

# Spectral Analysis of the Degradation of the Reactive Black 5 Dye Using Newly Developed Advanced Oxidation Process

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## Abstract

The present article discloses a new advanced oxidation process (AOP) to control organic Dye (Reactive Black (5) pollutants with all additives used in dye fabrication, which are discharged in running water streams. The new AOP mainly emphasizes to controlled urea used as a dye fixer on fabric in the textile industry. The AOP involves potassium permanganate as a potent oxidizing agent in which H<sub>2</sub>O<sub>2</sub> was applied to convert urea into urea - H<sub>2</sub>O<sub>2</sub> complex that also acts as an oxidizing agent to convert organic compounds into smaller fragments helpful in organic dye decolorization. It was recognized that newly developed AOP is effective due to the presence of three oxidizing species, namely, permanganate ion, nascent oxygen [O] and Urea - H<sub>2</sub>O<sub>2</sub> complex. The spectral analysis of all trials was conducted at room temperature at several parameters, including urea, H<sub>2</sub>O<sub>2</sub>, RB5 dye, oxidant concentrations, and pH, followed by the determination of the kinetics of the oxidation. Spectral analysis of dye wastewater showed that dye degradation takes place through complex formation with MnO<sub>4</sub><sup>-</sup> ions. A pseudo first order oxidation kinetics with KMnO<sub>4</sub> and urea while zero-order kinetics with dye and H<sub>2</sub>O<sub>2</sub> was established. The most significant advantage of this advanced oxidation process (AOP) is its optimal performance when potassium permanganate (KMnO<sub>4</sub>) is added at various pH levels in the last enduring H<sub>2</sub>O<sub>2</sub> in this innovation with urea, and KMnO<sub>4</sub> (3e) can synergistically act better with the traditional AOP to accomplish the resourceful speedy and septicity free degradation method.

**Keywords:** Spectral Analysis, AOP, Urea, H<sub>2</sub>O<sub>2</sub>

## 1. INTRODUCTION:

The recognition of the dyeing Textile industry is linked to its usage of water and chemicals for dye fabrication, where only a small amount, like less than 10%, is applied for fabrics or leather while the remaining discharges as dye wastewater, including the 75 % of unfixed dye[1]. The unfixed dye and additives are hazardous due to their high chemical oxygen demand (COD) and biological oxygen demand (BOD) contents. The dye effluent shows high electrical conductivity due to salts and heavy metals, which also alter the pH of the running stream. Azbar et al. [2] reported the composition of textile effluent (Table 1).

**Table 1:** Characteristics of a typical composite textile effluent Azbar [2]

S.No	Parameter	Value
1.	pH	6.0 - 10.1
2.	Temperature (°C)	35 - 50
3.	Chemical Oxygen Demand (mg/L)	1000-12,000
4.	Biochemical Oxygen Demand (mg/L)	300 – 6000
5.	Total Suspended Solids (mg/L)	15 – 8,000
6.	Total Dissolved Solids (mg/L)	2,900 -3,100
7.	Chloride (mg/L)	3000 – 6000
8.	Free Chlorine (mg/L)	<10
9.	Total Kjeldahl Nitrogen (mg/L)	70 – 80
10.	Silica (mg/L)	<15
11.	Oil and grease (mg/L)	10-30
12.	Free ammonia (mg/L)	<10
13.	Colour (Pt-Co)	50-2500

Advance oxidation processes (AOPs) are innovative water treatment procedures that are preferred over outdated systems due to the rapid degradation of organic waste colourant materials from main streams[3-8]. AOP uses progressive oxidation technologies to decompose complex organic compounds, such as dyes and pigments, into harmless carbon dioxide and water[2]. Most AOP consists of the generation of highly reactive OH radicals, which are powerful oxidizing species that have the ability to mineralize organic pollutants or convert them into less harmful sludge[9-15]. Several AOP methods are

available, generating  $\cdot\text{OH}$  radicals, including both non-photochemical and photochemical methods like Ozonation, Ozonation at elevated pH ( $> 8.5$ ) Ozone + hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ), Ozone + catalyst ( $\text{O}_3/\text{CAT}$ ), Fenton system ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ),  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ , Photo-Fenton/Fenton-like systems [15-22]. Among these, the Fenton reaction ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) is promising and has been primarily studied alone, as well as with UV systems that showed higher capability towards the mineralization of organic pollutants [10]. The catalytic decomposition of hydrogen peroxide via Fenton reagent produced a strong oxidant in the pH range of about 2-4 for controlling the hazards of solubilized organic compounds. Liu et al. [11] reported the oxidative capability of potassium permanganate and in situ delta  $\text{MnO}(2)$  adsorption for the treatment of dye wastewater. They observed the efficiency of the process towards decoloration, dissolved organic carbon (DOC), and increasing biodegradable oxygen demand of the two studied processes. Delta  $\text{MnO}(2)$  adsorption contributed to the maximum dissolved organic carbon (DOC) removal of 65.0% but exhibited limited capabilities of decolorizing and increasing biodegradability. While  $\text{KMnO}_4$  alone showed effective decoloration at a very low pH, it had limited application due to this pH(5). Potassium permanganate is famous as an oxidizing agent, an odourless, water-soluble solid with purple crystals where Mn (VII) is converted into Mn(II) with a 5e system [12-15]. Hydrogen peroxide is another oxidizing agent used in this research to control the hazardous effects of dye additive urea, a fixer of dye used during the textile dye process. The current article exposes the effectiveness of three oxidizing agents generated in permanganate oxidation with urea and hydrogen peroxide viz, nascent oxygen, urea hydrogen peroxide complex and permanganate ion, which proves to be a rapid dye wastewater controller with less sludge.

## 2. MATERIAL AND METHOD

All chemicals were purchased from Sigma Aldrich and used without any further purification, while solutions were prepared using the usual method of dilution. The dye Reactive Black 5 (RB5) was purchased from a local market and used without further treatment [12]. The molar ratio between Dye and  $\text{KMnO}_4$  was determined spectrophotometrically by the mole ratio method. The kinetics of the new advanced oxidation reactions were measured, keeping all reagents constant. One varied, including concentration of dye and oxidant, temperature, pH, and all additives of dye fabrication using UV/Visible spectrophotometer [12]. At the same time, the degradation of organic contaminates was checked through UV/Visible spectral analysis. The kinetics of the order of reaction was determined as described by [12]. pH of the reaction mixture was measured by HANNA-HI-1131 meter before and after the completion of the reactions. The Chemical oxygen demand of the reaction mixture before and after the reaction was determined by COD analyzer APHA 5220-C.

## 3. RESULTS AND DISCUSSION

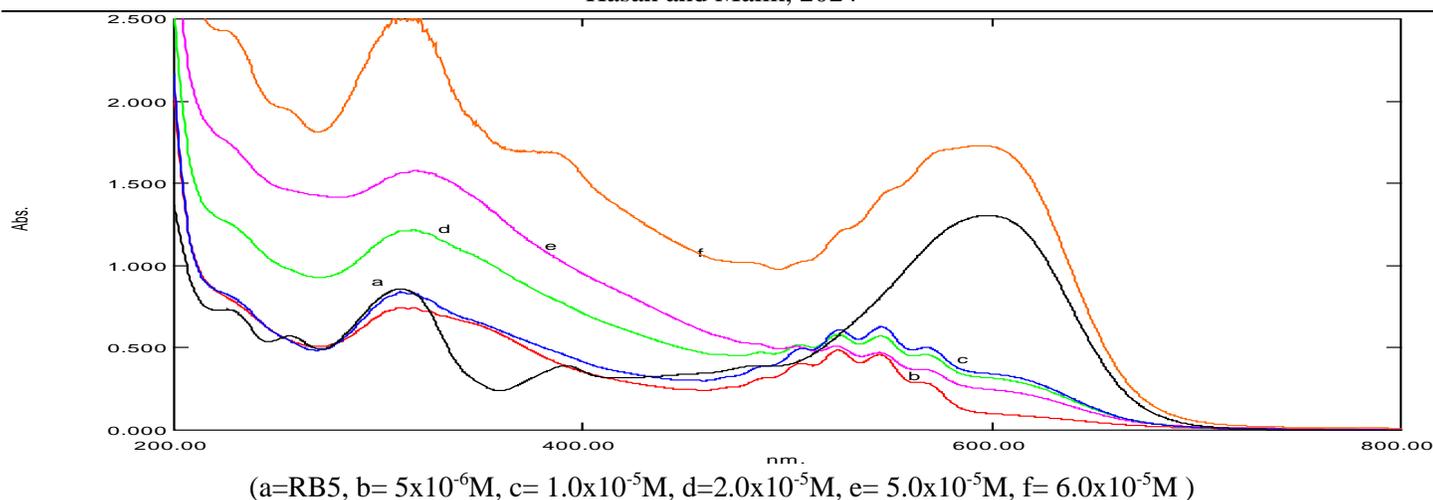
The advanced oxidation process is one of the probable substitutes to decolorize and reduce coloured wastewater burdens discharged from textile dyeing and finishing wastes. New AOP involves the generation of three oxidizing species. Decoloration of the RB5 was monitored at several parameters in a neutral medium (pH=7), suggesting that  $\text{KMnO}_4$  with Urea in an aqueous medium acts as the best oxidizing agent to control dye wastewater.

### 3.1 Monitoring the effect of change in RB5 concentration on the decoloration of RB5

The impact of change in RB5 concentration was observed, keeping a constant concentration of urea (0.075M) and  $\text{KMnO}_4$  ( $2.5 \times 10^{-4}\text{M}$ ) in a neutral (aqueous) medium and results are presented in Table (2). The spectral changes at elevated concentrations of RB5 were presented in Fig. (1), which showed a hyperchromic shift that may be related to the complex formation having high absorptivity, which later degraded into smaller fragments which are similar to the earlier reported [12]. Current results are according to the report of Xu et al. [14], who reported that  $\text{KMnO}_4$  oxidizes the chromophore of the dye, and the oxidation state changes from +7 to +4. Spectral changes clearly (Fig. 2), indicating the formation of a complex between dye and oxidant, which later decreases with time, and finally, the dye disappears, indicating reducing absorption ability of light due to the degradation.

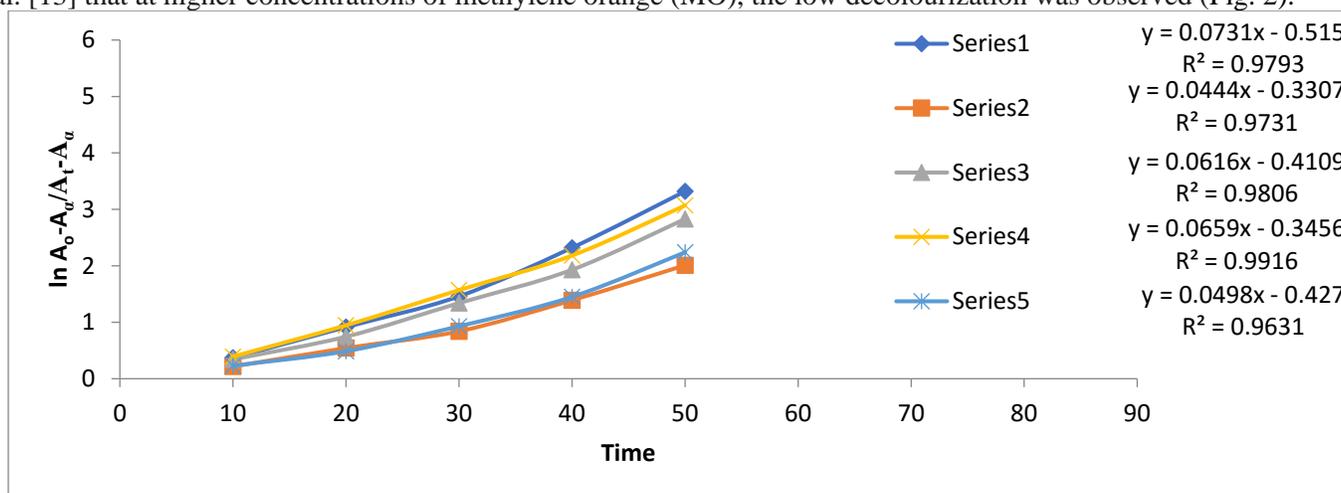
**Table 2.** Effect of change in RB5 concentration on decoloration (pH=7) Oxidant =  $\text{KMnO}_4$ , Temperature=298K, Urea=0.075M

Dye] $\text{mol.dm}^{-3}$ $10^5$	$(dx/dt)$ $\text{mol/dm}^3.\text{s}^{-1}$ $10^3$	$\log(dx/dt)$	$k_{\text{obs}}.\text{s}^{-1}10^3$	$k_{\text{sp}}.\text{s}^{-1}10^3$	% Decoloration
0.5	5.5	-2.25	24.0	73.1	74.87
1.0	4.0	-2.39	8.90	44.4	67.54
2.0	11.0	-1.95	19.2	61.6	41.12
5.0	17.8	-1.74	28.60	65.9	35.48
6.0	13.2	-1.87	6.30	49.8	30.91



**Figure 1:** UV/Visible spectral changes at an elevated concentration of RB5 with constant concentration  $\text{KMnO}_4$  after 60 min in aqueous medium

The result (Table 1) showed that no gradual increase or decrease was observed at an elevated concentration of the dye. At the same time, the rate declined at the highest concentration of the RB5 (Fig.1), which is similar to the reports of Trivedi et al. [13] that at higher concentrations of methylene orange (MO), the low decolourization was observed (Fig. 2).



**Figure .2:** Plot of  $\ln A_0 - A_\alpha / A_1 - A_\alpha$  versus time of various concentrations of RB 5 with  $\text{KMnO}_4$  in aqueous medium

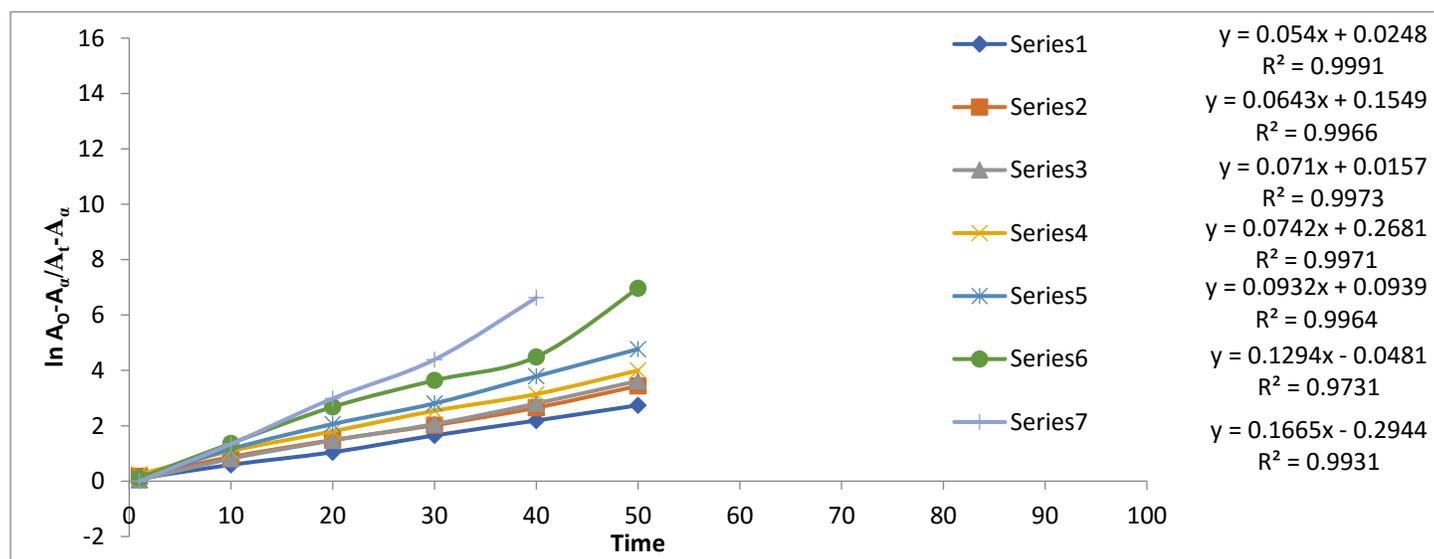
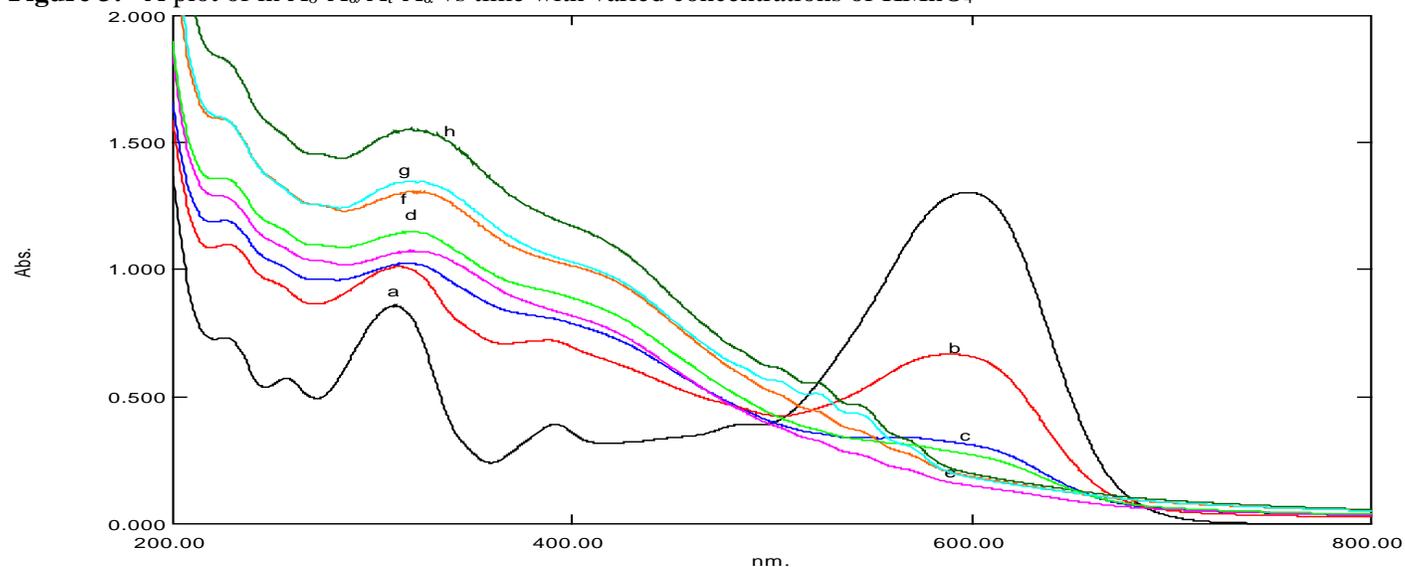
A plot of  $\ln A_0 - A_\alpha / A_1 - A_\alpha$  with respect to time is presented in Fig. (2), shows that the line is not passing through the origin, showing that the rate of reaction is independent upon the concentration of RB5 and zero order kinetics was established in between dye and  $\text{KMnO}_4$  in aqueous medium. Variations in values of  $k$  validated that the dye complex degraded into various small components over time, which may interfere with the reaction (Table 2). Due to this, varied rate constants were observed, while % decoloration decreased with the increase in dye concentration [11]. The % decoloration (74.87%) reaches the maximum extent at the concentration of RB5 ( $5 \times 10^{-6}$ ) while 30.91 % at  $6 \times 10^{-5}$ .

### 3.2 Monitoring the effect of change in $\text{KMnO}_4$ concentration on the decoloration of RB5

The decoloration of RB 5 was monitored under the influence of varied concentrations of  $\text{KMnO}_4$  [ $1.5 \times 10^{-4}$  M –  $3.5 \times 10^{-4}$  M] on the rate of oxidation of reactive black 5 in the presence of a fixed concentration of urea (0.075M) and RB 5 ( $5 \times 10^{-5}$  M) and temperature, respectively (Table 3). The results showed that an increase in the concentration of  $\text{KMnO}_4$  increases the rate of reaction [15-20] up to a certain extent; after that, the rate remains unaffected by the rise in the concentration of  $\text{KMnO}_4$ . The principal reactive species at neutral pH (7) was  $\text{MnO}_2$ , where three electrons ( $3e^-$ ) are released and used in oxidation. The order of reaction was determined through plots  $\ln A_0 - A_\alpha / A_1 - A_\alpha$  with respect to time presented in (Fig. 3), which shows that the line is passing through the origin and value of  $R^2$  suggesting that the rate of reaction is dependent upon the concentration of  $\text{KMnO}_4$  and pseudo first-order kinetics was established in between dye and  $\text{KMnO}_4$  in neutral medium with low sludge. The maximum % decoloration (85.83%) was observed at  $2.5 \times 10^{-4}$  M, while an increase or decrease showed a lower efficiency of decoloration. Spectral changes showed a hypochromic shift (Fig.4.), which showed lower absorptivity, and oxidation leading to degradation started as oxidant concentration increased.

**Table 3:** Effect of change in  $\text{KMnO}_4$  concentration on decoloration (pH=7)[RB5=  $5 \times 10^{-5}\text{M}$ ], Oxidant =  $\text{KMnO}_4$ , Temperature=298K, Urea=0.075M

$[\text{KMnO}_4]$ $\text{mol.dm}^{-3}$ $\cdot 10^4$	$(dx/dt)$ $\text{mol/dm}^3.\text{s}^{-1}$ $10^3$	$\log(dx/dt)$	$k_{\text{obs}}.\text{s}^{-1}10^3$	$k_{\text{sp}}.\text{s}^{-1}10^2$	% Decoloration
1.50	9.50	-2.02	0.30	5.40	44.82
1.87	14.2	-1.85	19.8	6.43	71.45
2.18	15.9	-1.80	23.6	7.10	77.27
2.50	16.5	-1.78	30.8	7.42	85.83
2.80	16.7	-1.78	28.3	9.32	84.11
3.10	16.1	-1.79	27.0	12.94	83.77
3.43	16.7	-1.78	26.6	16.65	84.00

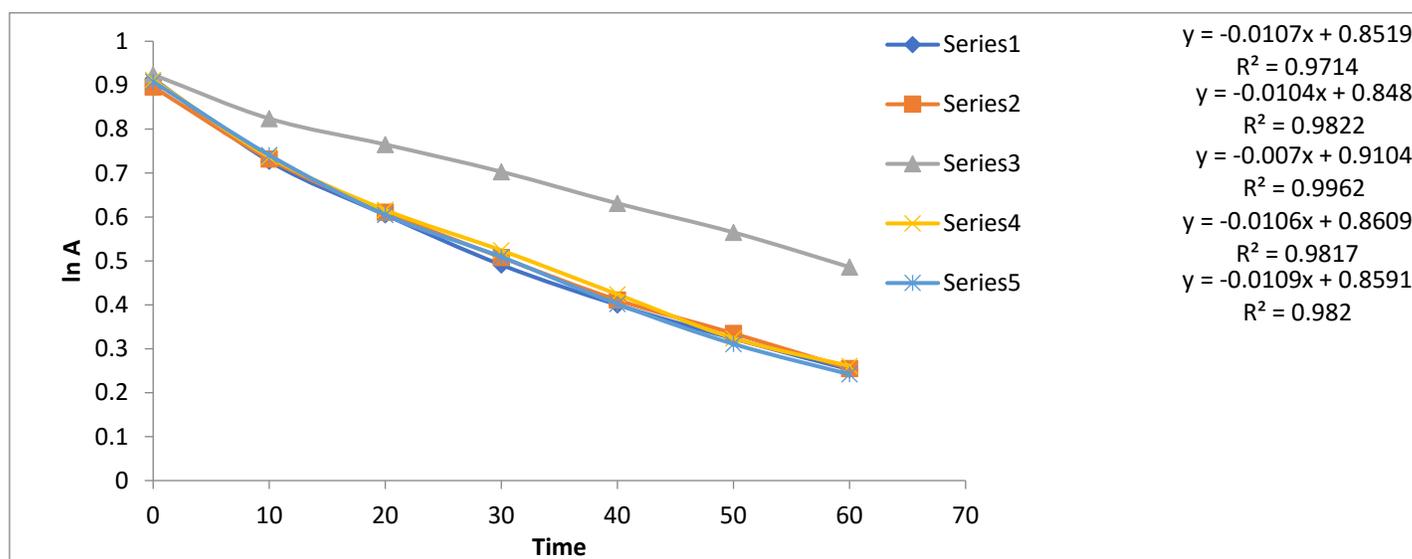
**Figure 3:** A plot of  $\ln A_0 - A_\infty / A_t - A_\infty$  vs time with varied concentrations of  $\text{KMnO}_4$ (a=RB5, b=  $1.50 \times 10^{-4}\text{M}$ , c=  $1.87 \times 10^{-4}\text{M}$ , d=  $2.18 \times 10^{-4}\text{M}$ , e=  $2.50 \times 10^{-4}\text{M}$ , f=  $3.10 \times 10^{-4}\text{M}$ , g=  $3.43 \times 10^{-4}\text{M}$ )**Figure 4:** UV/Visible spectral changes at an elevated concentration of  $\text{KMnO}_4$  with a constant concentration of RB5 after 60 min in aqueous medium

### 3.3 Monitoring the effect of change in H<sub>2</sub>O<sub>2</sub> concentration on the decoloration of RB5

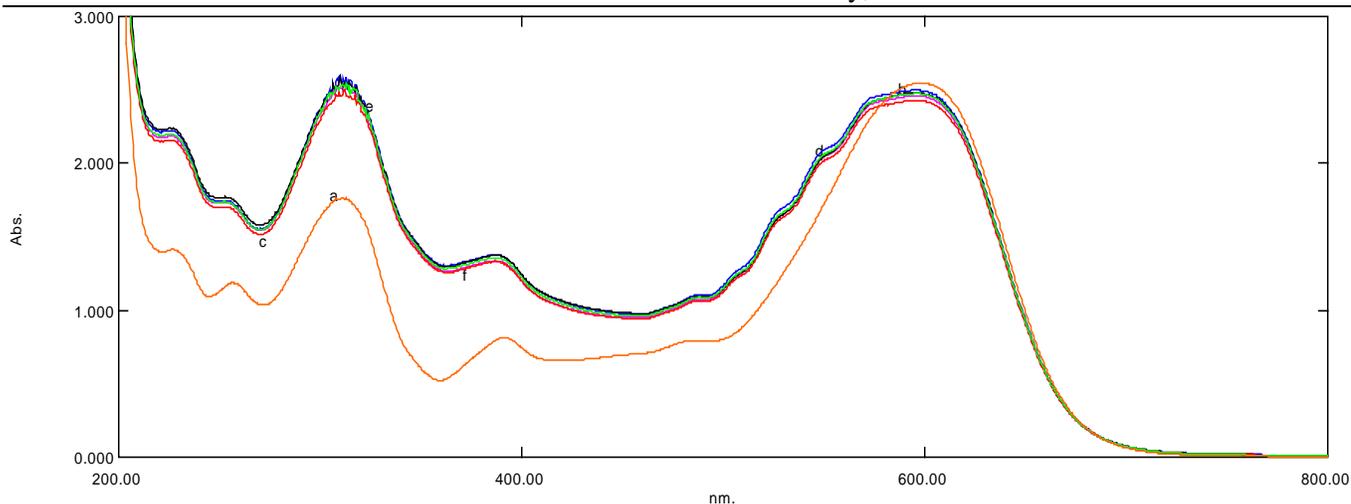
The kinetics of decoloration of RB5 at 597.5 nm and 298K under varied concentrations of the H<sub>2</sub>O<sub>2</sub> [3.75x10<sup>-4</sup>M -18.75x10<sup>-4</sup>M] and at a constant concentration of KMnO<sub>4</sub> (2.5x10<sup>-4</sup> M), RB5 (5x10<sup>-5</sup>M) and urea [0.075M] was studied and reported in Table (4). The result showed that an increase in the concentration of H<sub>2</sub>O<sub>2</sub> does not influence the rate of reaction Fig (5). The order of reaction was determined through plots ln A vs t Fig.(5), which is a straight line with a negative slope, while the value of R<sup>2</sup> showed the dependence of depletion of change in optical density with respect to time, with zero order kinetics aqueous medium, which was contrary to the earlier work of Ince [15] who reported first order kinetics with respect to the concentration of H<sub>2</sub>O<sub>2</sub> under UV irradiation. The prominent oxidizing species was molecular [O<sub>2</sub>] release on the dissociation of the H<sub>2</sub>O<sub>2</sub>, which was adequate for the decoloration of the dye. The maximum % decoloration (7.5 10<sup>-4</sup>) in 1 h (92.4%) was much higher with complete removal of all sludge in a particular time. The time-based resolution of the UV/Visible spectrum at the initial time (5min) and after 60 min were presented in Fig (6 &7). It was clearly observed from Fig.(6) that a complex is formed in between dye, oxidant and hydrogen peroxide, which degraded into small fragments as time passed and where no peak of dye was observed (Fig.7).

**Table 4:** Effect of change in H<sub>2</sub>O<sub>2</sub> concentration on decoloration (pH=7) [RB5= 5x10-5M] oxidant =[KMnO<sub>4</sub>= 2.5x10<sup>-4</sup>M] Temperature=298K urea = 0.075M

[H <sub>2</sub> O <sub>2</sub> ] mol.dm <sup>-3</sup> 10 <sup>4</sup>	(dx/dt) mol/dm <sup>3</sup> .s <sup>-1</sup> 10 <sup>2</sup>	log dx/dt	k <sub>obs</sub> .s <sup>-1</sup> 10 <sup>2</sup>	k <sub>sp</sub> .s <sup>-1</sup> 10 <sup>2</sup>	% Decoloration
3.75	1.91	-1.718	1.07	5.21	48.48
7.50	1.85	-1.732	1.04	4.91	92.40
11.25	1.42	-1.847	0.7	3.90	35.43
15.00	1.90	-1.721	1.06	5.34	47.83
18.75	1.94	-1.712	1.09	5.35	48.58

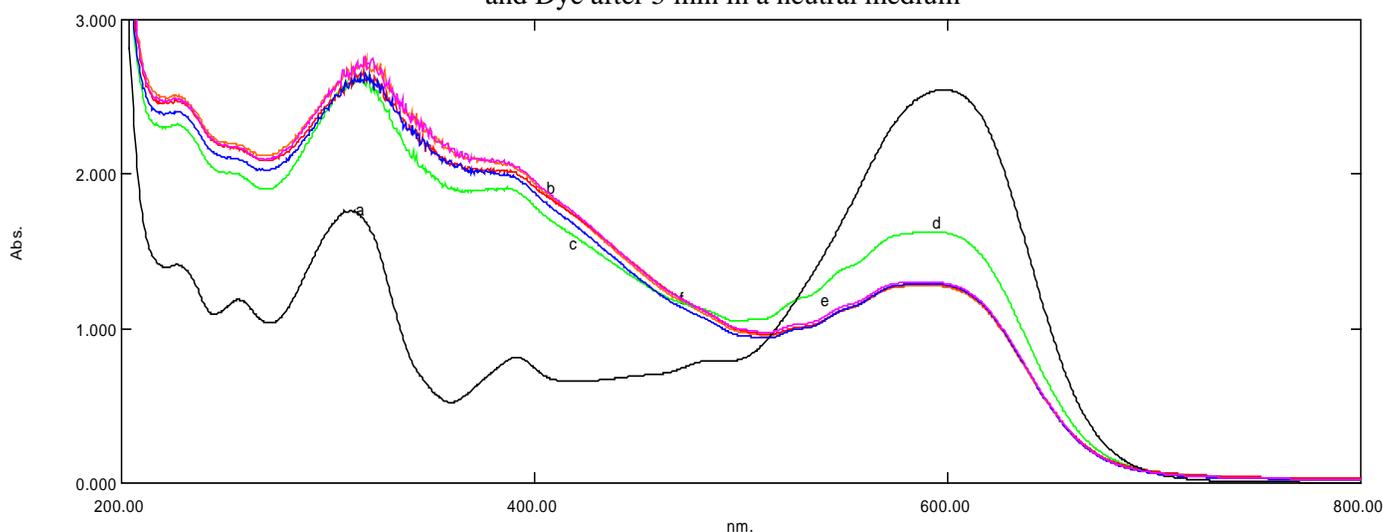


**Figure 5:** Plot of ln A versus time (t) of various concentrations of RB5 with KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> in a neutral medium



(a=RB5, b=  $3.75 \times 10^{-4}$  M, c=  $7.50 \times 10^{-4}$  M, d=  $11.25 \times 10^{-4}$  M, e=  $15.00 \times 10^{-4}$  M, f=  $18.75 \times 10^{-4}$  M, g=  $3.43 \times 10^{-4}$  M)

**Figure 6:** UV/Visible spectral changes at an elevated concentration of  $\text{H}_2\text{O}_2$  with constant concentration  $\text{KMnO}_4$ , Urea and Dye after 5 min in a neutral medium



(a=RB5, b=  $3.75 \times 10^{-4}$  M, c=  $7.50 \times 10^{-4}$  M, d=  $11.25 \times 10^{-4}$  M, e=  $15.00 \times 10^{-4}$  M, f=  $18.75 \times 10^{-4}$  M, g=  $3.43 \times 10^{-4}$  M)

**Figure 7:** UV/Visible spectral changes at an elevated concentration of  $\text{H}_2\text{O}_2$  with constant concentration  $\text{KMnO}_4$ , Urea and Dye after 60 min in a neutral medium

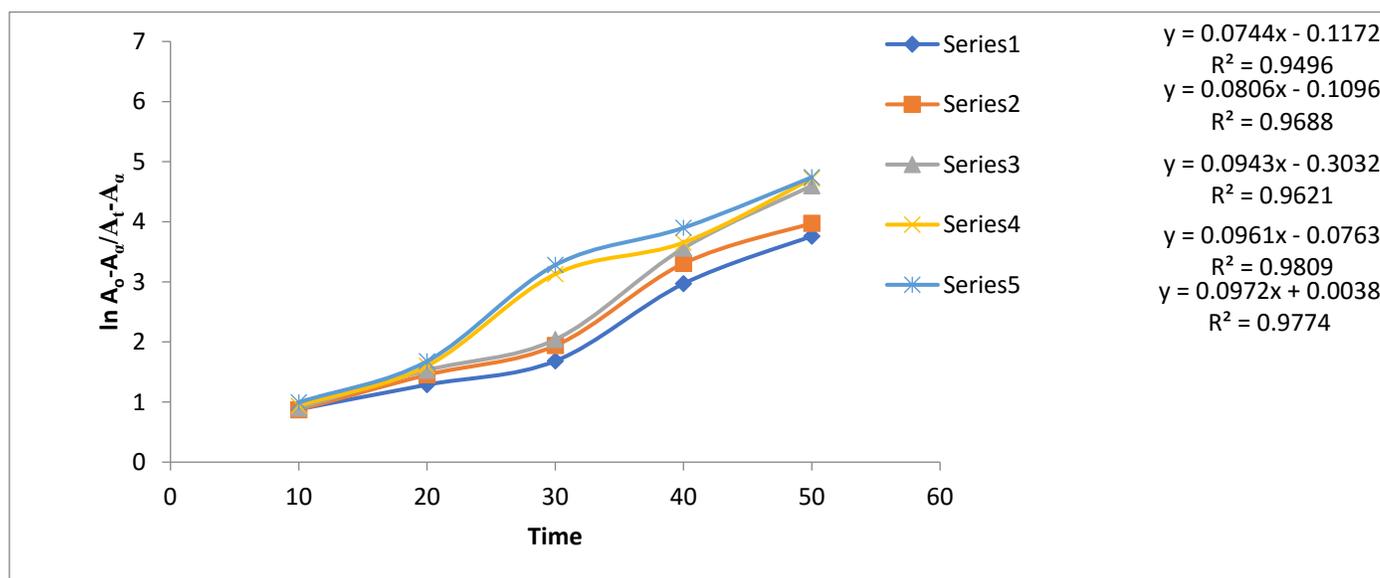
### 3.4 Monitoring the effect of varied concentrations of urea on oxidation of reactive black 5 with $\text{H}_2\text{O}_2$ and $\text{KMnO}_4$

The kinetics of dye decoloration was investigated by monitoring the change in optical density of the dye at 597.5 nm and at 298K under varied concentrations of urea [0.025M – 0.125M]. The rate constant was determined at constant concentrations of RB5,  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , i.e.  $5 \times 10^{-5}$  M,  $7.5 \times 10^{-4}$  M and  $2.5 \times 10^{-4}$  M, respectively. The result reported in Table (5) showed that an increase in the concentration of urea increases the rate of reaction. The order of reaction was determined through a plot of  $\ln A_0 - A_t / A_t - A_\infty$  with respect to the time (Fig. 8), which showed that the line is passing through the origin, showing that the rate of reaction is dependent upon the concentration of urea and first-order kinetics was established with respect to urea. Maximum dye decoloration (89.1%) was observed at 0.075M urea while decreasing with an increase in the concentration of the urea. The time-based resolution of UV/visible spectra (Fig 9 & 10) showed the initially high-intensity peak of the complex formation observed, which later on decreases as time passes or lower molar absorptivity than dye with time, reflected the decomposition of the complex into small fragments having lower  $\lambda_{\text{max}}$  than dye. The hypochromic shift demonstrates the degradation of the dye, due to which low absorptivity was observed. This may be due to the possible formation of a urea hydrogen complex, which is effectively involved in dye degradation.

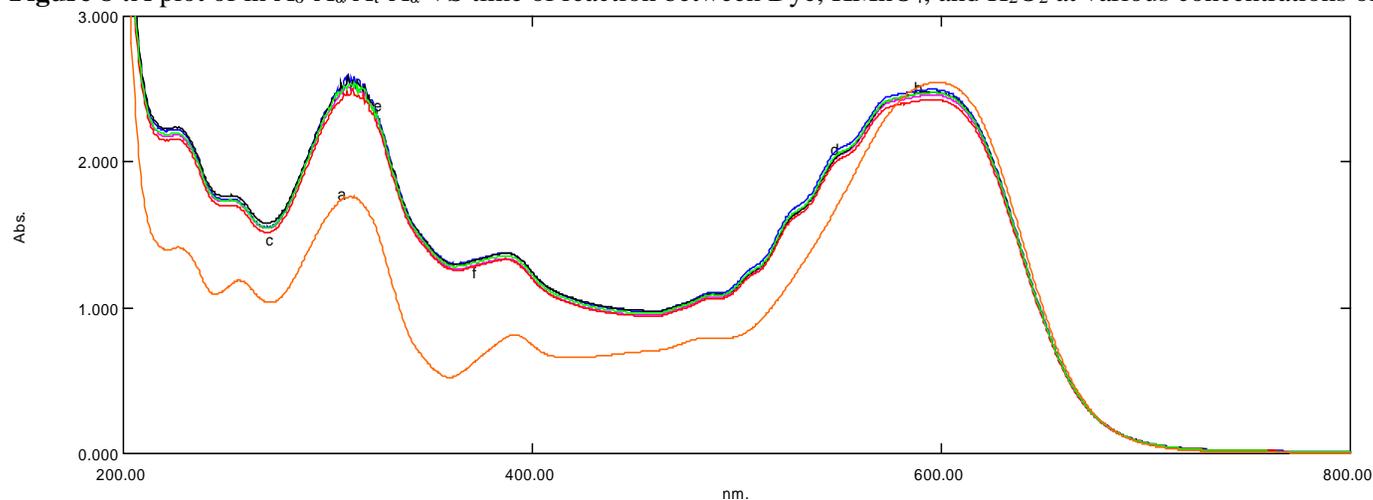
**Table 5:** Effect of change in Urea concentration on decoloration (pH=7)

[RB5=  $5 \times 10^{-5} \text{M}$ ], oxidant =  $[\text{KMnO}_4 = 2.5 \times 10^{-4} \text{M}]$ , Temperature=298K ,  $\text{H}_2\text{O}_2 = 7.5 \text{ M}$

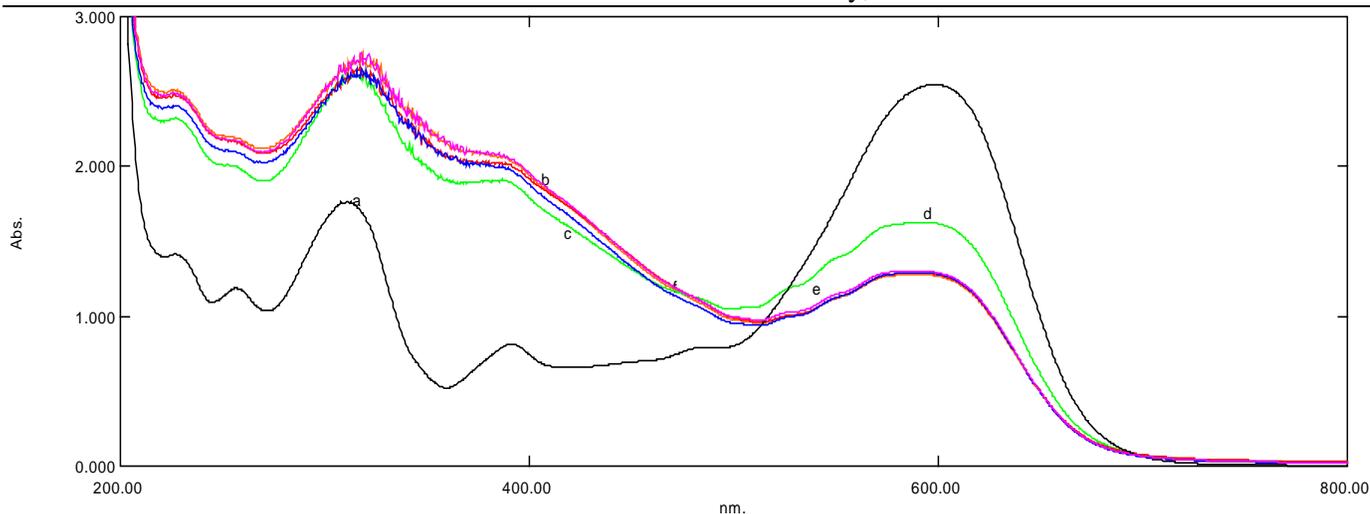
Urea] mol.dm <sup>-3</sup>	(dx/dt) mol/dm <sup>3</sup> .s <sup>-1</sup> 10 <sup>3</sup>	log (dx/dt)	k <sub>obs</sub> .s <sup>-1</sup> 10 <sup>3</sup>	k <sub>sp</sub> .s <sup>-1</sup> 10 <sup>2</sup>	% Decoloration
0.025	1.48	-1.83	-0.0236	7.44	80.54
0.050	1.52	-1.818	-0.0285	8.06	85.90
0.075	1.55	-1.809	-0.033	9.43	89.10
0.100	1.58	-1.801	-0.0338	9.61	87.20
0.125	1.59	-1.798	-0.0335	9.72	89.20



**Figure 8 :**A plot of  $\ln A_0 - A_\alpha / A_t - A_\alpha$  VS time of reaction between Dye,  $\text{KMnO}_4$ , and  $\text{H}_2\text{O}_2$  at various concentrations of urea



**Figure 9:** UV/Visible spectral changes at an elevated concentration of of urea with a constant concentration of  $\text{H}_2\text{O}_2$   $\text{KMnO}_4$ , and dye after 5 min in an neutral medium



**Figure 10:** UV/Visible spectral changes at an elevated concentration of urea with a constant concentration of  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$  and Dye after 60 min in an aqueous medium

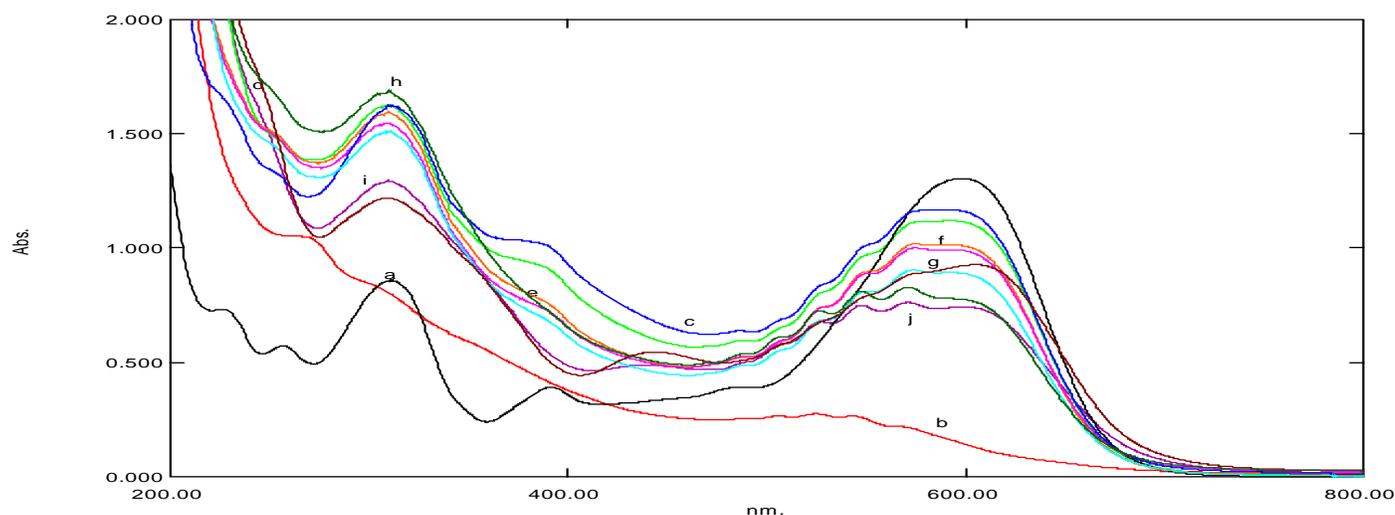
### 3.5 Effect of pH on oxidation of Dye with $\text{KMnO}_4$

The kinetics of oxidation of RB 5 under various pH (1–12) was monitored through spectral analysis and % decoloration using acetate and ammonium hydroxide and ammonium chloride buffer solution (Table 6). The findings revealed a decrease in percent decoloration with increasing pH in both acidic (pH 1-6) and basic ranges (pH 9-12), while the highest decoloration was observed at the lowest pH (pH 1). Hashim et al. [16] used an electrocoagulation (EC) reactor attached with Al electrodes, where they observed that RB5 removal efficiency was maximum at initial pH from 4 to 6 with a maximum decoloration rate of (96%). In contrast, the present investigation showed that maximum decoloration was 88-93% under varied pH of 1-5. Spectral analysis showed Fig (11&12) a decrease in coloration from lowest to high pH, revealing immediate degradation of the dye and no complex formation takes place at low pH with oxidant and dye, while at higher pH, a complex of dye with  $\text{KMnO}_4$  formed as reported earlier [12].

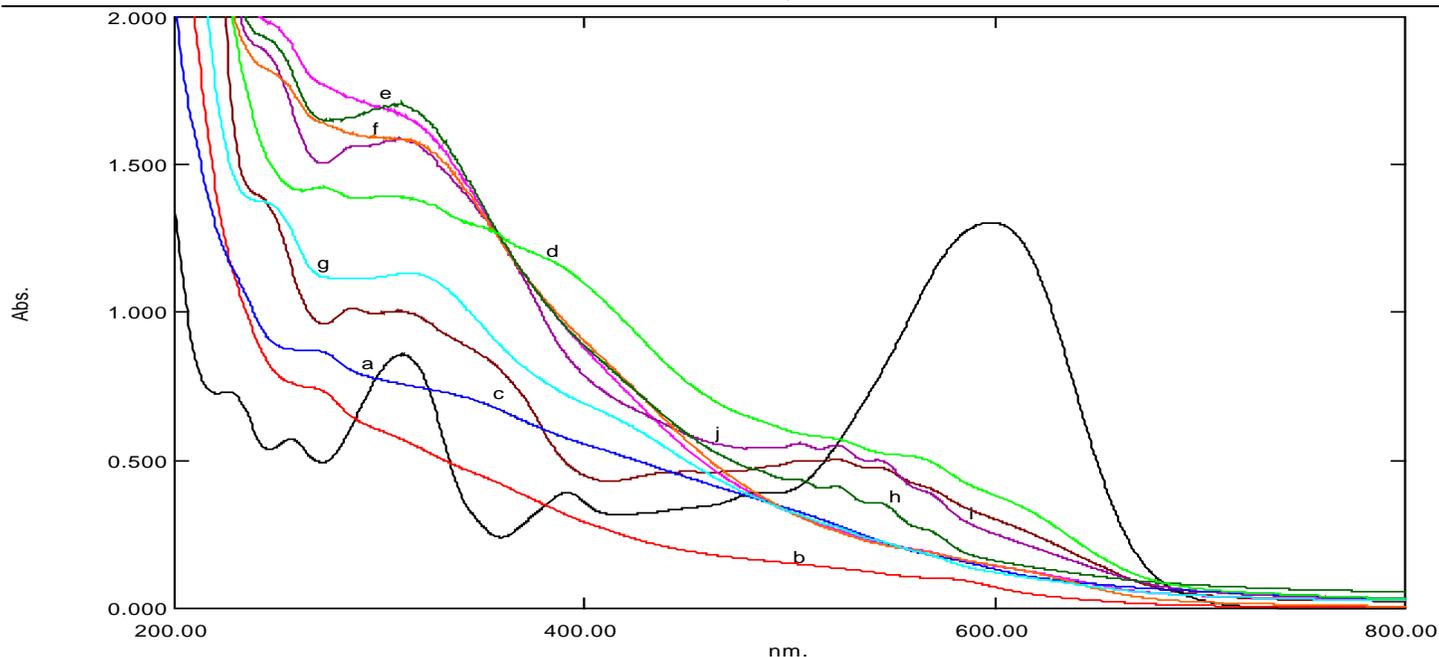
**Table 6:** Effect of variation in pH on decoloration of the RB5

[RB5=  $5 \times 10^{-5}\text{M}$ ], Reductant=[ $\text{KMnO}_4 = 2.5 \times 10^{-4}\text{M}$ ], Temperature=298K, pH = [1-12]

pH	1	2	3	5	6	7	9	10	11	12
% Decoloration	93.9	90.7	90.48	90.48	88.16	87.76	90.16	86.8	79.3	70.40



**Fig. 11** UV/ Visible Spectral changes at different pH with constant concentration  $\text{KMnO}_4$ , Urea  $\text{H}_2\text{O}_2$  and Dye after 5 min A=Dye b= 1, c= 2, d=3, e= 5, f= 6, g= 9, h= 10, i=11, j=12



**Fig. 12** UV/ Visible Spectral changes at different pH with constant concentration  $\text{KMnO}_4$ , Urea  $\text{H}_2\text{O}_2$  and Dye after 60 min A=Dye b= 1, c= 2, d=3, e= 5, f= 6, g= 9, h= 10 i=11, j=12

**3.6 Mechanism of the acceleration of the rate of oxidation**

The study was designed to develop a new AOP to control the dye wastewater and its oxidation products, which contaminate the running water streams. The new AOP is intended i) to speed up the oxidation, ii) to dye oxidation leading to complete mineralization, and iii) to control the sludge formation. For this purpose,  $\text{KMnO}_4$  was selected as a primary strong oxidant due to the variation in oxidation state. The rate of oxidation of RB5 by  $\text{KMnO}_4$  in a neutral medium was accelerated via  $\text{H}_2\text{O}_2$  in the presence of urea used as a dye additive for fixation of the dye on fabrics. The  $\text{H}_2\text{O}_2$  is also an oxidizing agent which chemically digests complex organic compounds into smaller, less toxic and more biodegradable fragments, employed for organic oxidation of various water-soluble polymers, carbohydrates, and nitrogen compounds; destroys phenols and chelants; hydrolyzes formaldehyde, carbon disulphide, organophosphorus and BTEX pesticides, solvents, plasticizers, and almost any other organic needful management [20-25].

Furthermore,  $\text{H}_2\text{O}_2$  affects the COD of running streams and oxidizes both organic and inorganic contaminants, which promotes BOD. This research was conducted in an aqueous medium, where an acceleration reaction was established through the addition of  $\text{H}_2\text{O}_2$ , which reacts with urea and forms a complex that acts as an oxidizing agent generated during reactions like nascent oxygen and  $\text{MnO}_4^-$ . Results showed that maximum decoloration was observed when  $\text{KMnO}_4$  was  $2.50 \times 10^{-4}$  M and  $\text{H}_2\text{O}_2$   $2.50 \times 10^{-4}$  M with lower COD (Table 7).

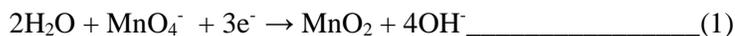
**Table 7.** Chemical oxygen Demand before and after treatment

<b>Dye wastewater (ppm)</b>	6000-7000
<b>After application of New AOP (neutral medium) (ppm)</b>	460

Results showed that the chemical oxygen demand of the dye wastewater was reduced by the application of AOP (Table 7). Therefore, the current AOP claims new ultra-advanced oxidation processes/systems that remove the dye and convert it into less harmful components without any UV irradiation and temperature. The spectral analysis showed a hypochromic shift (Fig.1,4,7,10,12), showing the reducing ability of the dye to absorb photons, revealing that the dye is degraded, establishing the effectiveness of AOP where dye decoloration related to electron transfer (e) from Mn, nascent oxygen and urea hydrogen peroxide complex, which makes AOP ultra-advanced with no dye peak even in minor quantity [22]. Therefore, the initial rapid part of oxidation may be attributed to a fast formation of an intermediate complex between the reactants and the dissociation of the complex leads to dye decolorization (Fig.1,6,9).

### 3.7 Oxidative species in new AOP

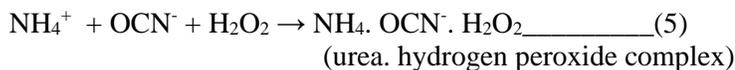
In water, probable oxidation of Mn occurs as follows.



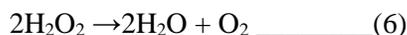
In chemical reactions, nascent oxygen [O] is produced from strong oxidizing agents like  $\text{KMnO}_4$ . Nascent oxygen [O] has a high tendency to react with other nascent oxygen and converted into the  $\text{O}_2$  molecule and can't exist as an independent entity



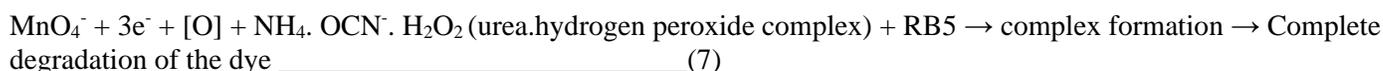
For urea probable reactions



The probable decomposition of  $\text{H}_2\text{O}_2$  yield



Dye decoloration occurs via three oxidizing species.



The probability of the presence of three oxidizing species in a neutral medium validates the fast decoloration of the dye without rising temperature and using any irradiation process. The AOP applied onsite dye wastewater collected from the dye shop, which resulted in the decoloration of dye wastewater with low sludge. The % decoloration was found to be maximum (92.4%) when compared with the reaction without  $\text{H}_2\text{O}_2$  (85%) in a neutral medium. The spectral changes corresponding to  $\text{H}_2\text{O}_2$  technology with urea in neutral mediums showed complete removal of dye with small degraded products.

### 4. CONCLUSION

The influence of  $\text{H}_2\text{O}_2$  and Urea in controlling dye waste in the presence of a strong oxidizing agent showed that newly developed AOP was cost-effective and beneficial to save the running streams. The oxidation kinetics of a reactive black 5 modelled by use of a nonlinear regression technique and found pseudo first order with respect to oxidant and urea. It is also suggested that dye degradation initially occurs through complex formation with urea hydrogen peroxide complex and is accelerated by the  $\text{O}_2$  molecules generated in the reaction, which degrades the dye immediately through the attack on chromophores of the dye.

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