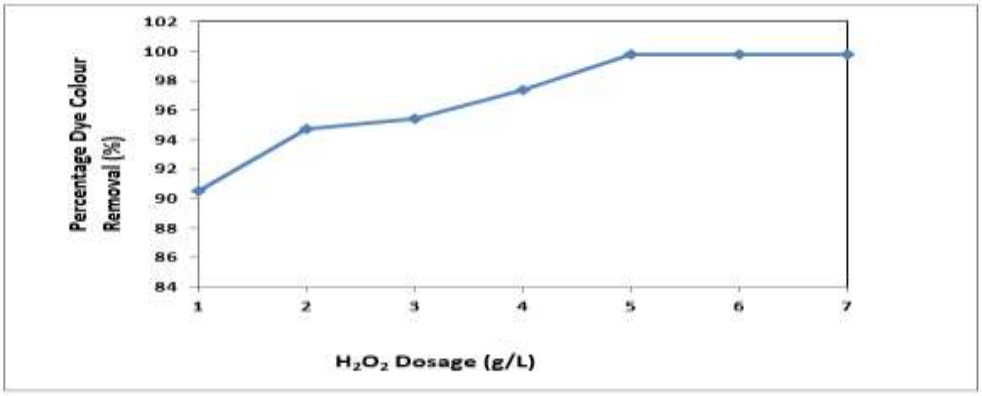

Figure - 8: Optimum Dosage of H_2O_2 in Presence of UV light

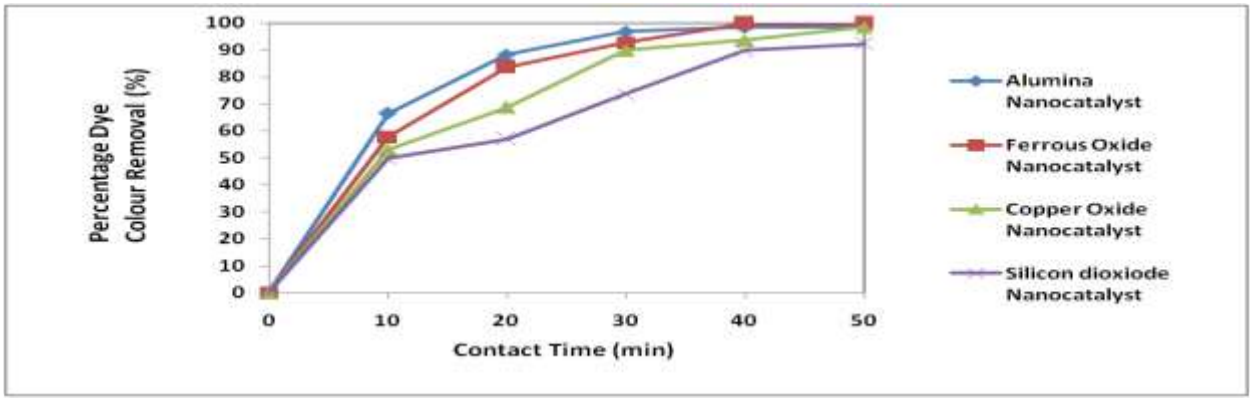

Figure - 9: Percentage colour removal by nano catalysts in presence of UV/H_2O

From Figure-9, In case of nano Al_2O_3 at 30 min irradiation time, 98.4% dye colour removal occurred at nanomaterial dosage of 0.15 g/L. In case of nano Fe_2O_3 at 30 min, 99.85% dye colour removal occurred at nanomaterial dosage of 0.15g/L. In case of nano CuO at 40 min, 98.42% dye colour removal occurred at nanomaterial dosage of 0.15g/L. In case of nano SiO_2 at 40 min, 92.14% dye colour removal occurred at nanomaterial dosage of 0.15g/L. Contact time got decreased from 150 min to 40 min in presence of UV and H_2O_2.

When hydrogen peroxide is exposed to UV radiation, particularly in the UV-C range, it undergoes photolysis, which means it's broken down by light. This process generates highly reactive hydroxyl radicals (·OH). These radicals break down complex dye molecules into simpler, less harmful substances, such as carbon dioxide (CO_2) and water (H_2O). Dyes such as Reactive Red-147 (Arshad et al., 2020), Direct Red-80, Methylene Blue (Javanbhakt& Mohammadian, 2021) were successfully degraded in the presence of UV/H_2O_2 .

4.4 Kinetic Studies

In Kinetic studies, the reaction rate would be found for 100 mg/L initial dye concentration, nanomaterials of varying dosages from 0.1 to 0.2 g/L, and H_2O_2 of 2 mL in presence of UV light. Dye concentration at regular

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https://theaspd.com/index.php

intervals of 5 min was considered in the presence and absence of nano materials. The linear form of first and second order kinetic models can be presented in (Eq.-6) and (Eq.-7) (El-Gawad et al., 2023, Su et al., 2022).

$$\text{Ln } C_t = K_1 t \quad (6)$$

$$1/C_t - 1/C_o = K_2 t \quad (7)$$

where Co be the initial concentration of dye and C_t be the concentration at irradiation time t, K_1 and K_2 were first and second order rate constants in min^{-1} and $L\ g^{-1}\ min^{-1}$, respectively, t being degradation time (in min). Figure-10 and Figure-11 gives plot Ln C_t and [$1/C_t - 1/C_o$] against time for each experiment leads to a straight line whose slope as K_1 and K_2, for UV/H_2O_2 based AOP respectively. The regression analysis of the concentration curves against degradation time marks that the rate of reaction can be depicted by means of first and second order kinetics and kinetic parameters were tabulated in Table-2.

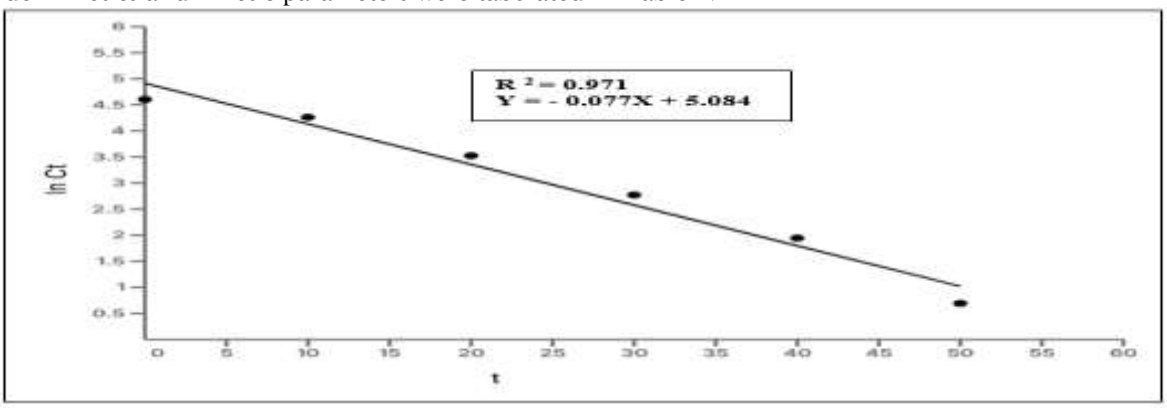

Figure-10: First order kinetics graph for UV /H_2O_2 based AOP at optimum parameters.

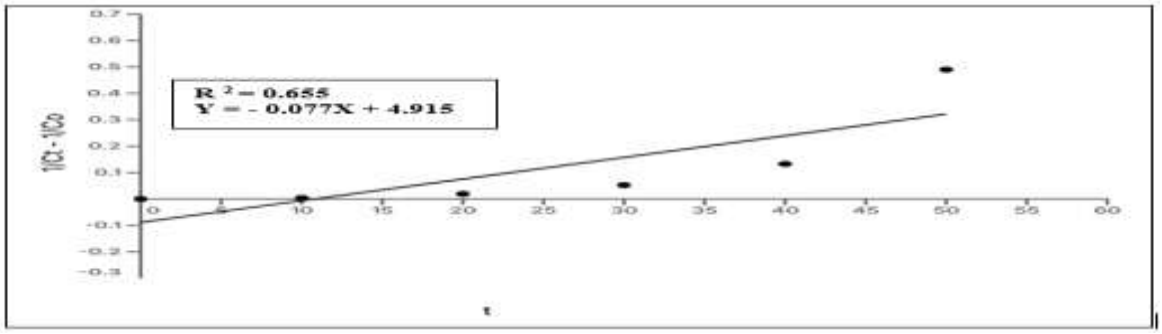

Figure-11: Second order kinetics graph for UV /H_2O_2 based AOP at optimum parameters.

Table-2: Rate Kinetics of UV/H_2O_2 for Acid Black-194

Type of kinetics	AOP	Kinetic Equation	Rate Constant	R^2
1st order kinetics	UV/H_2O_2	5.084=0.077X	0.077	0.971
2nd order kinetics	UV/H_2O_2	0.088=0.00819X	0.008	0.6553

From Table-2, in 1st order kinetics the R^2 value is 0.971 which was higher compared to R^2 value in 2nd order kinetics for the removal of Acid Black-194 dye by UV/H_2O_2. So1st order kinetics model fits well with the degradation of Acid Black-194 compared to 2nd order model. In degradation of industrial crude oil El-Gawad et al., 2023), Metronidazole (Su et al., 2022), Cibacron Red, Reactive Red-238 (Rasul et al., 2018)followed 1st order kinetics.1st order kinetics indicates that the dye degradation process is concentration-dependent. Initial degradation rate is faster with the high initial dye concentration. As dye concentration decreases, degradation rate also slows down (Haji & Al-Bastaki, 2023).

5. CONCLUSIONS

The conclusions for the degradation of Acid Black-194 in the presence of UV/H_2O_2 were as followed:

1. In case of H_2O_2, the favourable dosage of H_2O_2 found to be 8g/L; At pH-3 and optimum dosage of 4g/L, 98.57 % dye colour removal has occured.
2. In case of H_2O_2, at dosage of Nano Al_2O_3 is 0.1g/L at H_2O_2 Dosage of 2g/L, maximum dye colour removal of 97.6% has occurred. At dosage of Nano SiO_2 is 0.1g/L at H_2O_2 Dosage of 2g/L, maximum colour removal has occurred. i.e 94.52%. At dosage of Nano CuOis 0.15g/L at H_2O_2 Dosage of 2g/L, max dye colour removal has occurred. i.e 98.32%. At dosage of Nano $Fe_2O_3$is 0.1 g/L at H_2O_2 Dosage of 2g/L, maximum dye colour removal 98.29% has occured. All the nanomaterials performed well in reducing the dosage of H_2O_2. So if nano materials are used as catalysts, it enhances the degradation capacity of the oxidant.
3. In case of UV light alone, pH is varied as 3, 7 and 12 and reaction time is taken upto 150 min. Maximum colour removal is at pH-3 i.e 27.15%. At pH-3, Contact time of 150 min, the dosage of nano materials is varied to find the percentage dye removal. In case of nano Al_2O_3, at 0.1g dosage gives 97.39 % maximum dye colour removal. In case of nano Fe_2O_3, at 0.2g dosage gives 97.89 % maximum dye colour removal. In case of nano CuO, at 0.1g dosage gives 98.77% maximum dye colour removal. In case of nano SiO_2, at 0.15g dosage gives 34.98% maximum dye colour removal. Except nano SiO_2, ather nano materials performed well in removing dye colour.
4. In presence of UV/H_2O_2 dye colour removal of 99% was occured, using nanocatalyst Al_2O_3 at 30 min irradiation time, 98.4% dye colour removal occurred at nanomaterial dosage of 0.15g/L. In case of nano Fe_2O_3 at 30 min, 99.85% dye colour removal occurred at nanomaterial dosage of 0.15g/L. In case of nano CuO at 40 min, 98.42% dye colour removal occurred at nanomaterial dosage of 0.15g/L. In case of nano SiO_2at 40 min, 92.14% dye colour removal occurred at nanomaterial dosage of 0.15g/L.Contact time got decreased from 150 min to 40 min.
5. The removal of Acid Black-194 by H_2O_2, UV light and UV/H_2O_2 was in following order:

$$UV/H_2O_2 > H_2O_2 > UV$$

6. The colour removal of Acid Black-194 dye by UV/H_2O_2 followed 1st order kinetics. It indicate that the dye degradation process is concentration-dependent. Initial degradation rate is faster with the high initial dye concentration. As dye concentration decreases, degradation rate also slows down.

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