

A KINETIC SPECTROPHOTOMETRIC ANALYSIS OF OXIDATION OF A POTENTIAL POLLUTANT ORTHO AMINOPHENOL BY POTASSIUM MONOPERSULFATE FOR ITS CONVERSION INTO LESS TOXIC COMPOUND

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ABSTRACT

The current study focusses on the uncatalyzed potassium mono persulfate oxidation of ortho aminophenol to develop a method for its removal from water samples affected by it. Kinetic spectrophotometric analysis was done to study the effect of reaction pH, initial ortho aminophenol concentrations, initial oxone (potassium monopersulfate) concentrations, temperature, the effect of solvent and presence of ions in the reaction under study. All the kinetic parameters confirmed the fractional-order kinetic model. Thermodynamic parameters like change in enthalpy, change in entropy, pre-exponential factor, activation energy and Helmholtz free energy were investigated and it has concluded that this oxidation reaction was favorable and endothermic. The activation energy for removal of ortho aminophenol was found to be 74.096kJ/mol, which was compared with previous results. The optimum pH for this process was found to be 7.0 and the temperature was 32-38°C. Hence, the results suggested that this method could be applied as a low-cost effective method, considering the ease of availability of chemicals, their non-toxic nature, low cost and the period for completion of the reaction.

Keywords: Ortho Aminophenol, Oxone, Kinetic, Wastewater, Cost-effective, Less Toxic.

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INTRODUCTION

In this modern era, pollution is a prominent issue and the most dangerous type of this problem stands before us is water pollution. Saltwater covers 71% of the surface of the Earth and the remaining 29% freshwater, is used to sustain life. According to WHO (World Health Organization) reports, people more than 1 billion, are not getting clean water. Waterborne diseases are responsible for the death of approx 4000 children per day, as per Health Monitory Authorities. Increasing industrialization and activities of humans are the major factors for polluting the available water sources¹. The release of waste products as phenols due to the use of carcinogenic aromatic compounds in various industries² is a very serious topic to be discussed. The bulk of the chemical waste, which contaminates the water and environment, has created by the development of industries³. Many industries like paper, pulp, cosmetics, textile, food, and pharmaceuticals use azo dyes, which contaminates the wastewater by more than 15wt%⁴. The round off figure of commercial dyes is 1,00,000, while their annual worldwide production is 7 X 10⁵ metric tons.

The direct discharge of 2% of dyes in water bodies has been reported during their manufacturing process. 10% of the dyes get lost during the coloration process of textiles⁵. The largest consumer of dyes is textile industries since half of the dyestuff material of the world is consumed by itself only⁶. The treatment of industrial effluent becomes a major environmental problem. Moreover, the discharge of contaminated water to the environment is due to an increase in the growth of the textile industry worldwide⁷. It is because the dyes used in these industries are non-degradable and highly toxic for aquatic life, carcinogenic, and mutagenic to humans or adversely affect human health⁸. The other reasons reported for decreasing the

quality of water are the increased population, agricultural and domestic wastes, fast pace of industrialization etc. Moreover, the increasing demand for various products leads to environmental threats. Pollution of water and air has increased by the use of energy generated from fossil fuels⁹. Hence the effluent must be treated properly before it's discharged into water bodies. In this era of crisis of groundwater on earth, the treatment of wastewater and hence use in agriculture becomes an attractive option¹⁰.

Aminophenols are one of the harmful dyes, that have been used as a dyeing agent for furs, hairs, and leather^{11,12} and in the manufacturing of pharmaceuticals, resulting in their presence in groundwater of the area nearby to industrial plant and may be released in water streams¹³. The toxicity of aminophenols affects humans in more than one way. Skin allergy, headache, fatigue, dizziness, and blue color to the skin and lips^{11,12} are the major effects on humans. In plants, aminophenol disrupts the regular metabolic pathway, leading towards serious deformation as prove in the study¹⁴. Since the product formed due to oxidation of ortho aminophenol (OAP) i.e. Questiomycin A, having anti-microbial properties, is used for the synthesis of an antineoplastic agent Actinomycin D¹⁵. Mixed metastatic embryonal carcinoma of the testes, Wilm, gestational choriocarcinoma, etc. are some of the examples of tumors, which are treated by Actinomycin D¹⁶⁻¹⁸. Hence, the study becomes all the more important to be seriously explored.

In this way, many physical, chemical, and biological methods are used. These methods are reported as follows-

- **By Metallic Oxidation**

Using transition metal complexes for the conversion of OAP to 2-amino-3H-phenoxazin-3-one (APX) for the biosynthesis of actinomycin D has become an area of great interest. Many metals were used in their compound form, as a catalyst for the oxidative process of OAP. Many compounds of copper have been used as catalysts for the oxidation of OAP in DMF at 60°C with dioxygen as an oxidant, for example- $\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{OCH}_3)(\text{Cl})$, CuSO_4 , CuCl , CuCl_2 , $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ ¹⁹. Copper (II) catalyzed oxidation of OAP in aqueous solution has also investigated through spectrophotometer²⁰. By using cobalt (II) phthalocyaninetetrasodiumsulfonate as a catalyst, oxidation of OAP has been done²¹. By forming an intermediate as o-benzoquinone imine, oxidation of OAP has performed by using $\text{K}_3\text{Fe}(\text{CN})_6$ ²². Ti has been used as TiO_2 during heterogeneous UV photolysis in the removal process. Some enzyme-catalyzed methods were also used in this way. The Use of tyrosinase as a catalyst for the mechanistic study of OAP has been reported²³. Haemoglobin, catalase etc., for the oxidation purpose of OAP, have the efficient quality to act as catalysts²⁴. Ag as Ag electrode by using SERS (Surface-enhanced Raman scattering) technique²⁵ and Pt as a Pt electrode was used in the electrochemical oxidation of para, ortho and meta aminophenols in acidic medium by spectroelectrochemical method²⁶.

- **By Adsorption Method**

Adsorption on activated carbons has been investigated to oxidize phenols²⁷. The kinetic study by using groundnut shells as the biomass was also investigated²⁸. Novel adsorbents as carbon were used for removal of OAP and to investigate its kinetic study²⁹.

- Ozone (O_3) had been used during the oxidative process for the generation of hydroxyl free radical²⁴. Moreover, it has been applied for the investigation of the degradation of 4-chloro-2-aminophenol by the help of ultrasonic reactors and photolysis process³⁰.
- Radiolysis was another way out, by using a source of radiation having high energy²⁴.
- Wet air oxidation is also applied for the oxidation of OAP. It involves oxidation at elevated temperature (125-320°C) and pressure (0.5-20MPa), using air²⁴.

- **By Using Nanoparticles as a Catalyst**

Mn-doped ZrO_2 nanoparticles have been used for the abatement of degradation of dye³. Carbon-based nanocomposites like Carbon quantum dots have been used for environmental remediation⁹. TiO_2 -hybrid nanomaterials have been used for enhanced photocatalysts for water remediation⁴.

- **MBSPs Technique**

This technique of remediation of pollutants covers microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO). It includes membrane bioreactors and photocatalytic membrane reactors (PMRs) also¹.

Due to the strong oxidizing nature, caroat or oxone has a wide range of applications. The sulfur atom present in its structure is tetrahedrally surrounded by per hydroxyl and hydroxyl groups³¹. A triple salt of potassium monopersulfate, potassium hydrogen sulfate, and potassium sulfate, has a long storage life. Since it does not contain any halogen, by-products after the oxidative process do not contain any halogen. Along with use for denture cleaners, metal treatment and metal extraction, etching of printed circuit boards, repulping of papers, pretreatment of wool, and swimming pool water treatment³², it has wide applications in processes of removal of toxic chemicals from wastewater. Oxone associated metalloporphyrins were used for oxidizing acetaminophen and ellipticine derivatives³³. Pharmaceutical compounds like acetaminophen, antipyrine, doxycycline, etc have been oxidized by oxone in both catalyzed and uncatalyzed manner³⁴. Kinetic spectrophotometric method for determining doxycycline hyclate was performed by using Mn (II) as catalyst³⁵. Degradation of ibuprofen has carried out by oxone³⁶. For oxidative cyclization of 2-aminobenzoic acid and aryl aldehydes to aryl 4H-3,1-benzoxazin-4-ones, environmentally benign oxidant oxone has been used³⁷. It was also used to improve sludge dewaterability along with the use of Fe(II)³⁸. Salts like diaryliodonium was synthesized by using oxone³⁹.

Removal of NO from flue gas by the help of sulfate and hydroxyl free radicals was achieved by activating oxone with cobalt⁴⁰. It has also been used for studying reactions of alkynylsilane⁴¹. Its use as an oxidant for synthesizing a variety of carbamates from amines, alcohols, and carbon mono oxide by Rh as a catalyst⁴². Synthesis of indeno[1,2,3-de]chromenes class of compounds has been done using oxone as a terminal oxidant⁴³. The use of oxone has also been reported for the synthesis of Ni-based water oxidizing electrode⁴⁴. Oxidation of phenols in water was carried out by sulfate radicals by the support of Ru catalysts. These sulfate radicals were generated from oxone⁴⁵. Degradation and mineralization processes of Acid Blue (113) wastewater was done by UV/oxone and UV/persulphate⁴⁶. Oxidative cyclization of 2-92-arylidenhydrazinyl pyridines chemoselectively has been done by RuCl₃/oxone. It acts as an efficient homogeneous catalyst⁴⁷. The use of oxone in wet air oxidation of landfill leachates has been reported⁴⁸. Till now, oxone has not been used for oxidizing OAP. Here, we have attempted removing OAP and to convert it to actinomycin D.

In the present work, we have investigated the removal of OAP, by using low-cost chemicals at normal temperature condition, conducted the kinetic and thermodynamic studies to understand its behavior. This way of removal is performed at low operational cost and found to be eco-friendly in all respects.

Limitation and Novelty

Although the removal of pollutant OAP has been done by using various chemical and adsorptive methods, but its kinetic study of removal by using oxone is not found in the literature. Oxone acts as a potent oxidizing agent, which readily oxidizes OAP into product APX. It does not require any catalyst during the reaction. Furthermore, the chemicals used for the present work were non-toxic and easily available. Although the present work is very rapid and accurate, but still it has some limitations.

- The suitable pH range for reaction mixture, when the medium is buffered by phosphate buffer, is 6-7⁴⁹ at 32°C.
- Highly concentrated buffer is a must, since the product HSO₄⁻, after decomposition of oxone, is a much stronger acid than the reactant HSO₅⁻. A highly concentrated buffer maintains the constant pH of the reaction mixture.
- The concentration of oxone must be at least 10 times higher than [OAP].

EXPERIMENTAL

Materials

Reagent "OAP" was Sigma Aldrich make. "Oxone" i.e. KHSO₅ was also Sigma Aldrich make. Other chemicals such as potassium dihydrogen orthophosphate (KH₂PO₄), sodium hydroxide (NaOH), acetone, and sodium chloride (NaCl) were obtained from Fischer Scientific. All of them were of AR grade. Triply distilled water was used during all the experiments. All the solutions were freshly prepared before use.

Apparatus

UV-VIS spectrophotometer (SYSTRONICS-118) was used for the analysis. The water bath used for maintaining temperature and for proper mixing of the reaction mixture. The pH of the reaction mixture

was maintained by using SYSTRONICS-Digital pH meter - 335. The Infrared spectra of solid APX were recorded in the wavelength ranges between $4000\text{--}400\text{ cm}^{-1}$ at room temperature in KBr powder on SHIMADZU FTIR-8400S.

Preparation of Buffer

Potassium dihydrogen orthophosphate buffer of 0.5M strength having pH 4.0, was prepared in a 100ml volumetric flask. 6.8045gm of KH_2PO_4 was dissolved in triply distilled water and made up to 100ml in a volumetric flask. The pH of this buffer was maintained to be 7.0 by using sodium hydroxide solution, prepared by dissolving NaOH pellets in triply distilled water.

Experiments for Kinetic Study of Oxidation of OAP

A reaction mixture was prepared to determine the absorption maxima and to understand the order w.r.t. the substrate as well as oxidant, the effect of pH, effect of temperature, the effect of solvent and effect of ionic strength on the rate of reaction. For the determination of absorption maxima, a reaction mixture was prepared, which was having a concentration of OAP as $3 \times 10^{-3}\text{M}$, while KHSO_5 as $2 \times 10^{-5}\text{M}$, in a phosphate-buffered medium for the reaction. The reaction was proceeded at 32°C for 240 minutes for wavelength ranges from 200 to 800nm. This experiment gave a value of absorption maxima at which absorbance of each concentration and each variation of parameters was determined.

For determining the pH effect on the oxidation of OAP, a reaction mixture having substrate strength as $2 \times 10^{-5}\text{M}$, while oxidant strength as $2.0 \times 10^{-4}\text{M}$ was prepared for different initial pH ranging from 4.5 to 10.0. The optimum pH for removal of OAP was determined by this experiment.

The order of reaction concerning substrate was investigated by preparing a reaction mixture, in which concentration of oxidant was kept to be constant i.e. $2 \times 10^{-5}\text{M}$, while the concentration of the substrate was varied from $3 \times 10^{-4}\text{M}$ to $9 \times 10^{-4}\text{M}$. The order of the reaction was determined and all the subsequent experiments were performed for the order of the reaction. The order of reaction concerning oxidant was investigated similarly, by keeping the strength of the substrate to be constant i.e. $2 \times 10^{-5}\text{M}$ and varying the concentration of oxidant from $2 \times 10^{-4}\text{M}$ to $7 \times 10^{-4}\text{M}$. The pH for this experiment was maintained as obtained from the previous experiment.

The effect of temperature on the removal of OAP was investigated at 305, 307, 309, and 311K. In this experiment, the concentration of OAP was $2 \times 10^{-5}\text{M}$ and KHSO_5 was $2 \times 10^{-4}\text{M}$. The data obtained was used for calculating all the thermodynamic parameters.

Investigating the effect of solvent on reaction, a reaction mixture having substrate concentration $4 \times 10^{-5}\text{M}$ and oxidant concentration $4 \times 10^{-4}\text{M}$, was prepared. Keeping all other conditions constant, here the concentration of acetone was varied as 2.5%, 5.0%, 7.5% and 10.0%. Since the reaction mixture was a binary and contained some amount of acetone along with water, hence it was needful to discuss the effect of acetone on oxidation of OAP.

To investigate the effect of ions on the oxidation process of OAP, Na ions were taken in its chloride form (NaCl). During this experiment, the concentration of Na ions was varied from $2 \times 10^{-1}\text{M}$ to $5 \times 10^{-1}\text{M}$. The reaction mixture for this experiment was containing $4 \times 10^{-5}\text{M}$ OAP and $4 \times 10^{-4}\text{M}$ KHSO_5 . The pH was remaining the same and the experiment was performed at room temperature i.e. 305K.

Experimental Calculation

The order of the reaction was determined by the slope of the graph plotted between $\log k_{obs}$ and $\log [\text{reactant}]$. As the k_{obs} (pseudo-fractional-order rate constant) values were essential to determine all the kinetic parameters, Guggenheim method⁵⁰ had been applied to find k_{obs} values.

Guggenheim method: Guggenheim suggested this method of obtaining rate constant in cases where the final concentration of product or reactant is failed to be calculated experimentally. In this method, a series of absorbance readings (which is equivalent to the concentration of product), A_t , where t is time with equal intervals, are noted down. Another series of readings $A(t + \Delta t)$ is made, each at the time $(t + \Delta t)$, here Δt is arbitrary chosen constant time interval. Now a plot between $\log [A(t + \Delta t) - A_t]$ and t should give a straight line, having slope as $-k_{obs}/2.303$.

Evaluation of overall rate constant:

$$k_{cat} = k_{obs} / [S] \cdot [\text{catalyst}]$$

Where, [S] is concentration of reactant taken in excess and k_{cat} was calculated overall rate constant. Since this oxidation process was uncatalyzed, hence-

$$k_{cat} = k_{obs} / [S]$$

The unit of k_{cat} was given in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Evaluation of Thermodynamic Parameters

The plot relating temperature and the specific rate was drawn between $\log k_{cat}$ and $1/T$ for testing the validity of Arrhenius equation viz.

$$\log k_{cat} = [-E_a / 2.303 RT] + \text{Constant}$$

Where E_a - Activation energy, R- Gas constant and T- Temperature

The slope of this curve gave E_a , which was also calculated by following formula-

$$\log [(k_{cat})_2 / (k_{cat})_1] = [E_a / 2.303 R] \cdot [1/T_1 - 1/T_2]$$

Where $(k_{cat})_1$ and $(k_{cat})_2$ were calculated overall rate constants at temp. T_1 and T_2 . The unit of E_a was given in kJmol^{-1} .

Other thermodynamic parameters were as follows-

Frequency factor (A),

$$k_{cat} = A \cdot e^{(-E_a/RT)}$$

The unit of A was given in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Helmholtz free energy (ΔF),

$$k_{cat} = [K_b T/h] \cdot e^{(-\Delta F/RT)}$$

Where K_b - Boltzmann constant and h - Planck's constant. The unit of ΔF was given in kJmol^{-1} .

Entropy of activation (ΔS),

$$k_{cat} = (K_b T/h) \cdot e^{(-E_a/RT)} e^{(-\Delta S/R)}$$

The unit of ΔS was given in $\text{Jmol}^{-1}\text{s}^{-1}$.

Enthalpy of activation (ΔH)

$$\Delta H = \Delta F + T \cdot \Delta S$$

The unit of ΔH was given in kJmol^{-1} .

Evaluation of Dielectric Constant

For a binary reaction mixture, having acetone and water, the effect of acetone on the rate of oxidation of ortho aminophenol was determined. It was calculated by the following equation:

$$D = [(V_a \times D_a) + (V_w \times D_w)] / (\text{total volume of reaction mixture})$$

Where, V_a - the volume of acetone present in the reaction mixture, D_a - dielectric constant of acetone at 305K, V_w - the volume of water present in the reaction mixture, D_w - dielectric constant of water at 305K.

Evaluation of Ionic Strength

Ionic strength i.e. the effect of Na ions on the rate of oxidation was determined by varying the concentration of sodium chloride (NaCl) in the reaction mixture. The ionic strength was calculated by the following equation-

$$\mu = 1/2 \cdot \sum (C_i Z_i^2)$$

Where C_i - concentration of ions, Z_i - charge on ions.

RESULTS AND DISCUSSION

UV-VIS Analysis

To identify the possible intermediates, an absorption spectrum of the reaction mixture was recorded at different time intervals. The spectrum is given in Fig.-1. An absorption band was observed nearby 200nm,

when it was recorded for mixture having KHSO_5 (oxidant) in buffer i.e. in the absence of OAP, whereas when recorded for mixture having OAP and oxone in phosphate buffer, a redshift occurred. An adduct established here. The characteristic wavelength for this adduct in the visible range was found to be 434nm, which was attributed to the product APX (2-aminophenoxazin-3-one)⁵¹, where the substrate has no absorption.

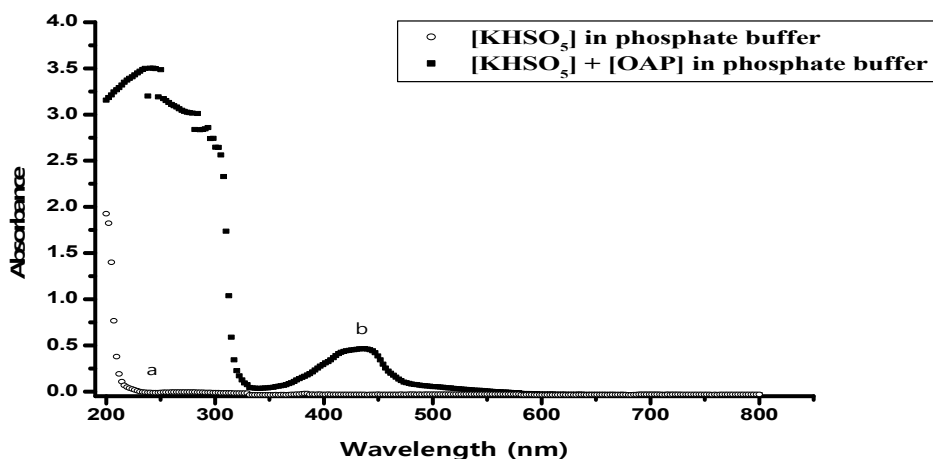


Fig.-1: UV-VIS Absorption Spectrum of Uncatalyzed OAP Degradation by PMS.

(a) Absorption Spectrum of $[\text{KHSO}_5]$ ($2 \times 10^{-5} \text{ M}$) + Phosphate Buffer (0.5M), (b) Absorption Spectrum of $[\text{OAP}]$ ($3 \times 10^{-3} \text{ M}$) + $[\text{KHSO}_5]$ ($2 \times 10^{-5} \text{ M}$) + Phosphate Buffer (0.5M).

IR-Analysis

The IR spectra of the reaction mixture was having peaks in the region 3487.42, 3161.43, 1749.49, 1550.82, 1176.02 and 1018, which was compared with the literature data⁵². 1749.49 peak lied in the range of stretching for the $\text{C}=\text{O}$ group. The stretching frequency for the $\text{N}-\text{H}$ bond was indicated by 3487.42. Similarly, the stretching frequency for the $\text{C}-\text{N}$ bond lies in the range 1080-1360. The ether group present in the product was having a peak range of 1000-1300. All the peaks mentioned above was lying within these ranges, which resembled the structure to be APX.

Rate Law

The order of the reaction was determined to understand the path or mechanism of the process. The orders concerning substrate and oxidant were shown in Fig.-2 and Fig.-3.

A simple rate law for the uncatalyzed reaction of OAP with KHSO_5 was given as-

$$-\frac{d[\text{OAP}]}{dt} = \frac{d[\text{APX}]}{dt} = k [\text{OAP}]^{n_1} [\text{KHSO}_5]^{n_2} \quad (1)$$

Where n_1 was the order of reaction w.r.t. substrate while n_2 was the order of reaction concerning oxidant.

To find the order concerning substrate and oxidant, kinetic runs were performed by using different oxidants [Table-1: Experiment no. 1 to 6] and substrate concentrations [Table-1: Experiment no. 7 to 13]. Assuming constant concentration of oxidant, pseudo-fractional-order rate law was derived, where,

$$k_{obs} = k [\text{KHSO}_5]^{n_2} \\ -\frac{d[\text{OAP}]}{dt} = k_{obs} [\text{OAP}]^{n_1} \quad (2)$$

The plot between $\log k_{obs}$ and $\log [\text{OAP}]$ was linear with a correlation coefficient of $R=98.84\%$, indicating that the reaction was of fractional-order concerning substrate concentration. k_{obs} and k_{cat} indicated the observed and calculated rate constant values. This indicated that $n_1=0.60$ (Fig.-2).

Similarly, assuming the constant concentration of substrate, again pseudo-fractional-order rate law was derived, where,

$$k_{obs} = k [\text{OAP}]^{n_1} \\ -\frac{d[\text{OAP}]}{dt} = k_{obs} [\text{KHSO}_5]^{n_2} \quad (3)$$

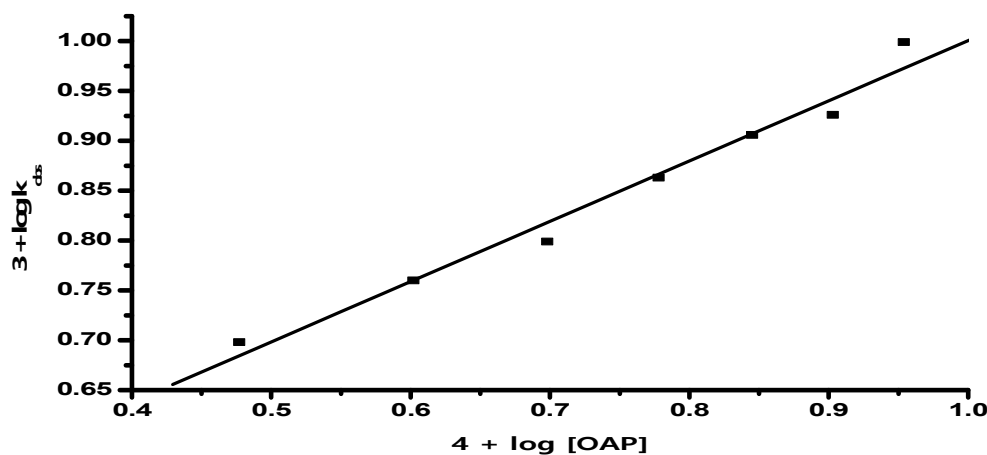


Fig.-2: Plots between $\log k_{\text{obs}}$ Vs $\log [\text{OAP}]$: Determination of Order
Conditions: $[\text{KHSO}_5] \times 10^5 = 2.0 \text{ M}$, $\text{pH} = 7.0$, $\lambda_{\text{max}} = 434\text{nm}$, $\text{Temp.} = 32 \pm 0.1^\circ\text{C}$

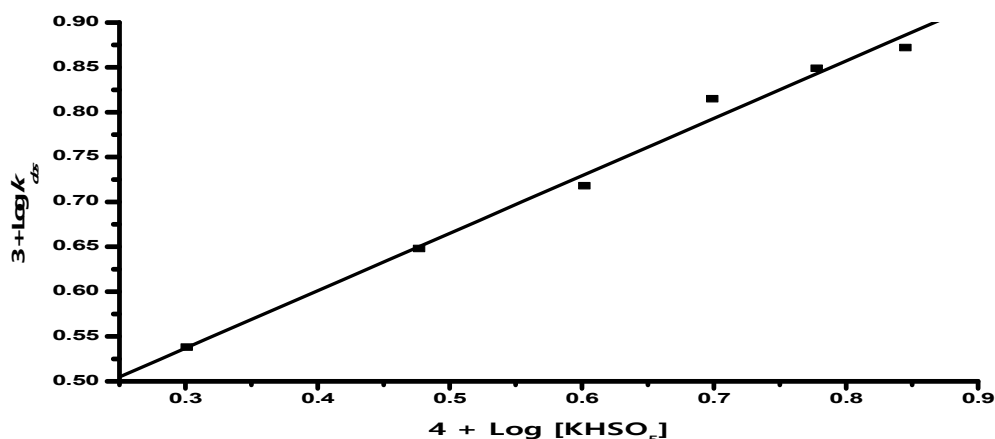


Fig.-3: Plots between $\log k_{\text{obs}}$ vs $\log [\text{KHSO}_5]$
Conditions: $[\text{OAP}] \times 10^5 = 2.0 \text{ M}$, $\text{pH} = 7.0$, $\lambda_{\text{max}} = 434\text{nm}$, $\text{Temp.} = 32 \pm 0.1^\circ\text{C}$

Experiments for different oxidant concentrations [Table-1: Experiment no.- 1 to 6] showed that the reaction was again fractional-order concerning oxidant. Again graph plotted between $\log k_{\text{obs}}$ and $\log [\text{KHSO}_5]$ came out to be a straight line with a correlation coefficient of $R=99.47\%$ (Fig.-3), through which the order was found to be $n_2=0.64$. Hence the obtained kinetic data revealed that the overall order of oxidation of OAP by oxone was 1.24 with $n_1=0.60$ and $n_2=0.64$ in equation (1); through which mean value of kinetic constant $k = 1.304 \times 10^{-1} \text{ mol/L/s}$ at 305K was found (Table-1). Table-1 shows a kinetic data for variation of initial OAP concentrations, initial oxone concentrations, the effect of pH, the effect of change in acetone concentration and effect of change in concentration of competitive ions.

Table-1: Kinetic Data for Potassium monopersulfate Oxidation of OAP at 32°C

Experiment No.	$10^4 [\text{KHSO}_5]^a$ (mol dm^{-3})	$10^4 [\text{OAP}]^a$ (mol dm^{-3})	pH	Acetone% ^a (V/V)	NaCl% ^a (W/V)	$10^3 k_{\text{obs}}$ /sec	$10^{-1} k_2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
1	2.0	0.2	7.0	-	-	3.448	1.724
2	3.0	0.2	7.0	-	-	4.452	1.484

3	4.0	0.2	7.0	-	-	5.220	1.305
4	5.0	0.2	7.0	-	-	6.525	1.305
5	6.0	0.2	7.0	-	-	7.062	1.177
6	7.0	0.2	7.0	-	-	7.446	1.064
7	0.2	3.0	7.0	-	-	4.99	1.663
8	0.2	4.0	7.0	-	-	5.76	1.440
9	0.2	5.0	7.0	-	-	6.29	1.258
10	0.2	6.0	7.0	-	-	7.29	1.215
11	0.2	7.0	7.0	-	-	8.06	1.151
12	0.2	8.0	7.0	-	-	8.44	1.055
13	0.2	9.0	7.0	-	-	9.98	1.109 1.304 ^b
14	2.0	0.2	4.5	-	-	1.228	6.141
15	2.0	0.2	5.0	-	-	1.842	9.212
16	2.0	0.2	5.5	-	-	2.994	14.969
17	2.0	0.2	6.0	-	-	2.764	13.818
18	2.0	0.2	6.5	-	-	2.994	14.969
19	2.0	0.2	7.0	-	-	15.584	77.918
20	4.0	0.4	7.0	2.5	-	5.22	13.05
21	4.0	0.4	7.0	5.0	-	6.986	17.465
22	4.0	0.4	7.0	7.5	-	8.291	20.728
23	4.0	0.4	7.0	10.0	-	9.673	24.183
24	4.0	0.4	7.0	-	0.2	4.376	10.939
25	4.0	0.4	7.0	-	0.3	5.527	13.818
26	4.0	0.4	7.0	-	0.4	6.909	17.272
27	4.0	0.4	7.0	-	0.5	7.370	18.424

a in 25 ml reaction mixture.

b mean value of kinetic constant *k*.

Effect of pH

A plot between k_{cat} , calculated by the Guggenheim method, as a function of different initial pH of the reaction mixture, ranging from 4.5 to 7.0, is shown in Fig.-4. The figure depicted that the highest value of $\log k_{cat}$ has been obtained at neutral pH. The value was increased on increasing the pH of the reaction mixture and found maximum as $\log (60.26) = 1.780$ at pH 7.0. Hence, the optimum value of pH is found to be 7.0. Beyond pH 7.0, the aqueous solution of CAROAT i.e. oxone, becomes unstable³².

Although KHSO_5 is more stable in acidic conditions, when its aqueous solution was added to the reaction mixture, it is assumed that its maximum stability is found at pH 7.0, where it is dissociated into its ionic form i.e. the hydrogen sulfate content is increased and maximum amount of oxygen is generated and hence rate of the reaction becomes maximum at pH 7.0, while in alkaline conditions, the decomposition is delayed due to a drop in the stability of oxone.

Above pH 7 or apparently above 8, phosphate buffer was less effective. The average rate constant in acidic stream i.e. in phosphate buffer for the decomposition of KHSO_5 was found to be maximum at 33.2°C, whereas in basic stream i.e. in carbonate buffer, it was maximum at 25°C⁴⁹. Since we had performed all the experiments at 32°C in phosphate buffer, hence the acidic range was more appropriate. Between pH 7-10, the decomposition of KHSO_5 was second-order, between 6-8 and 10.5 to 12, in the basic stream, it was the first order⁴⁹. Hence, a medium of neutral pH was found to be an optimum condition for the maximum degradation of OAP.

Effect of Solvent

The effect of dielectric constant on the reaction rate was studied by adding varying proportions of acetone (2.5% - 10% v/v). On increasing concentration of acetone, the rate also increases⁵³, and results are shown in table (1). A linear plot with $R = 98.57\%$ with a positive slope is obtained between $\log k_{obs}$ and $1/D$, which is shown in Fig.-5.

The change in the concentration of acetone in the reaction mixture had a positive effect on the degradation of OAP. The plot between $\log k_{obs}$ and $1/D$ is linear with a positive slope, which indicates a positive ion and a dipole nature of rate-determining step⁵⁴.

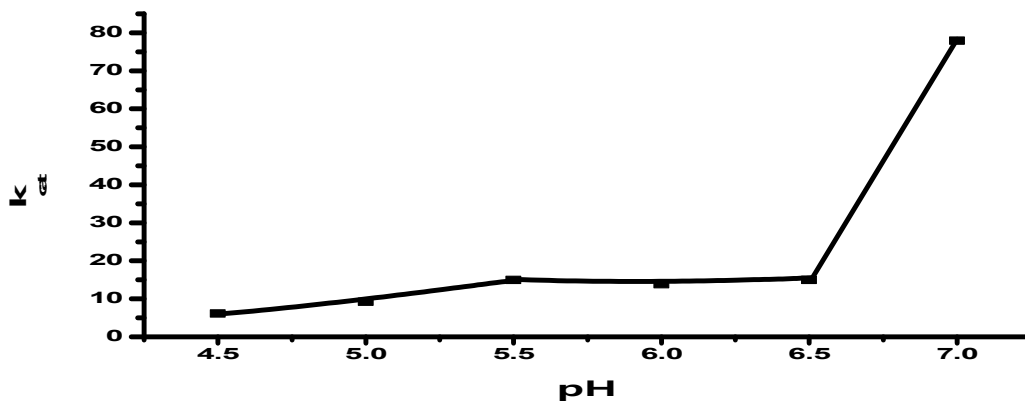


Fig.-4: Effect of pH on Reaction Rate

Conditions: $[OAP] \times 10^4 = 0.2M$, $[KHSO_5] \times 10^4 = 2.0 M$, $\lambda_{max} = 434nm$, Temperature = $32 \pm 0.1^\circ C$

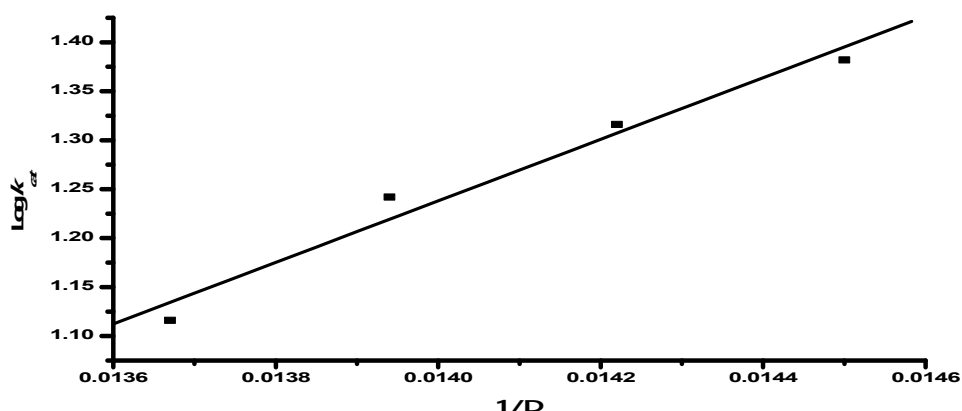


Fig.-5: Effect of Dielectric Constant on Reaction Rate

Conditions: $[OAP] \times 10^4 = 0.4 M$, $[KHSO_5] \times 10^4 = 4.0 M$, pH = 7.0, $\lambda_{max} = 434nm$, Temp. = $32 \pm 0.1^\circ C$

Effect of Ions

The present study shows that removal of OAP from wastewater in the presence of other cations like Na^+ , becomes easy. We had studied this by taking Na^+ in the form of NaCl and varying the concentrations of Na^+ in the reaction mixture. The results are shown in Fig.-6. It can be seen that as the concentration of Na^+ increases, the rate of removal of OAP also increases. The maximum rate of this removal process is found at 0.5M concentration of ions in the NaCl solution.

Effect of Temperature

To determine the optimum temperature, experiments were performed in a series. The range followed was 25 to $40^\circ C$. It was observed that below $32^\circ C$, the activation energy required for the reaction to proceed was not enough, although oxone had some rate constant of decomposition. As the temperature reached to $32^\circ C$, the decomposition rate became maximum⁴⁹. Since low temperature favors the degradation by $KHSO_5$ when the medium is buffered by phosphate⁴⁹, hence the variation was allowed below $40^\circ C$. It was observed that increasing temperature, increased the rate of degradation of OAP. The activation energy for the present study was calculated to be 74.096kJ/mol. This was compared to other compounds, degraded by $KHSO_5$. For example; glycine and alanine are having activation energies as 112.13kJ/mol and 101.67kJ/mol⁵⁵.

The values of rate constants were determined at four different temperatures (32.0 – 38.0°C) by the Arrhenius plot which is shown in Fig.-7.

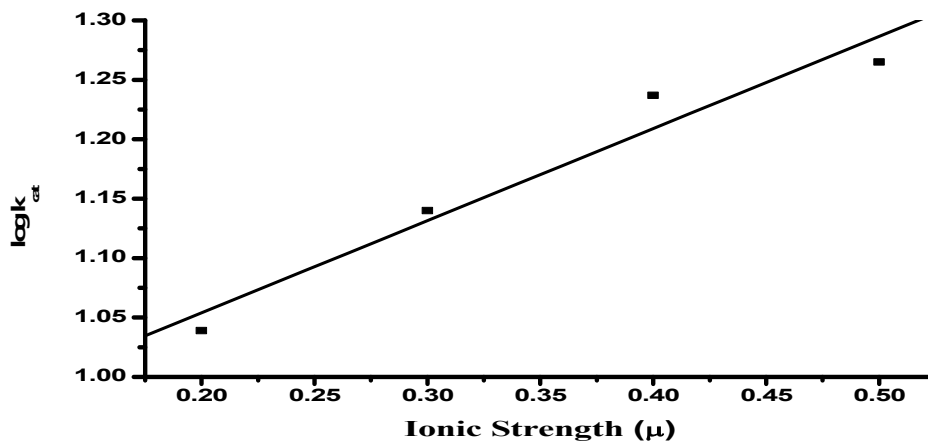


Fig.-6: Effect of Ionic Strength on Reaction Rate

Conditions: [OAP] $\times 10^4 = 0.4$ M, [KHSO₅] $\times 10^4 = 4.0$ M, pH = 7.0, $\lambda_{max} = 434$ nm, Temp. = $32 \pm 0.1^\circ\text{C}$

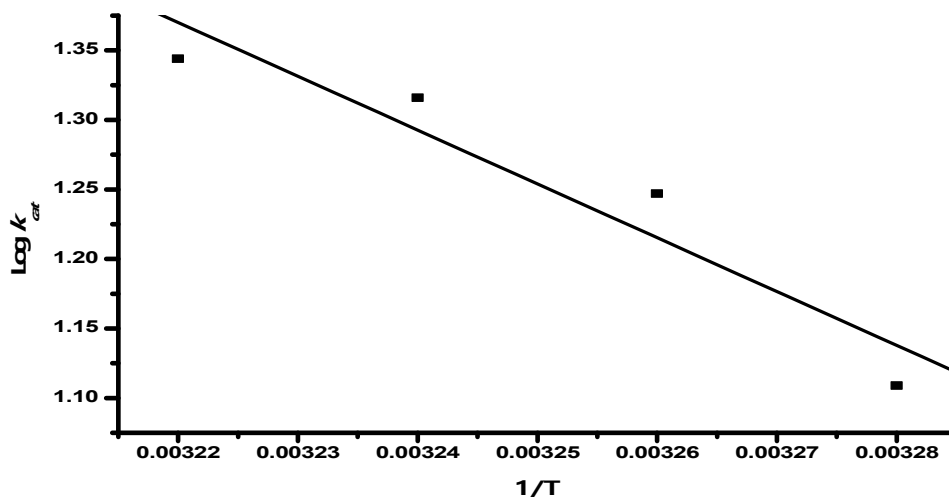


Fig.-7: Arrhenius Plot

Conditions: [OAP] $\times 10^5 = 2.0$ M, [KHSO₅] $\times 10^4 = 2.0$ M, pH = 7.0, $\lambda_{max} = 434$ nm

The study of all the thermodynamic parameters calculated for the removal of OAP by using KHSO₅ confirms that the reaction is characterized by a comparatively low value of activation energy (E_a). Other thermodynamic parameters like Enthalpy of activation (ΔH) and value of Arrhenius parameter were also calculated from the slope and intercept of a graph plotted between $\log k_{cat}$ versus $1/T$ and shown in Fig.-7. The formulas applied for the determination of these parameters have already discussed earlier. Table-2 shows the values of all these parameters. The positive value of enthalpy of activation (ΔH) is evidence for the endothermic process of oxidation of OAP. The negative value of entropy of activation (ΔS) indicates the decrease in the randomness of particles during the oxidation process which further promotes the formation of the product. This high value also suggests the involvement of solvent interactions⁵⁶. The low positive value of activation energy (E_a) indicates the bi molecularity of the process. It can also be assumed that the oxidizing power of oxone i.e. KHSO₅ is very much responsible to decrease the minimum required

energy for the reaction. Hence, KHSO_5 seems to be very effective for the removal of OAP in a low-cost effective way. Moreover, the value of the pre-exponential factor (A) gives an idea of the number of times the reacting species collide with each other. The high value of Helmholtz free energy (ΔF) is evidence for the high rate of reaction. The high value indicates the high internal energy of OAP and that of KHSO_5 , due to which the collision frequency is also high and hence, effective collision is again high. This may be one of the reasons for the swift rate of the reaction.

Table-2: Kinetic Parameters for Peroxymonosulphate Oxidation of OAP
[OAP] $\times 10^5 = 2.0$ M, $[\text{KHSO}_5] \times 10^4 = 2.0$ M, pH = 7.0, $\lambda_{\text{max}} = 434\text{nm}$

Temp. (°C)	k_{cat} ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	E_a (kJmol^{-1})	$A \times 10^{13}$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	$-\Delta S^\ddagger$ ($\text{Jmol}^{-1}\text{s}^{-1}$)	ΔH^\ddagger (kJmol^{-1})	ΔF^\ddagger (kJmol^{-1})
32	12.858	-	1.577042624	10.85770946	25.90358686	29.71398407
34	17.655	123.42628650	1.806276293	11.84376560	25.88695964	29.73913383
36	20.725	63.23053871	1.772870085	13.09474480	25.87033243	29.76428358
38	22.070	25.12227445	1.582160049	14.50329563	25.85370521	29.78943340
Mean Values		70.59303323	1.684587263	12.57487879	25.87864604	29.75170871

E_a from graph: 74.0959458 kJ/mol

Comparison of Uncatalyzed Monopersulfate Oxidation of OAP with Previously Applied Methods

Several methods were applied for the removal of OAP from water samples. In these processes, several metals like Cu (II), Co (II), Ti as TiO_2 , Ag as Ag electrode, and Pt as Pt electrode have been used. The use of copper as a catalyst is more pronounced as compared to other metals may be due to its low cost, but on the other hand, some serious diseases like Wilson disease and Minimata can be credited to copper. Hence, it seems to be a toxic alternative and is not an eco-friendly catalyst. Although the use of cobalt does not lead to any toxicity but in respect of expenditure, it is comparatively much costly. The use of tyrosinase, hemoglobin, catalase, etc also seems to be comparatively costly. The cost of Ag and Pt electrodes is also very high. Ozone itself acts as a bleaching agent and its solution contains toxicity, hence its use at a commercial scale must be thought twice. Wet air oxidation seems to be eco-friendly, but it works at very high temperature and pressure. Hence, it can be followed only at specific conditions only under controlled conditions in expert hands.

Now, the present method seems to be more favorable in all respects as compared to the other methods discussed previously. All the chemicals used in this method, are easily available. All of them are cheap enough to use at the commercial level. They all are eco-friendly i.e. free of any toxicity, both in respect of their own or their solution. Due to the strong oxidizing property of oxone, the reaction completes in a very short period. Most importantly, the reaction can be easily proceeded at low temperatures, even at room temperature also, as compared to other methods. Thus, this method seems to be eco-friendly, can be performed at low operational cost at an industrial scale, and completes in a very short period.

Comparative Review

Various methods have been reported which deal with the removal of pollutants by generating sulfate radicals^{55, 57-60}. These methods can be compared with the present study in Table-3, since it also involves the reaction between sulfate radicals and OAP during the reaction.

Table-3: Comparison of Results

Authors	Target Compound	Activation Energy
S. M. Rayappan <i>et al.</i>	Glycine ⁵⁵	112.13 kJ/mol
S. M. Rayappan <i>et al.</i>	Alanine ⁵⁵	101.67 kJ/mol
Y. Ji <i>et al.</i>	Atrazine ⁵⁷	97.98 kJ/mol
C. Tan <i>et al.</i>	Diuron ⁵⁸	166.7 ± 0.8 kJ/mol
A. Ghauch <i>et al.</i>	Naproxen ⁵⁹	155 ± 26.4 kJ/mol
A. Ghauch <i>et al.</i>	Bisoprolol ⁶⁰	119.8 ± 10.8 kJ
Present Study	Ortho Aminophenol	74.096 kJ/mol

CONCLUSION

In this study, uncatalyzed potassium mono persulfate oxidation of OAP was carried out to develop a method for its removal from water samples affected by it. To identify the optimum levels of different operating parameters, a kinetic spectrophotometric study was conducted in a phosphate-buffered medium. The results revealed that the removal of OAP by using monopersulfate, follows fractional-order kinetics concerning substrate and oxidant both and follows overall first-order kinetics. It is an endothermic process for which the value of activation energy is found to be 74.096 kJ/mol, which is comparatively low. The optimum values of pH and temperature were 7.0 and 32 to 38±0.1°C. The product formed due to oxidation of OAP is Questionmycin A, which is used to synthesize Actinomycin D, an anti-neoplastic agent, which is used in the treatment of tumors. This method could not only prove instrumental in the research about the treatment of deadly disease of cancer but also can form the basis of an effective method of removal of aminophenols in water samples having a hazardous concentration of this pollutant in it which might lead to some serious health problems as far as the human race is concerned. Further insight into this method is still being explored by us to make this more effective. Moreover, the ease of availability of all the chemicals, their non-toxicity, and low cost, insists this way of removal of OAP be performed at the laboratory as well as in industrial scale.

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