

DEGRADATION KINETICS OF P,P'-DDT IN AQUEOUS MEDIUM BY FENTON'S AND ELECTRO GENERATED FENTON'S OXIDATION

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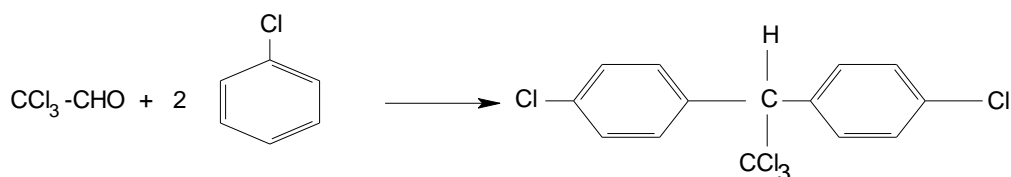
Abstract.

p,p'-DDT[(1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane)] is an organochlorine insecticidewidely used by American troops during World War II for controlling illness like malaria, typhus, yellow fever, bubonic plague, especially in Italy and in tropical regions like the South Pacific. The degradation of *p,p'-DDT* in water by different types of oxidation methods viz. Fenton's (H_2O_2 / Fe^{2+}) oxidation method and electro generated Fenton's oxidation method was carried out in this study. In classical Fenton's reaction externally added Fe^{2+} facilitate the generation of hydroxyl free radical. In electro generated Fenton's method, in situ generated Fe^{2+} facilitate the oxidative cleavage of *p,p'-DDT*. In classical Fenton's reaction, 76.38% of *p,p'-DDT* was degraded within 5 minutes of contact time at pH4. Further extending the contact time up to 75minutes, 98% of *p,p'-DDT* was degraded. In electro generated Fenton's reaction even in the absence of externally added hydrogen peroxide 50.54% of *p,p'-DDT* was degraded with in 30minutes of contact time. The degree of degradation was increased to 71.23% with the external addition of 0.5ml of 50% hydrogrn peroxide. Kinetics data obtained from electro generated Fenton's reaction fitted with pseudo first order kinetics. This study is a baseline study for the removal of *p,p'-DDT* from industrial effluent system.

Key words: *p,p'-DDT* ; Fenton's oxidation; sacrificial anode.

1. INTRODUCTION

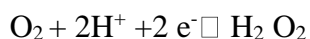
Pesticides are chemical substances intended for preventing, destroying, repelling and mitigating any pest, although they can also be used as a plant regulator, defoliant or desiccant. Due to the high consumer expectation and the ever increasing world population, pesticide production and its uses have been increased progressively worldwide during the last decades. DDT is an Organochlorine pesticide and was first synthesised in 1874, but its insecticide property was discovered by Muller in 1939. For that discovery, Muller was awarded the Nobel Prize in 1948. DDT was widely used by American troops during World War II (Brooks, 1976). DDT manufactured by the condensation reaction between chloral (Trichloro acetaldehyde) and monochlorobenzene.



At present, in India DDT is banned for agricultural purposes but still using for controlling vector borne diseases. Soil half-life of DDT is 2 years to 15 years (U. S. Department of Human Health and Human Services 1994). Half-life of DDT in aquatic environment is about 150 years (Callahan et al., 1979). Since DDT is soluble in organic solvent (lipophilic), they tend to accumulate in fatty tissue of ingested organism along the food chain. DDT breaks down into DDD and DDE by microorganism present in the soil or water (Ashish Chauhan and Jashwant Sing, 2015). The distribution and environmental behaviour of pesticides in water stream depends upon season especially rain fall and temperature (Yihan Chen et al., 2018).

In addition to normal methods, many advanced technologies have been reported in recent years for the treatment of pesticide containing waste water. These include microbial degradation technology and membrane bio filtration. But the microbial degradation processes are time consuming and require special kind of microorganism. Recently researchers have given considerable interest in the degradation of pesticides by advanced oxidation processes such as photo catalytic degradation, sonolysis, sonophotolysis, photo Fenton, Electro Fenton, Electro Fenton process with advanced electrode, etc. This study is mainly concentrated on the removal of an organochlorine insecticide p,p'-DDT by an inexpensive and easy method via advanced oxidation processes (AOP) simple Fenton's reagent, Electro generated Fenton oxidation process. Advanced oxidation process (AOPs) are considered clean technologies for treatment of effluent water that apply concept of producing hydroxyl free radicle (OH^\cdot), which will attack the organic molecules. In this study the AOPS techniques are used for the degradation of p,p'-DDT from aqueous system. The efficiency of AOPs is based on the generation of these highly reactive hydroxyl free radicle that are unselective and power full oxidizing species ($E^0 = 2.80\text{V}$) Vs Normal Hydrogen Electrode (NHE) (Aaron and Oturan, 2001).

Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electro chemical processes constitute the emergent methods for the degradation of pesticides. These methods are environmentally friendly and they do not form new toxic wastes (Youssef Samet et al., 2012). One of the advanced Fenton's process is electro-Fenton's process, in this process, electric current used for in situ generation of H_2O_2 by O_2 reduction in presence of dissolved Fe^{2+} (equations 4 & 5) (Nihal outran et al., 2009). Electro - Fenton's process do not create any secondary pollutant because the catalytic cycle convert Fe^{3+} to Fe^{2+} (Olalla Iglesias et al., 2014). In recent years, electro - Fenton's processing has been shown to be an effective alternative for the removal of several substances such as refractory organic compounds from stabilized land fill leachate (Bashir et al., 2013).



2. Materials and methods

2.1 Experimental

a) Classical Fenton's Reaction

Experimental solutions of 1000 ppb p,p'-DDT in distilled water was prepared using 100 ppm p,p'-DDT stock solution. All the experiments were carried out in the same experimental procedure which includes optimisation of pH, optimisation of quantity of hydrogen peroxide and contact time followed by kinetic study. 1ml of 100 ppm stock solution was spiked in 100ml distilled water used, to this varying amount of

FeSO₄ and hydrogen peroxide (50%) was added under uniform shaking. Kinetic study was conducted with the optimum dose of Fenton's reagent for 30 minutes in an interval of 5 minutes. After the reaction the entire reaction mixture was then extracted as per APHA (2012) method. Progress of the degradation reaction was monitored by analysing the sample in Gas chromatography with electron capture detector (Agilent GC 7890A).

b) Electro generated Fenton's reaction

Influence of electric current in the degradation of p,p'-DDT was explored by conducting electrochemical experiments with iron as sacrificial anode and graphite rod as cathode. The electrode was connected to power source of 9 volt, 150 MA current. In addition to in situ generated hydrogen peroxide, balance amount of hydrogen peroxide was added drop wise with agitation provided by magnetic stirrer (Nidheesh, Gandhimathi .,2012). During electrochemical reaction, current flowing through the system was monitored. pH of the solution was adjusted with sulphuric acid and supply of air was rendered from air cylinder. Kinetic study was conducted with optimum dose of hydrogen peroxide up to 75 minutes with the interval of 15 minutes and analysis was carried out in the interval of 15 min.

2.2 Analytical method

Gas chromatographic method was used for the analysis of p,p'-DDT. After the reaction, entire reaction mixture was extracted as per APHA (2012) method. Hexane layer was injected in Agilent GC7890A provided with electron capture detector (ECD) equipped with split/splitless capillary injection system and with HP- 5 column (30m X 0.32mm X 0.25µm film thickness). The operating conditions were as follows: The column was held at 214^oC (isothermal). The temperature of injector and detector were maintained 250^oC and 300^oC respectively. Nitrogen gas was used as a carrier gas at a flow rate of 0.8 ml/min (5.0 psi) and injection was made in split mode with a split ratio of 1:10.

2.3 Reagents

All the reagents used were of analytical grade. All the glassware's used were of Borosil. Distilled water was used for making synthetic effluent water. All the glass wares were cleaned and dried at 110^oC for 5hr. Standard p,p'-DDT 99% procured from SIGMA – ALDRICH was used for the entire experiments.

3. Results and discussion

3.1 Optimisation of pH in Fenton's reaction

Fenton's reaction was carried out in synthetic effluent water containing 1000ppbp,p'-DDT under different pH. The appreciable degree of degradation was observed at pH 4. At pH 4, 93.28% of p,p'-DDT was degraded with the Fenton's reagents combination of 0.25g FeSO₄ + 0.5ml of H₂O₂ in 30 minutes of contact time. Degree of degradation of p,p'-DDT with pH is depicted in the Figure 1. At acidic pH, H₂O₂ decomposes to produce hydroxyl free radical, whereas at pH > 4 iron precipitate to form ferric hydroxide (VrushaliPawar and SagarGawande, 2015). At higher pH, lesser hydroxyl free radicals are generated due to the presence of lesser Fe²⁺ ions (ArjunanBabuponnusami and KaruppanMuthukumar, 2014).

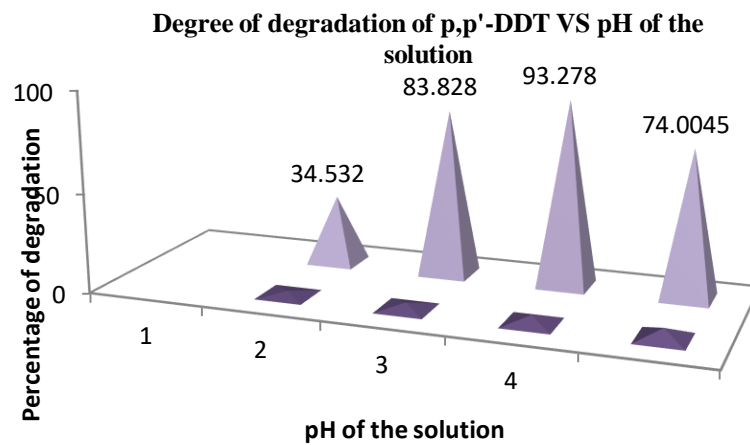


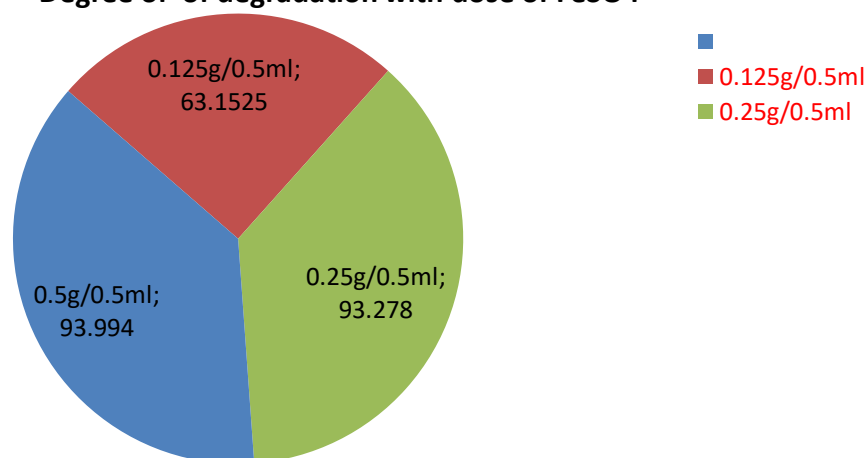
Fig 1 Degree of degradation of p,p'-DDT with pH

3.2 Optimisation of hydrogen peroxide in Fenton's reaction

To study the effect of hydrogen peroxide in the degradation of p,p'-DDT, Fenton's reaction was carried out by using 0.25g FeSO₄ at optimized pH (pH4) with varying amount of hydrogen peroxide. It was observed that maximum degradation (93.28%) was achieved by Fenton's reaction with the dosage 0.5ml of hydrogen peroxide (50%). The degree of degradation of p,p'-DDT was increases with increasing hydrogen peroxide from 0.1 ml to 0.5ml, there after starts to decreases with increasing in the amount of hydrogen peroxide. The lower degree of degradation at higher dose of hydrogen peroxide is due to scavenging effect of excess hydrogen peroxide over hydroxyl free radical (Kavitha and Palanivelu, 2005). More over the excess and unreacted hydrogen peroxide in the treated water is again creating toxicity threat to the aquatic environment.

3.3 Optimisation of FeSO₄ in the degradation of p,p'-DDT by Fenton's reaction

Ferrous ion concentration plays an important role in the Fenton's reaction. Hydroxyl free radicals are generated by decomposition of hydrogen peroxide in the presence of Fe²⁺ ions. To optimize the quantity of hydrogen peroxide in the degradation of p,p'-DDT, Fenton's reaction was carried out with different concentration of Fe²⁺ ions at optimized pH and optimized quantity of hydrogen peroxide. From this study it was observed that, degree of degradation of p,p'-DDT was increasing with increasing in the amount of FeSO₄ and reached maximum value 93% . On further extending the dose of FeSO₄, there was no remarkable increase in the degree of degradation. According to Kang and Hwang, 2000 and Lin et al., 1999, the extent of increase in the degradation rate is limited to certain concentration of FeSO₄ in the Fenton's reaction, on further increase in the dose of Fe²⁺ has no positive effect in the degree of degradation. In addition to that the excess un reacted FeSO₄ will adversely affect quality of treated effluent water as there is increase in the total dissolved solids concentration

Degree of degradation with dose of FeSO₄Fig 2 Degree of degradation in p,p'-DDT with FeSO₄

3.4 Kinetics of Fenton's degradation reaction of p,p'-DDT

Kinetics studies of Fenton's degradation reaction of p,p'-DDT was studied under optimum experimental conditions. Change in the initial concentration of p,p'-DDT with time is tabulated in the Table 1.

Table 1 Degradation of p,p'-DDT with time

Initial concentration	Fenton's reagent FeSO ₄ / H ₂ O ₂	pH of the solutions	Time in min	Amount of DDT remaining in solution			Percentage of degradation
				Expt No 1	Expt No 2	Average	
1000	0.25g/0.5ml	4	0	1000	1000	1000	0
1000	0.25g/0.5ml	4	5	226.91	245.5	236.21	76.38
1000	0.25g/0.5ml	4	15	152.30	140.64	146.47	85.35
1000	0.25g/0.5ml	4	30	68.65	65.79	67.22	93.28
1000	0.25g/0.5ml	4	45	35.45	34.12	34.79	96.52
1000	0.25g/0.5ml	4	60	21.8	22	21.90	97.81
1000	0.25g/0.5ml	4	75	20.1	20	20.05	98.00

From this table it was observed that, 76.38% of p,p'-DDT was degraded within 5 minutes of contact time. Further extending the contact time up to 75minutes, 98% of p,p'-DDT was degraded. Rate equation for p,p'-DDT can be written as follows.

$$d[A]/dt = -k[c]^n \quad (1)$$

'[A]' is the molar concentration of p,p'-DDT, 'k' represents the rate constant of the reaction and 'n' represent the order of the reaction.

For zero order reaction, the rate equation can be represented as follows.

$$d[A]/dt = -k_0 \quad (2)$$

According to zero order reaction equation no (2), rate of a reaction does not depend up on the initial concentration of reactant and depends up on other factors like catalyst so that, plot of [A] with time should be a straight line.

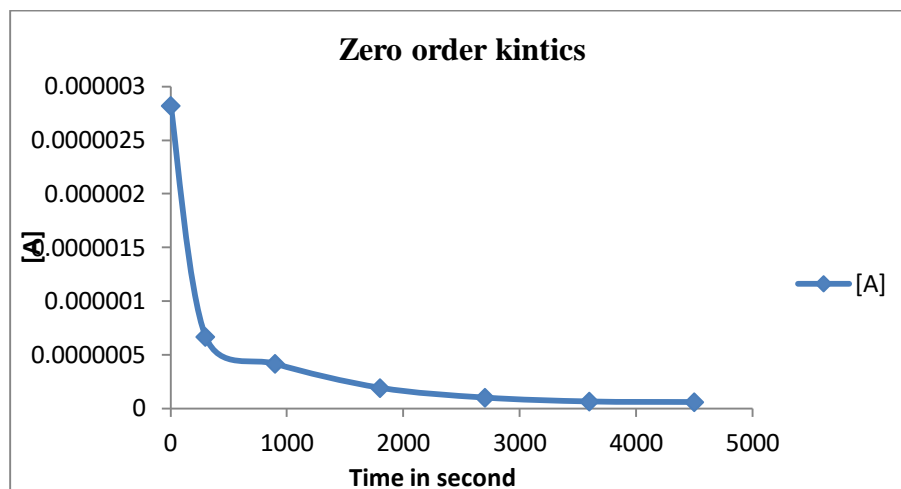


Fig 3 Zero order kinetics of p,p'-DDT degradation with Fenton's reaction

Molar concentration of p,p-DDT is plotted against time in the Figure 3. From the Figure 3, it was observed that, initial concentration of p,p'-DDT was not linearly varied with time which confirms that degradation of p,p;-DDT by Fenton's reaction does not follows zero order reaction. The R^2 values obtained from the first order and second order kinetics graphs indicated that, degradation of p,p-DDT with Fenton's reaction does not follows either first order or second order kinetics but follows pseudo second order reactions.

Table 2 Regression coefficients (R^2) of first order and second order reaction

Experiment	Order of reaction	Regression coefficients (R^2)
Without aeration	First order kinetics	0.8729
	Second order	0.9724

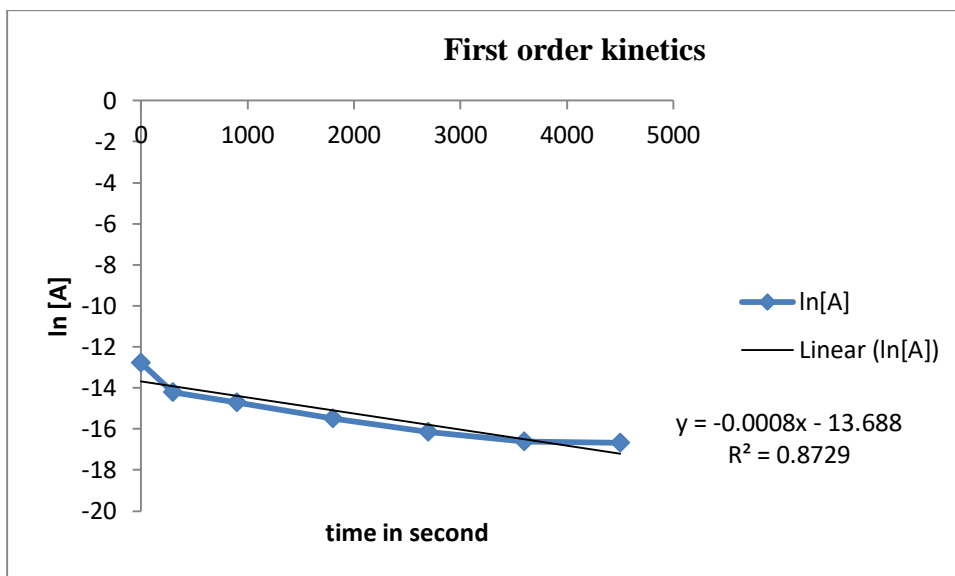


Fig 4 First order kinetics of p,p'-DDT degradation with Fenton's reaction

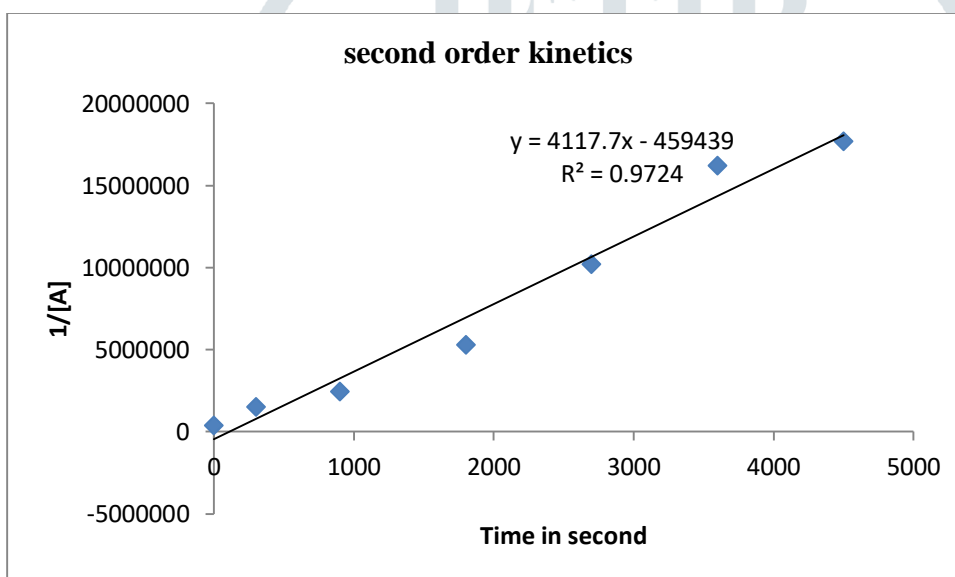


Fig 5 Second order kinetics of p,p'-DDT degradation with Fenton's reaction

3.5 Optimisation of hydrogen peroxide

When electric current is passed through the synthetic effluent water containing 1000ppb p,p'-DDT having Fe rode and anode and graphite as cathode, DDT was degraded with in situ generated hydrogen peroxide and Fe^{2+} ion. But the extant of degradation was limited only to 50.54%. By the external addition of hydrogen peroxide, the degradation percentage was increased to 72.7%. Variation in the degree of degradation of p,p' DDT with external added hydrogen peroxide under electro-generated Fenton reaction was tabulated in the Table 3. From the Table 3 it was observed that degree of degradation increased to the maximum value 72.4% with the addition of 0.5ml of 50% hydrogen peroxide and there after decreases with further extending the dose of external added hydrogen peroxide.

Table.3 Degree of degradation in p,p'-DDT with hydrogen peroxide under electro-generated Fenton's reaction

Initial concentration of DDT in ppb	Contact time in minutes	Amount of Hydrogen peroxide in ml	pH	concentration of DDT remaining in ppb			Degradation percentage %
				Expt NO 1	Expt No2	Average	
1000	30	0	3	509.9	479.3	494.6	50.54
1000	30	0.5	3	266.16	290.42	278.29	72.17
1000	30	1	3	492.65	492.41	492.53	50.75
1000	30	1.5	3	479.04	470.99	475.015	52.50

3.6 Kinetics of p,p'-DDT degradation with electro-generated Fenton's reaction

Electro generated Fenton's reaction facilitate the use of in-situ generated Fe^{2+}/Fe^{3+} and hydrogen peroxide. Fe^{2+} continuously supplied to the solution from the oxidation of Fe anode (sacrificial electrode) by the reaction



The Fe^{2+} produced at anode got converted in Fe^{3+} by Fenton's reaction. Since entire experiments was carried out at pH 3, the chance of $Fe(OH)_3$ formation was ruled out. From the Table 4 it was observed that 64.97% of p,p'-DDT was degraded within 15 minutes of contact time. On further extending the contact time up to 75 minutes, degree of degradation of p,p'-DDT was found to be 72.5%.

Figure 4.6 represents zero order kinetics graphs. From the Figure 6 it was observed that plot of molar concentration against time was not follows zero order kinetics. Figure 7 and Figure 8 represents first order and second order kinetics of p,p'-DDT with electro-generated Fenton's reaction. Regression coefficients of the first order and second order kinetics graphs are plotted in the Table 5. R^2 values obtained from the both first order and second order kinetics graphs indicates that degradation of p,p'-DDT with electro-generated Fenton's was not following either first order or second order kinetics, but follows pseudo second order kinetics.

Table 4 Degradation of p,p'-DDT with time under electro-generated Fenton's reaction

Initial concentration of DDT in ppb	Contact time in minutes	Amount of Hydrogen peroxide in ml	pH	Concentration of DDT remaining in ppb			Degradation percentage %
				Expt NO 1	Expt No2	Average	
1000	0	0.5	3	1000	1000	1000	0.00
1000	15	0.5	3	348	352.6	350.3	64.97
1000	30	0.5	3	284.9	290.42	287.66	71.23
1000	45	0.5	3	283.2	282.9	283.05	71.70
1000	60	0.5	3	284.89	270.77	277.83	72.22
1000	75	0.5	3	283.5	265.12	274.31	72.57

Zero order kinetics

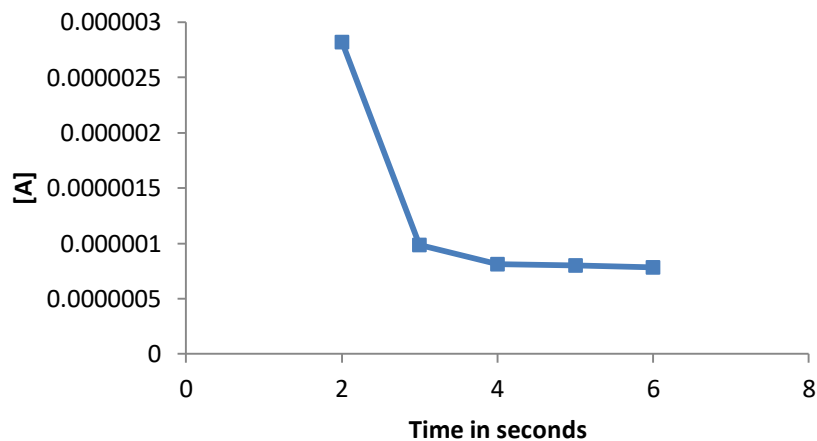


Figure 6 Zero order kinetics of p,p'-DDT under electro-generated Fenton's reaction

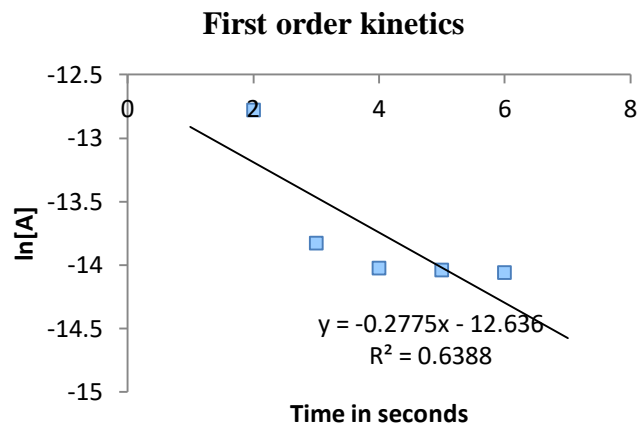


Figure 7 First order kinetics of p,p'-DDT under electro-generated Fenton's reaction

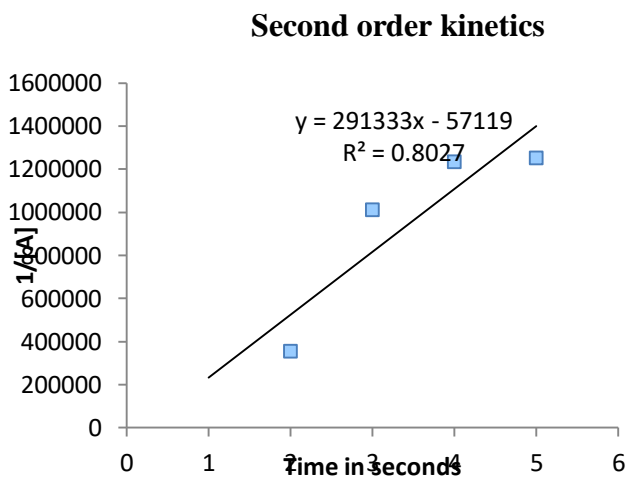


Figure 8 Second order kinetics of p,p'-DDT under electro-generated Fenton's reaction

Table 5 Regression coefficient with order of reaction

Experiment	Order of reaction	Regression coefficients (R ²)
Electro generated Fenton's Reaction	First order kinetics	0.6388
	Second order	0.8027

4. Conclusions

- ❖ Optimum pH in classical Fenton's reaction was found to be 4. At this pH 93.28% degradation of p,p'-DDT was achieved with the Fenton's reagent 0.50mg Fe²⁺/ ml and 0.029g H₂O₂ /ml within 30 minutes of contact time.
- ❖ In electro generated Fenton's reaction 50.54% degradation of p,p'-DDT was achieved even in the absence of externally added hydrogen peroxide but 71.23% of degradation was attained with dosage of 0.0029g of H₂O₂ /ml in 30 minutes of contact time.
- ❖ Kinetic study reveals that, during classical and electro generated Fenton's reaction p,p'-DDT degradation does not follow either first order or second order kinetics, and is found to obey pseudo second order kinetics.
- ❖ In Electro generated Fenton's reaction supply of Fe²⁺ is rendered by sacrificial Iron anode.

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