



KINETIC AND THERMODYNAMIC STUDIES OF OXIDATIVE DEGRADATION OF CHLORO-DERIVATIVES OF PHENOL IN AQUEOUS PHASE BY CLASSIC FENTON AND PHOTO-FENTON PROCESSES

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Abstract : Fenton oxidation offers itself as plausible treatment technology for complete removal or reduction of concentration of priority organic pollutants within permissible limits specified by environmental protection agencies. In the present investigation classic and UV assisted Fenton and Fenton-like oxidation of some chlorophenols have been studied. Experiments were carried out in a batch scale laboratory photoreactor to evaluate the kinetic and thermodynamic parameters. These studies show that maximum degradation of chlorophenols took place at pH = 3, initial chlorophenol concentration = 3×10^{-4} mol/L, $H_2O_2/COD = 3.5$, $[H_2O_2] = 1.7$ mol/L and $Fe^{++}/Fe^{+++} = 0.0093$ mmol/L. The concentration decay profile could be better described by the pseudo-first-order model. The energy of activation of both Fenton and Fenton like process for 2CP and 4CP are very small as compared to the activation energy for noncatalytic oxidation of phenol in aqueous solution indicating a rapid degradation reaction path having very low energy of activation. The positive ΔH^\ddagger values indicating that an external source of energy is required to raise the energy level of reactants for the formation of transition state. The negative values of entropy of activation indicate a more ordered and rigid transition state than the ground state. The oxidative degradation rate constants obtained are of the order of $\approx 8 \times 10^{-4} \text{ sec}^{-1}$ at 298 K and Gibbs free energy of activation ΔG^\ddagger values around 80 kJ/mol^{-1} implying a reaction with half life of $t_{1/2} \approx 15 - 20$ min and corresponds to a typical reaction that proceeds to completion within few hours.

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Index Terms - AOP, Classic Fenton, UV-Fenton, Fenton-like, UV-Fenton-like, Degradation, Chlorophenols, Reaction Kinetics, Thermodynamic parameters.

INTRODUCTION

Even though 3/4th part of earth is covered by water, only about 1% is appropriate for drinking. The domestic, agricultural and industrial use of water further leads to generation of wastewater in ever-increasing quantities. The presence of organic priority pollutants namely phenols and its derivatives in wastewater in unacceptable quantities makes it mandatory to subject the wastewater to efficient treatment methods to eliminate or bring down the concentration of pollutants below permissible limits stipulated by environmental protection agencies without transferring them to another phase.

Presence of non-biodegradable organic compounds in wastewaters precludes conventional biological methods of treatment. Under such situations advanced chemical oxidation can be used to decrease the toxicity before applying a conventional biological. AOPs can also be used as a post-treatment to oxidize non-biodegradable residues present in wastewater pretreated by conventional biological processes [1]. In this context, Advanced Oxidative Degradation Processes (AOPs) comprise a set of techniques that, under certain conditions, could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions, which involve transitory oxidant species OH^\cdot free radicals. Literature abounds itself in data related to AOPs, but there are very few reports provided on kinetics, mechanism and thermodynamics of the process [2].

Chlorophenols constitute a group of chemicals widely used to produce pesticides, herbicides, insecticides and synthetic dyes and are released into water due to their industrial applications [3]. Chlorophenols (CPs) are hazardous, bio-refractory, stable in water and persists in soil and ground water and impart objectionable taste and odor [4]. Their presence in water results in objectionable taste and

odor and are carcinogenic. Due to the toxic and low biodegradable nature of chlorophenols, biological treatment methods are not adequate to treat the wastewater efficiently. Considerable interest therefore manifest itself in working out a treatment technology that can efficiently and economically remove the hazardous and refractory organics present in wastewater and treated waters from conventional treatment plants. Advanced oxidation processes (AOP) offer themselves as an excellent treatment alternative for complete oxidation and mineralization of pollutants without transferring them from one phase to another [5,6]. During AOPs, OH· free radicals having very high oxidation potential of 2.8 V [7] are produced in situ, which can destroy organic contaminants non-selectively.

The objective this study was to evaluate the treatability of 2-Chlorophenol and 4-Chlorophenol in aqueous phase by classical Fenton ($\text{H}_2\text{O}_2 + \text{Fe}^{++}$) and UV assisted Photo-Fenton ($\text{UV} + \text{H}_2\text{O}_2 + \text{Fe}^{++}$) oxidation. The efficiency of Fenton like processes ($\text{H}_2\text{O}_2 + \text{Fe}^{+++}$ and $\text{UV} + \text{H}_2\text{O}_2 + \text{Fe}^{+++}$) was also studied. Experiments were conducted in a laboratory scale batch photoreactor to study the oxidative degradation of 2-CP and 4-CP at five different temperatures between 293 – 313 K to evaluate the reaction kinetics, rate constant, energy of activation and thermodynamic parameters associated with the process. Since AOPs are strongly dependent on process parameters like pH, temperature, substrate and oxidant concentration, Fe^{++} and Fe^{+++} concentration, the same were first optimized experimentally. The obtained results prove that the Fenton process holds good promise for the efficient treatment of effluents. The abbreviations used in the text for convenience are : 2CP – 2 chlorophenol, 4CP – 4 chlorophenol, F- Fenton process, FL - Fenton like process, UV-F - Photo-Fenton process and UV-FL - Photo-Fenton like process

MATERIALS AND EXPERIMENTAL METHODS

2.1 Chemicals

Hydrogen peroxide (30% w/v H_2O_2), 2-CP, 4-CP and 2,4 DCP, sulphuric acid (98% H_2SO_4), NaOH, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ used were of AR/GR grade Merck/S.D. Fine chemicals and were used as such without further purification. The aqueous phase solubility of all substrates used in these studies are summarized in the Table 2.1. The stock solutions of the pollutants were prepared in freshly boiled and cooled distilled water and were stored in amber coloured bottles. 0.005 M solutions of 2-CP and 4-CP were prepared by dissolving the required amount of these compounds in 1000 ml volumetric flask. The stock solutions were then diluted to required concentration using distilled water for subsequent use.

2.2 Spectrophotometric Method

Chlorophenols show strong absorption bands in UV- region with a high molar extinction coefficient value in their aqueous solutions and hence, UV-Visible spectrophotometric technique was employed for determination of the concentration of the substrates in water. LABMAN UV-VIS double beam spectrophotometer with auto scanning microprocessor was used during these studies. This instrument has an optical bandwidth of 1nm, with D2 and W-Lamp as source and silicon photodiode as detector. The absorbance measurements were carried using 1cm path length well matched quartz cuvettes. According to Beer's law:

$$A = \epsilon c l = \epsilon c \quad (1)$$

where, A = the absorbance or optical density,
l = optical path length, cm [1 cm in this case]
 ϵ = molar extinction coefficient $\text{M}^{-1} \text{cm}^{-1}$,
c = the concentration of sample under investigation ML^{-1} .

Pollutant concentration versus absorbance plot at the wavelength of maximum absorbance (λ_{max}) were plotted for all the chlorophenols. Linear regression analysis of the experimental data of the concentration versus absorbance showed excellent linearity up to a certain concentration range. The reproducibility of the Beer's law plot was also tested regularly.

H_2O_2 reacts with potassium titanium oxalate sulphate solution to give a yellow coloured solution having wavelength of maximum absorption at 420 nm. Stock solution of known concentration of H_2O_2 was prepared by diluting 30% w/v H_2O_2 solution and its concentration was determined by titration against standard KMnO_4 solution [8]. After standardising the prepared H_2O_2 solution, it was used for making several solutions in the concentration range of 6 – 60 mg $\text{H}_2\text{O}_2/\text{L}$ by appropriate dilutions of the stock solution for the Beer's law plot. Table 2.2 summarises λ_{max} , ϵ and Beer's law validity range for chlorophenols and hydrogen peroxide.

Table 1 : Physical properties of Chlorophenols

Compound	2-Chlorophenol	4-Chlorophenol
Abbreviation used	2-CP	4-CP
Molecular weight	128.56	128.56
Aq. Solubility at 25°C, mg/L	29000	27000
Melting point (°C)	9.4	42.8
Boiling point (°C)	174.9	220
Density (g/cm^3)	1.257	1.26
dissociation constant, pKa	8.65	9.57
PubChem CID*	7245	4684
CAS Number**	95-57-8	106-48-9

*PubChem CID - is compound ID number giving database of chemical molecules and their activities in biological assays.

**CAS Number - is unique numerical identifier assigned by the Chemical Abstracts Service to every chemical described in the open scientific literature

Table 2 : λ_{\max} and molar extinction coefficient values of studied pollutants.

No.	Pollutant	λ_{\max} , nm	ϵ , $M^{-1} \text{ cm}^{-1}$	Beer's law validity range
1	2-Chlorophenol	272	1828	0 – 0.0010 ML^{-1}
2	4-Chlorophenol	224	1426	0 – 0.0009 ML^{-1}
4	H_2O_2	420	868	0 – 0.002 ML^{-1}

Percentage degradation of the synthetic pollutant and wastewater was calculated by the formula:

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Where C_0 and C_t are the concentrations at time $t = 0$ and $t = t$, respectively.

2.3 Batch degradation experiments in Photoreactor

All experiments were carried out in a 1.0 liter jacketed thermostatic batch photo reactor (Figure 1) equipped with low pressure mercury lamp (8 W, UV-C) placed in its center, external exposure of UV light was cut-off by placing the reactor in a wooden box having internal coating of aluminum foil. The reactor was placed over a magnetic stirrer and a teflon coated magnetic needle was used for stirring the solution at the constant rate. All the experiments were performed at atmospheric pressure. The desired temperature ($T \pm 0.2 \text{ }^\circ\text{C}$) was maintained by circulating water from a cryostat bath (Fourtech systems, Mumbai, India). All the experiments were carried out in batch mode. Photoreactor was charged with 800 ml of $3 \times 10^{-4} \text{ M}$ solution. The required pH of solution was adjusted initially by using dilute 0.01 N HCl or NaOH. The required concentrations of iron Fe^{2+} (salt $FeSO_4 \cdot 7H_2O$) or $(Fe_2(SO_4)_3 \cdot 7H_2O)$ in case Fe^{3+} was added when necessary. Required quantity of hydrogen peroxide solution was injected into the reactor and the UV-light was switched on at the same time. During the experiments, samples were withdrawn from the reactor with the help of syringe at regular time intervals for concentration determination. Experiments were carried out for optimizing process parameters like pH, H_2O_2 concentration, Fe^{2+} , Fe^{3+} . For evaluating the activation energy and thermodynamic parameters chlorophenol degradation experiments were carried out at five different temperatures between 293-313 K. This range was selected because the real treatment process temperatures are in this range. Systronics LED display Digital pH meter Model No. MK-VI was used for pH determination. This instrument was calibrated before use with the buffer solutions of pH 4.0, 7.0 and 9.5. Remi 2 ML magnetic stirrer Model No. Q-19 A was used for stirring the reactor contents during experiments.

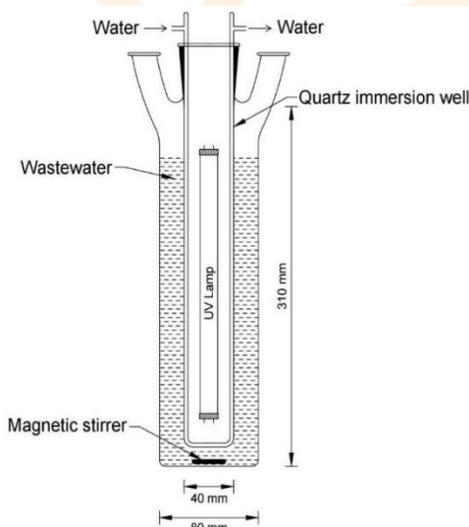


Figure 1: UV Photo reactor assembly

3. Results and Discussion

From the preliminary experimental studies, the optimal conditions determined for degradation of chlorophenols were: 1.7 mmol/L of H_2O_2 , 0.0093 mmol/L of Fe^{2+}/Fe^{3+} and $pH=3$. Figure 4 shows a representative plot of optimization of Fe^{+++} concentration, similar experiments were carried out for optimizing other process parameters. The initial concentration of chlorophenols was kept at $3 \times 10^{-4} \text{ mol/L}$. These optimal process parameters gave highest degradation efficiency and hence were maintained constant during present investigation.

3.1 Kinetic studies

About 90-95% of the substrate underwent oxidative degradation within an hour. The experimentally observed substrate concentration decay profile against time was examined by first and second order kinetics. The obtained rate data could be best explained by pseudo first order kinetics particularly during initial 60-70 minutes of contact time and subsequently deviated from linearity. Thus, using the integrated form of first order rate equation:

$$\ln [C_0/C_t] = k t \quad \text{--- (3)}$$

Hence, $\ln [C_0/C_t]$ values were plotted against t to evaluate the pseudo first order reaction rate constant k . Fig. 2 shows concentration decay profile and Fig. 3 shows the pseudo first order kinetics plot for degradation of 2-chlorophenol by UV/ H_2O_2 , UV/ H_2O_2/Fe^{+++} and UV/ H_2O_2/Fe^{+++} processes. Fig. 4 shows the optimization of $[Fe^{+++}]$ concentration and corresponding first order plots.

3.2 Activation Energy

Activation energy is minimum amount of energy required for formation of activated complex, which then will lead to the formation of product or return to the reactant stage by liberating energy. The rise in temperature increases the kinetic energy of the reactant molecules increasing the probability of activated collisions leading to the formation of activated complex thereby increasing the rate of reaction [9]. To evaluate the energy of activation, the experimentally obtained pseudo first order rate constants 'k' at five different temperatures 293 K, 298 K, 303 K, 308 K and 313 K were plotted according to Arrhenius equation :

$$\ln k = \ln A - (E_a/R).(1/T) \quad \text{--- (4)}$$

which showed excellent linearity with regression coefficient ($R^2 \geq 0.97$) as shown in Figs. 5 and 6. The energy of activation 'E_a' was then calculated from the slope. The experimental data on effect of temperature on reaction rate constant and the Arrhenius equation obtained by linear regression of ln k versus (1/T) plot for AOP processes studied are reported in Table 3 and in corresponding Figs. 5 and 6.

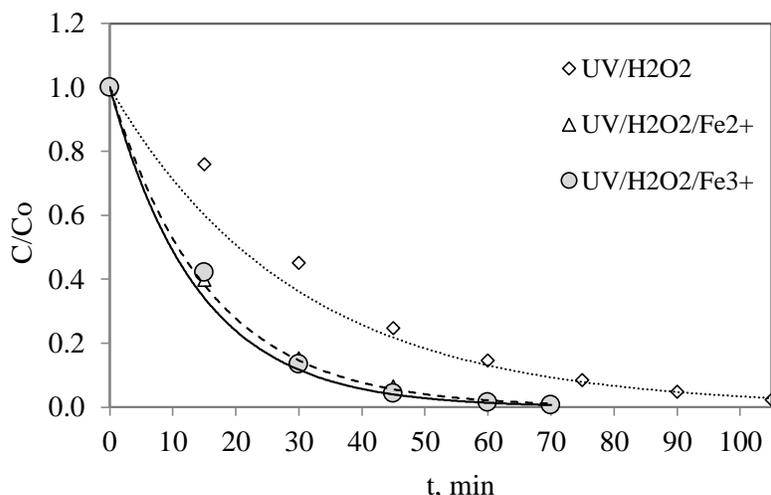


Fig. 2 : Concentration decay of 2-chlorophenol as a function

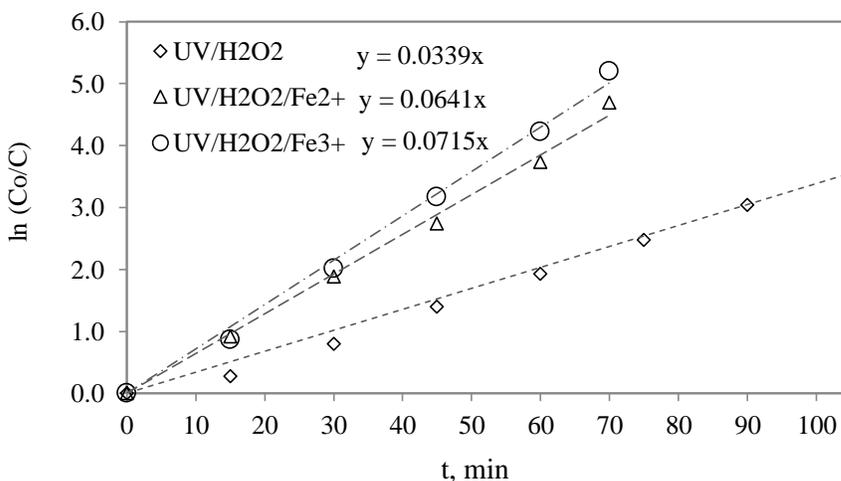


Fig. 3 : Pseudo first order kinetic plot for 2-chlorophenol

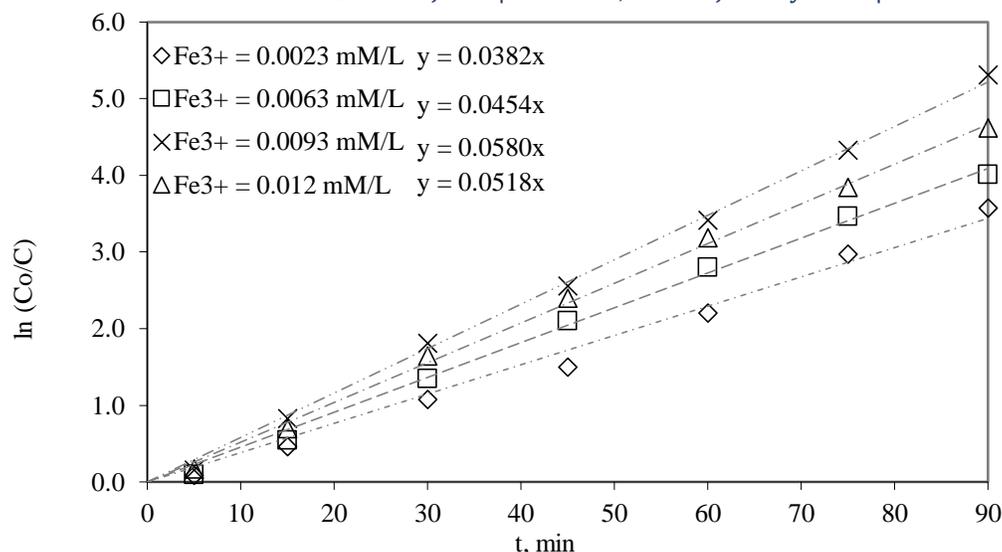


Fig. 4 : Pseudo first order kinetics plot for 2-chlorophenol (optimization of Fe^{3+} dose)

3.3 Evaluation of thermodynamic parameters

During Fenton and Fenton like oxidation, substrate molecule is attacked by the $\text{OH}\cdot$ free radicals generated in situ, forming a transition state complex SOH^\ddagger , and can be well represented by the transition state theory [10].



The Equilibrium constant K^\ddagger is given by:

$$K^\ddagger = \frac{[\text{SOH}^\ddagger]}{[\text{S}][\text{OH}\cdot]} \quad \text{or} \quad [\text{SOH}^\ddagger] = \frac{k_f}{k_r} K^\ddagger [\text{S}][\text{OH}\cdot] \quad (5)$$

In Eqn. (4), the first step is an equilibrium between the substrate, oxidant $\text{OH}\cdot$ and the transition state complex which subsequently gives products. The intermediate transition state complex SOH^\ddagger is very short lived and hence it is logical to assume that $(k_f + k_2) \gg k_r$ and at any given instant of time the concentration of SOH^\ddagger will be very small. According to transition state theory, one vibrational degree of freedom of the activated complex $[\text{SOH}^\ddagger]$ is quite unstable and breaks the transition state complex (vibrating at the top of the barrier) into products. The frequency of such vibration 'v' will be low and average energy will be of the order of $k_b T$ (where, k_b = Boltzmann constant, T = Temperature and h = Planck's constant)

$$\text{i.e. } E_{vib} = k_b T = h \cdot \nu \quad (6)$$

Rate of reaction depends upon (i) $[\text{SOH}^\ddagger]$ and (ii) frequency of vibration of activated complex 'v'. Hence,

$$\text{Rate of reaction} = r = \nu \cdot [\text{SOH}^\ddagger] = \nu \cdot [\text{S}] \cdot [\text{OH}\cdot] K^\ddagger \quad (7)$$

$$\text{From (3), (6) and (7), rate of the reaction, } r = \frac{k_b T}{h} K^\ddagger [\text{S}][\text{OH}\cdot] \quad (8)$$

The well-known Eyring equation derived from the transition state theory describes the relation between rate of a reaction and Gibb's free energy of activation as $k = (k_b T/h) \exp(-\Delta G^\ddagger / RT)$. Transition state theory assumes a chemical equilibrium between reactants and transition state complex and is often successfully used for calculating the standard enthalpy of activation (ΔH^\ddagger), the standard entropy of activation (ΔS^\ddagger), and the standard Gibbs energy of activation (ΔG^\ddagger) for any reaction if its rate constant has been experimentally determined. The Gibbs free energy contains an entropic and enthalpic term. In case of Arrhenius equation, entropic term is accounted for by pre-exponential factor A . The linearized from the Eyring equation is (9),

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{k_b}{h} + \frac{\Delta S^\ddagger}{R} \quad (9)$$

where, $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ (molar gas constant value)

$h = 6.626 \times 10^{-34} \text{ Js}$ (Planck constant)

$k_b = 1.38 \times 10^{-23} \text{ JK}^{-1}$ (Boltzmann constant).

The thermodynamic parameters were then evaluated by plotting $\ln(k/T)$ versus $(1/T)$, which was linear with a high regression coefficient ($R^2 \geq 0.97$) as shown in Figs. 7 and 8. The slope of the plot $(-\frac{\Delta H^\ddagger}{R})$ and intercept $(\ln \frac{k_b}{h} + \frac{\Delta S^\ddagger}{R})$ values were then used to calculate K^\ddagger standard enthalpy of activation (ΔH^\ddagger), the standard entropy of activation (ΔS^\ddagger), and the standard Gibbs energy of activation (ΔG^\ddagger) for the AOPs studied are reported in Table 4.

Table 3: Effect of temperature on rate constant and Arrhenius plot equation for AOPs studied.

No.	Temperature	$1/T \times 10^3, K^{-1}$					Arrhenius Plot Equation
		3.41	3.36	3.33	3.25	3.19	
	System	Rate constant k, min^{-1}					
1	2-CP+H ₂ O ₂ +Fe ²⁺	0.0429	0.538	0.0676	0.0828	0.0992	$\ln k = - (3866.3/T) + 10.053$
	2-CP+H ₂ O ₂ +Fe ³⁺	0.0427	0.0545	0.0695	0.0842	0.1042	$\ln k = - (4073.0/T) + 10.756$
	2-CP+UV+H ₂ O ₂ +Fe ²⁺	0.0534	0.0654	0.0753	0.0846	0.0983	$\ln k = - (2714.0/T) + 6.3554$
	2-CP+UV+H ₂ O ₂ +Fe ³⁺	0.0543	0.0648	0.0773	0.0886	0.1024	$\ln k = - (2901.8/T) + 6.9944$
2	4-CP+H ₂ O ₂ +Fe ²⁺	0.0208	0.0289	0.0375	0.0485	0.0586	$\ln k = - (4756.7/T) + 12.395$
	4-CP+H ₂ O ₂ +Fe ³⁺	0.0257	0.0336	0.0442	0.0551	0.0681	$\ln k = - (4486.0/T) + 11.662$
	4-CP+UV+H ₂ O ₂ +Fe ²⁺	0.0321	0.0412	0.0589	0.0726	0.0898	$\ln k = - (4818.5/T) + 13.013$
	4-CP+UV+H ₂ O ₂ +Fe ³⁺	0.0343	0.0436	0.0609	0.0795	0.0931	$\ln k = - (4770.6/T) + 12.911$

Table 4 : Energy, Enthalpy, Entropy and Gibbs Free Energy of activation values

No.	System	A	E _a , kJ/mol	ΔH^\ddagger , kJ/mol	ΔS^\ddagger , J/mol K ⁻¹	ΔG^\ddagger , kJ/mol
1	2-CP+H ₂ O ₂ +Fe ²⁺	10.053	32.25	29.63	-169.8	80.22
	2-CP+H ₂ O ₂ +Fe ³⁺	10.756	33.97	31.35	-163.9	80.20
	2-CP+UV+H ₂ O ₂ +Fe ²⁺	6.355	22.64	20.05	-194.6	78.03
	2-CP+UV+H ₂ O ₂ +Fe ³⁺	6.994	24.2	21.61	-195.2	79.78
2	4-CP+H ₂ O ₂ +Fe ²⁺	12.395	39.69	37.03	-150.3	81.82
	4-CP+H ₂ O ₂ +Fe ³⁺	11.662	37.42	34.78	-156.4	81.39
	4-CP+UV+H ₂ O ₂ +Fe ²⁺	13.013	40.19	37.54	-145.2	80.80
	4-CP+UV+H ₂ O ₂ +Fe ³⁺	12.911	39.79	37.15	-146.0	80.66

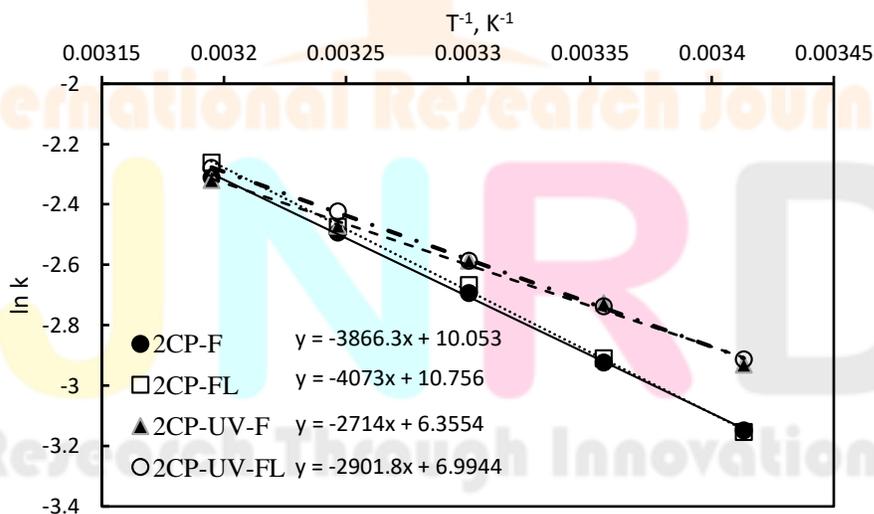


Fig. 5 : Arrhenius plot for 2CP-Fenton processes

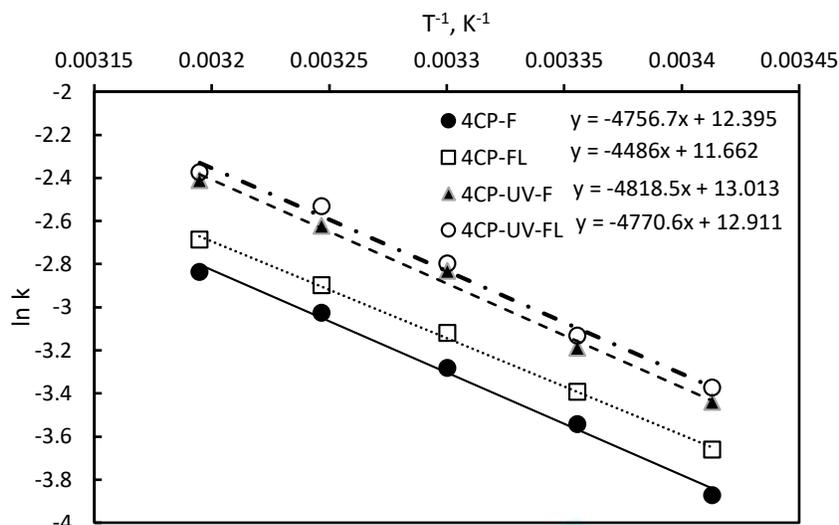


Fig. 6 : Arrhenius plot for 4CP-Fenton processes

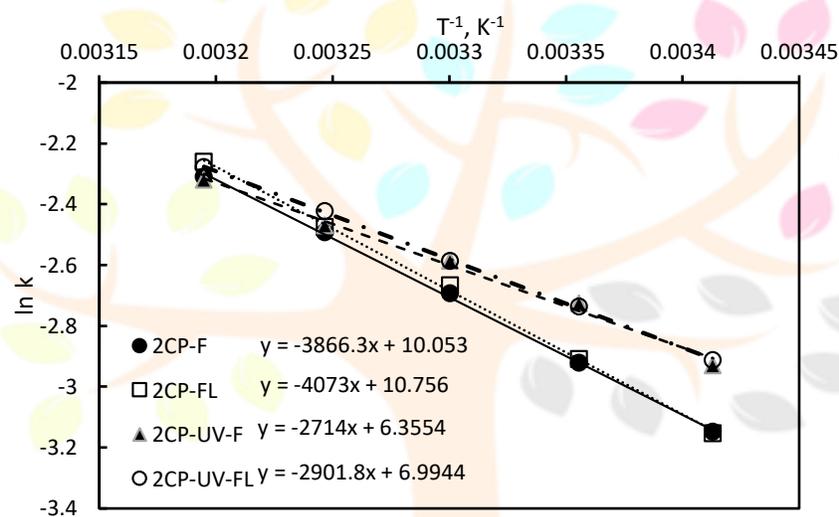


Fig. 7 : Eyring plot for 2CP-Fenton processes

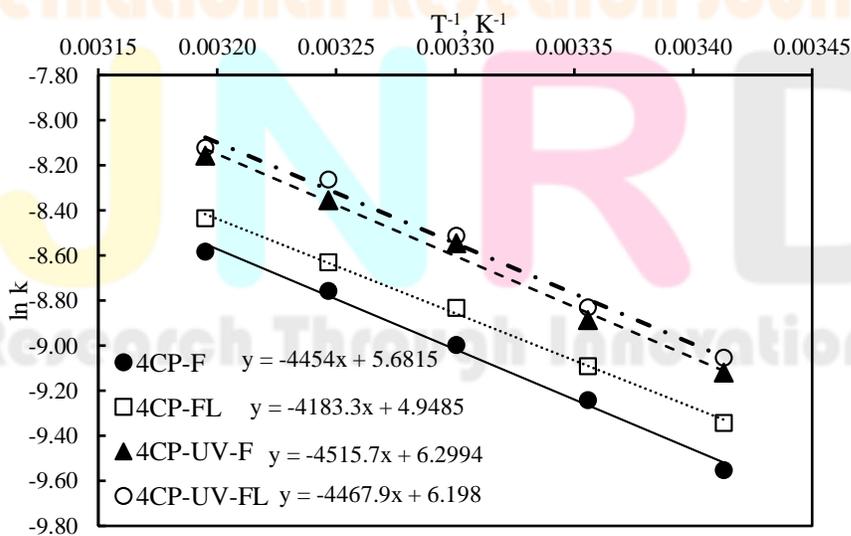


Fig. 8 : Eyring plot for 4CP-Fenton processes

4. Conclusions

Activation energy is minimum amount of energy required for formation of activated complex, which then will lead to the formation of product or return back to the reactant stage by liberating energy. The rise in temperature increases the kinetic energy of the molecules taking part in the chemical reaction, hence the probability of activated collisions leading to the formation of activated complex increases thereby increasing the rate of reaction [9]. Levenspiel [11] stated that reactions with values ranging between 40 and 400 kJ mol⁻¹ are considered low and high activation energy, respectively. The energy of activation of both Fenton and Fenton like process for 2CP and

4CP are very small compared to the activation energy of 170 kJ/mol for noncatalytic oxidation of phenol in aqueous solution below 463 K [12]. This indicates that the Fenton and Fenton-like processes are much faster at ambient temperature and follow a reaction path having very low energy of activation.

In Table 4, positive ΔH^\ddagger values indicating that an external source of energy is required to raise the energy level of reactants for the formation of transition state. Thus, the higher the value of enthalpy of activation, the greater the oxidative stability. The entropy of activation ΔS^\ddagger signifies the extent to which the transition state is disordered as compared to starting materials. The negative values of entropy of activation indicate a more ordered and rigid transition state than the ground state. The Eyring-Polanyi equation, gives a straightforward relationship between ΔG^\ddagger and first-order reaction rate constant. In the AOPs studied in present work, the rate constants are of the order of $\approx 8 \times 10^{-4} \text{ sec}^{-1}$ at 298 K and ΔG^\ddagger values around 80 kJ/mol⁻¹ implying a reaction with half-life of $t_{1/2} \approx 15 - 20$ min. A free energy of activation of this magnitude will correspond to a typical reaction that proceeds to completion within few hours. Increase in the temperature shows positive influence on the oxidative degradation of pollutants and the increase in degradation rate at higher temperatures is mainly due to higher probability of formation of activated complex and the availability of abundant $\cdot\text{OH}$ which enhanced the degradation of pollutants [13]. These results also bring out the advantages of Fenton and Fenton-like processes as they can be performed at ambient temperature and pressure. They show excellent potential of treating water and wastewater at enhancement of degradation efficiency.

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