

Degradation of Pendimethalin in aqueous medium by Fenton's and Electro generated Fenton's oxidation

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Abstract

Pendimethalin (*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) is a selective herbicide used to control most of the annual grasses and many annual broad leaved weeds. The degradation of Pendimethalin 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 Pendimethalin. In classical Fenton's reaction, complete degradation of Pendimethalin was observed at pH 3 with 30 minutes of contact time and follows pseudo first order kinetic model.

In Electro generated Fenton's reaction, under aeration, 88.4% of Pendimethalin was degraded within 30 minutes of contact time even in the absence of externally added hydrogen peroxide and complete degradation was observed after 120 minutes with externally added hydrogen peroxide. Kinetics data obtained from electro generated Fenton's reaction were fitted with first order kinetics.

Keywords: Pendimethalin; Fenton's oxidation; sacrificial anode.

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 increased progressively worldwide during the last decades. Pendimethalin (*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) is one of the widely used selective herbicides in the world. It is used to control most of the annual grasses and many annual broad leaved weeds¹⁴.

The structure of Pendimethalin is shown in fig. 1. Due to the excessive and indiscriminate uses of pesticides, water streams have been contaminated which may be either by rain fall or leaching. An unguarded and important compartment of environment is water and the contamination of water is a major environmental issue.

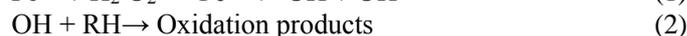
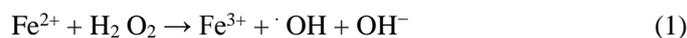


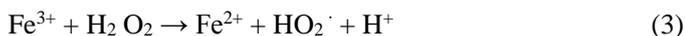
Figure 1: Pendimethalin molecule.

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 herbicide, Pendimethalin by an inexpensive and easy method via advanced oxidation processes (AOP) simple Fenton's reagent and Electro generated Fenton oxidation process.

For the removal of persistent organic pollutants (POPs) form contaminated water, advanced oxidation process is employed. AOP is environmentally friendly method based on the *in situ* production of $\cdot OH$ (Hydroxyl free radicle). Hydroxyl free radicle is the second strongest oxidant known after fluorine with $E^\circ(\cdot OH/H_2O) = 2.8 \text{ V vs. NHE}$ (normal hydrogen electrode)¹. These techniques are applied when conventional oxidation techniques become insufficient by kinetic reasons or because contaminants are refractory to chemical oxidation in aqueous medium or are partially oxidised yielding stable byproducts showing even greater toxicity than the starting pollutants.

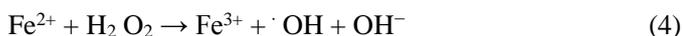
In contrast, $\cdot OH$ generated in AOPs can selectively destroy most organic and organometallic pollutants until total mineralization. These radicals react rapidly with organics mainly either by abstraction of a hydrogen atom (dehydrogenation) or by addition to a non-saturated bond (hydroxylation) equations (1, 2 and 3)³.





Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electrochemical processes constitute the emergent methods for the degradation of pesticides. These methods are environmentally friendly and they do not form new toxic wastes¹⁵. One of the advanced Fenton's process is electro-Fenton's process. In this process, electric current is used for *in-situ* generation of H_2O_2 by O_2 reduction in presence of dissolved Fe^{2+} (equations 4 and 5)³. Electro-Fenton's process does not create any secondary pollutant because the catalytic cycle converts Fe^{3+} to Fe^{2+} ¹².

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 leachate⁶.



Material and Methods

Classical Fenton's Reaction: Experimental solutions of 1000 ppb Pendimethalin in distilled water were prepared using 100 ppm Pendimethalin 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 FeSO_4 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 APHA² method. Progress of the degradation reaction was monitored by analysing the sample with gas chromatography with electron capture detector (Agilent GC 7890A).

Electro generated Fenton's reaction: Influence of electric current in the degradation of Pendimethalin 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 stirrer¹⁰. 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 120 minutes with the interval of 15 minutes and analysis was carried out in the interval of

15min. Schematic diagram of lab-scaled electrochemical system with open and magnetic stirred two-electrode undivided reactor setup for electro generated Fenton's reaction is represented in figure 2.

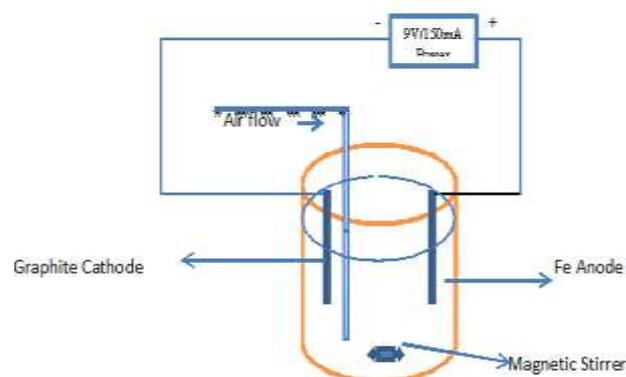


Figure 2: Lab – scaled two-electrode undivided electrochemical system

Analytical method: Gas chromatographic method was used for the analysis of Pendimethalin. After the reaction, entire reaction mixture was extracted as per APHA² method. Hexane layer was injected in Agilent GC7890A provided with electron capture detector (ECD) equipped with split/split less capillary injection system and with HP- 5 column (30m X 0.32mm X 0.25 μm film thickness). The operating conditions were as follows: The column was held at 214 $^{\circ}\text{C}$ (isothermal). The temperature of injector and detector were maintained 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ 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. Chromatogram of Pendimethalin reference standard analyzed in the above condition is given in figure 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 glasswares were cleaned and dried at 110 $^{\circ}\text{C}$ for 5hr. Standard Pendimethalin 98.8% obtained from SIGMA – ALDRICH was used for the entire experiments.

Results and Discussion

Optimisation of pH in Fenton's reaction: Effect of pH on the degradation of Pendimethalin by Fenton's process is shown in table 3. The experimental data reveals that 90.88% of Pendimethalin was degraded at pH 3. Variation in the percentage degradation with pH is illustrated in figure 4. Generation and subsequent reaction of hydroxyl free radicals in Fenton process involve complex chain reactions⁹. The first step in this reaction is chain initiation and it requires proton and hence is a proton abstraction step.

At higher pH, >4 it has a tendency to form ferric ion which will lead to the formation of relatively inactive ferric hydroxo complexes. In addition to that, hydrogen peroxide

is also unstable in basic solution and may decompose to give oxygen and water there by losing its oxidation ability.

Amount of Pendimethalin remaining in the solution against pH after degradation is shown in table 1.

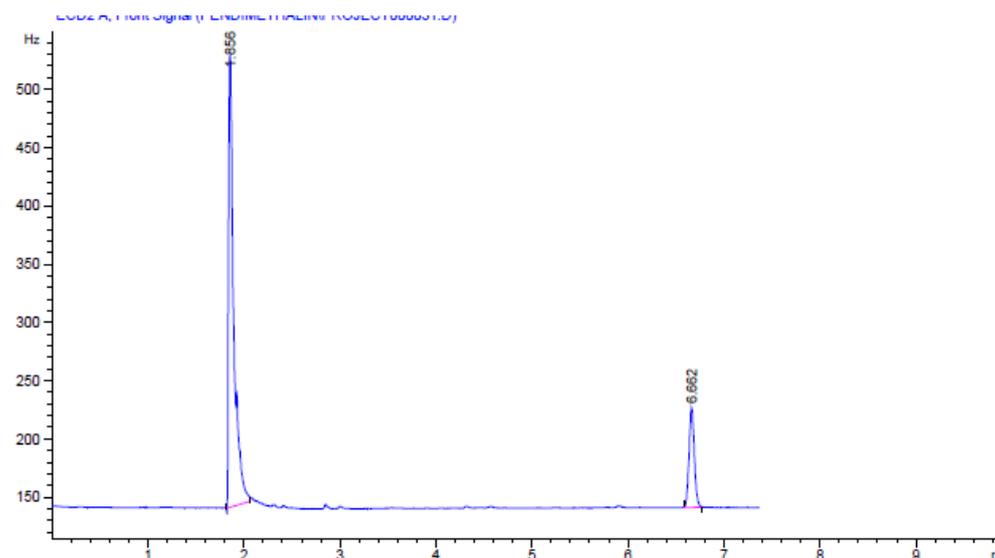


Figure 3: Reference standard chromatogram of Pendimethalin

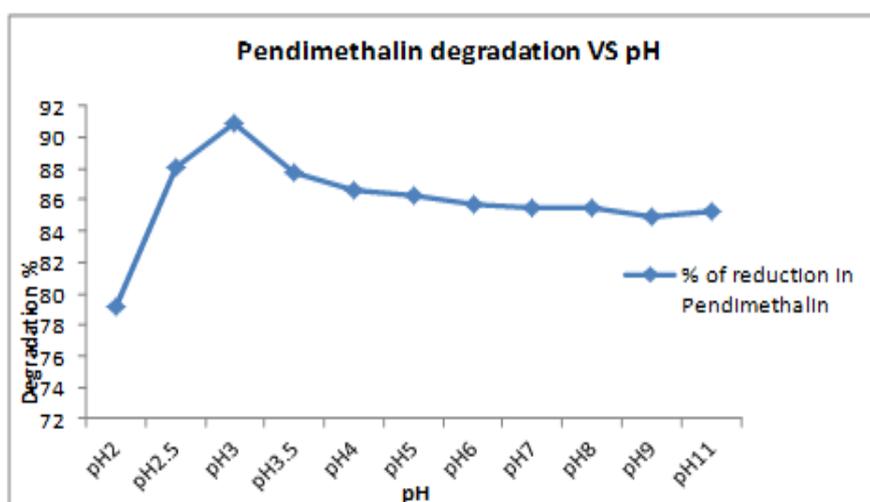


Figure 4: Effect of pH in the degree of degradation in Pendimethalin

Table 1
Effect of pH in the degradation of Pendimethalin

Initial concentration of Pendimethalin in ppb	pH of the reaction mixture	Contact time in minute	Pendimethalin remaining in the solution (ppb)
1000	2.0	30	208.16
1000	2.5	30	119.85
1000	3.0	30	91.15
1000	3.5	30	122.36
1000	4.0	30	135.00
1000	5.0	30	137.60
1000	6.0	30	143.15
1000	7.0	30	145.36
1000	8.0	30	152.40
1000	9.0	30	150.98
1000	11.0	30	143.71

The oxidation potential of the hydroxyl radical was known to decrease with increasing pH¹¹. Another reason for the inefficient degradation at pH >3 is the dissociation and auto decomposition of H₂O₂⁵. For pH values below 2.5, the reaction of hydrogen peroxide with Fe²⁺ is seriously affected causing reduction in hydroxyl radical production due to hydroxyl radical scavenging H⁺ ions¹¹. From the optimisation study, it was observed that better pH for degradation of Pendimethalin is pH 3.

Optimisation of hydrogen peroxide in Fenton's reaction:

Concentration of hydrogen peroxide played a crucial role in the degradation of Pendimethalin. The dosing rate of hydrogen peroxide is considered to be one of the most important factors in Fenton's process. Unconsumed hydrogen peroxide is not only harmful to organisms, which also acts as scavenger for hydroxyl free radical⁸. The degradation percentage of Pendimethalin was increased from 78.71% to 100% with increase of hydrogen peroxide (50%) dosage from 0.5ml (0.59g/100 ml) to 5ml (5.98g/100ml) at an optimum pH value 3 and is illustrated in figure 5.

The experimental study reveals that 100% degradation of Pendimethalin occurred with the Fenton's combination of 50

mg of Fe²⁺/5ml H₂O₂ per 100 ml at 30°C. The change in concentration of Pendimethalin with dose of hydrogen peroxide is tabulated in table 2. From this study it was observed that optimum value of hydrogen peroxide for the complete degradation of Pendimethalin was found to be 5ml/100ml.

Kinetics of degradation of Pendimethalin in Fenton's reaction:

Series of experiments were carried out with different concentration of Fe²⁺ ion varying from 5mg to 60 mg per 100ml under the same dose of 5 ml (5.98g/100ml) H₂O₂ for 30min. It was observed that the extent of 100% degradation was obtained at 50mg Fe²⁺/2.5g H₂O₂. Kinetic studies were carried out with optimum value of Ferrous ion concentration 50mg /100ml, 5 ml H₂O₂ (5.98g/100ml) and at pH 3. The change in initial concentration of Pendimethalin with time is tabulated in table 3.

Figure 6 shows that 95% degradation attains within 10 minute of reaction time and after extending the reaction time up to 30 min, the degradation percentage of Pendimethalin was found to be 100%. From the graph, a sharp increase in the percentage of degradation was observed up to 10 min and after 10 min, degradation rate was found to be almost constant.

Table 2
Degradation of Pendimethalin with the dose of hydrogen peroxide

Initial concentration of Pendimethalin in ppb	Fenton's Reagent		Amount of Pendimethalin remaining (in ppb)		
	Fe ion in mg/100ml	Hyrogenperoxide in ml	Expt No 1	Expt No 2	Mean
1000	50	0.50	185.73	240.00	212.87
1000	50	1.00	103.40	78.90	91.15
1000	50	1.50	51.80	37.70	44.75
1000	50	2.00	26.27	39.50	32.89
1000	50	3.00	29.00	34.29	31.65
1000	50	4.00	19.40	29.00	24.20
1000	50	5.00	0.00	0.00	0.00

Table 3
Change in initial concentration of Pendimethalin with time

Initial concentration of Pendimethalin in ppb	Contact time in minute	Amount of Pendimethalin remaining (in ppb)		
		Expt No 1	Expt No 2	Mean
1000	0	1000	1000.00	1000.00
1000	1	543.2	521.80	532.50
1000	5	185.16	151.08	168.12
1000	10	45.53	36.64	41.09
1000	15	13.29	16.45	14.87
1000	20	15.71	14.32	15.02
1000	25	9.17	11.20	10.19
1000	30	0	0.00	0.00

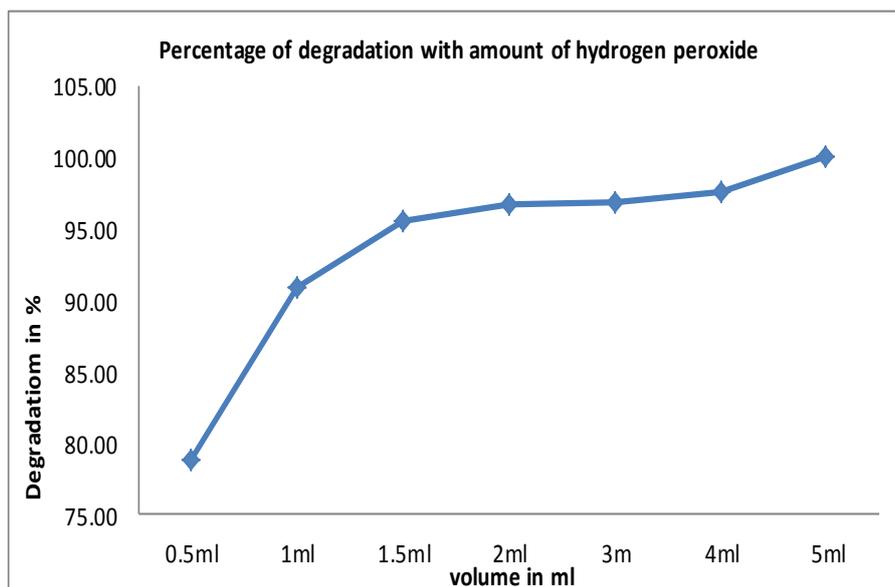


Figure 5: Degradation percentage of Pendimethalin with hydrogen peroxide

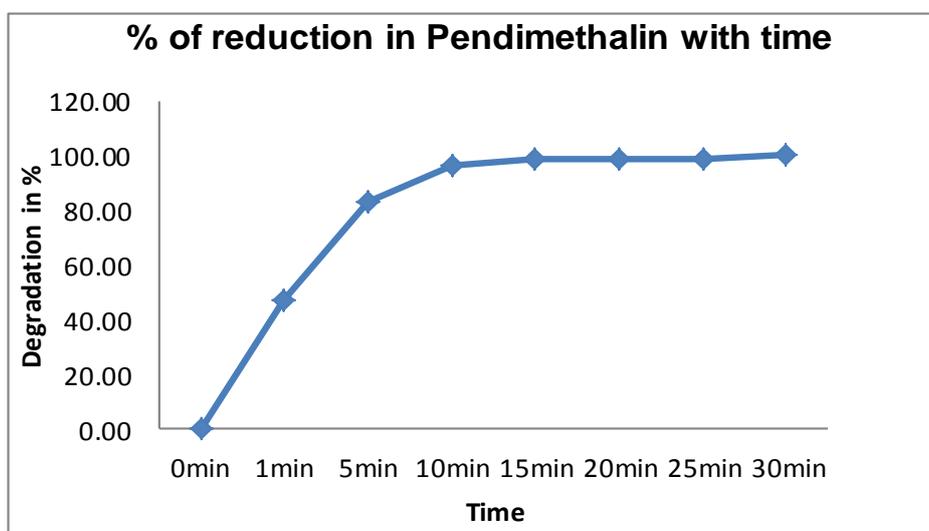


Figure 6: Degradation percentage of Pendimethalin with time

The Fenton's reaction for Pendimethalin can be represented by the following n th order reaction kinetics.

$$dC/dt = -kC^n \quad (6)$$

where C represents the concentration of Pendimethalin, n is the order of the reaction, k represents the rate constant and t the reaction time. For first order reaction, the above equation becomes:

$$C = C_0 \exp(-kt) \quad (7)$$

where C_0 represents the initial concentration of Pendimethalin.

For second order, the integrated equation becomes:

$$C = C_0 / (1 + k C_0 t) \quad (8)$$

Figures 7 and 8 represent first order and second order kinetic graphs for the degradation of Pendimethalin respectively. From figures 6 and 7 it was observed that correlation coefficients (R^2) are found to be 0.8989 and 0.8569 for first order and second order kinetics respectively. The first order and second order kinetics do not fit the data very well for the whole classical Fenton's reaction due to the lower regression coefficients (<0.96). Several investigations have found that Fenton's reaction follows pseudo - first order kinetics⁷ which was quite similar to the results obtained in this study.

Optimisation of hydrogen peroxide in Electro generated Fenton's reaction: When electric current of 150MA was passed through the synthetic effluent water containing 1000ppm Pendimethalin having Fe as anode and graphite as cathode, Pendimethalin degraded with the *in-situ* generated Fe^{2+} and hydrogen peroxide. The percentage of Pendimethalin degradation with *in-situ* generated hydrogen

peroxide was around 46.4%. When hydrogen peroxide was added externally, degree of degradation increases and reaches maximum value that is 85.31% with 1ml 50% hydrogen peroxide. When external supply of hydrogen

peroxide increased more than 1ml, it adversely affect Pendimethalin degradation. Figure 9 represents the percentage of degradation with the amount of hydrogen peroxide.

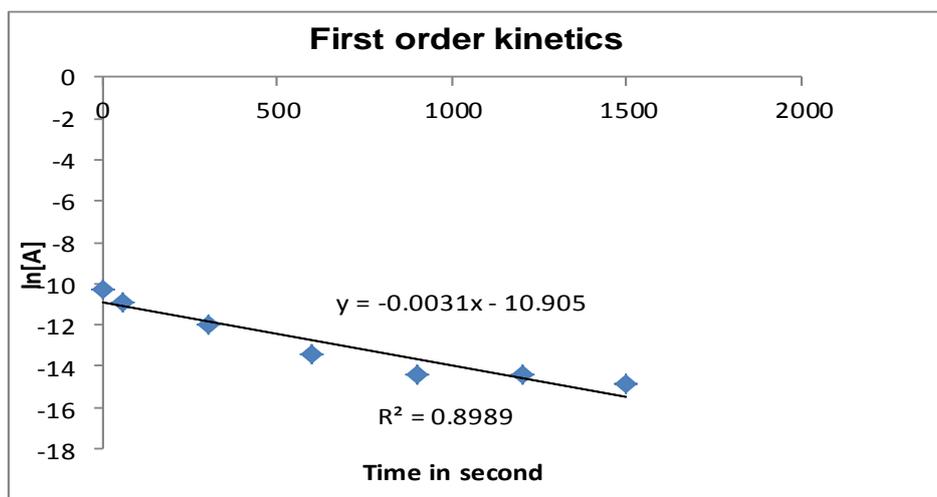


Figure 7: First order kinetics of Fenton's reaction

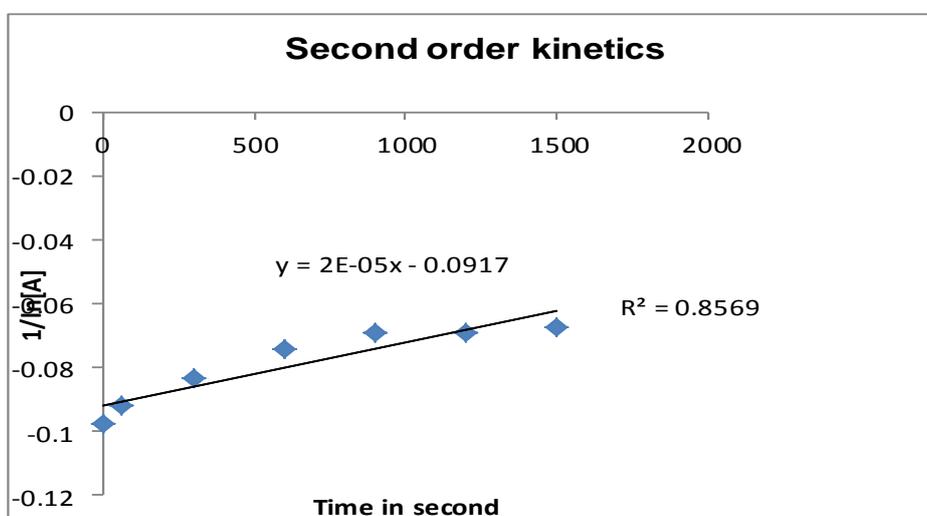


Figure 8: Second order kinetics of Fenton's reaction

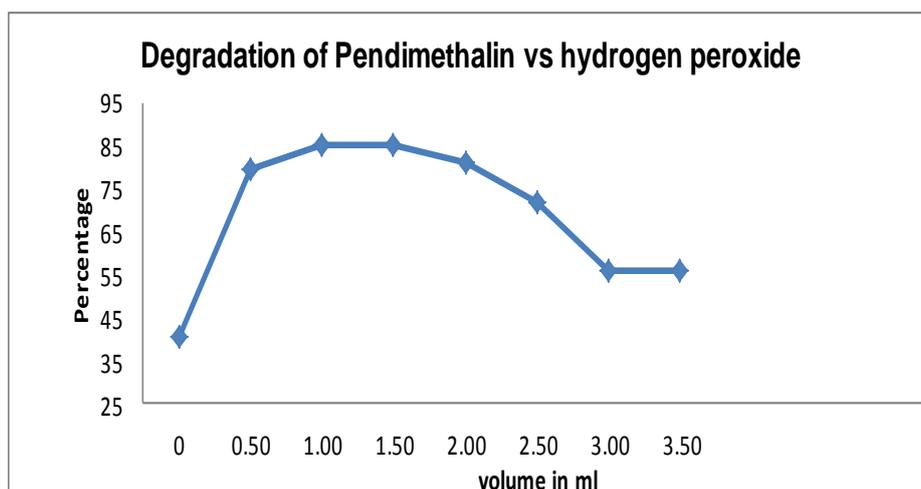


Figure 9: Degree of degradation of Pendimethalin with hydrogen peroxide

Same experiment was carried out with externally added hydrogen peroxide with aeration. Variation in degree of degradation of Pendimethalin was plotted in figure 9. Degradation without addition of hydrogen peroxide was found to be 88.4%, by adding 0.5ml of 50% hydrogen peroxide (0.59 g), the extent of degradation reached 91.39%. On further adding, hydrogen peroxide degree of degradation tends to decrease because the unconsumed hydrogen peroxide is also acting as a scavenger of hydroxyl free radicle⁸.

Degradation of Pendimethalin by electro generated Fenton's oxidation method carried out under external supply of hydrogen peroxide is tabulated in table 4. While considering inhibition property and poisonous nature of hydrogen peroxide at higher dosage, its dosage was optimised to a lower dose of 0.5ml (0.59g/100ml) in both electrochemical reactions with aeration and without aeration.

Kinetics of Pendimethalin degradation in Electro generated Fenton's reaction: The electro generated indirect cleavage proceeds under the action of strong oxidants, similar to the chemical incineration, moreover, *in situ* electro-generation allows better efficiency of the organic substrates destruction and avoids the need for transportation and storage¹³. Electro generated Fenton's reaction facilitates 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+} released from anode undergoes Fenton reaction leading to the generation of Fe^{3+} . The entire experiments were conducted at acidic pH by supplying dilute sulphuric acid. With increase in pH of the solutions, excess ferric ions got precipitated as $Fe(OH)_3$. The combined action, coagulation of $Fe(OH)_3$ and degradation by hydroxyl radical enhance the removal of pesticides⁴. Optimisation of hydrogen peroxide data reveals that in addition to *in-situ* generated hydrogen peroxide at graphite cathode, 0.5ml of 50% hydrogen peroxide (0.25g/100ml) was added externally¹⁶.

Rate of reaction was monitored by analyzing Pendimethalin remaining in the solution using GC with electron capture detector. Amount of Pendimethalin remaining in the solution with reaction time is tabulated in the table 5 and degree of degradation is plotted in figure 10. From the table 5, it was observed that complete degradation of Pendimethalin occurred after 120 minutes in both the experiments that is with and without aeration.

Table 4
Comparison of Pendimethalin degraded during Electro generated Fenton reaction

Initial concentration in ppb	Volume of Hydrogen peroxide in ml	Amount of Pendimethalin degraded without aeration in ppb	Amount of Pendimethalin degraded with aeration in ppb
1000	0.00	464.00	884.42
1000	0.50	796.28	913.97
1000	1.00	852.65	827.05
1000	1.50	853.08	860.64
1000	2.00	808.00	871.09

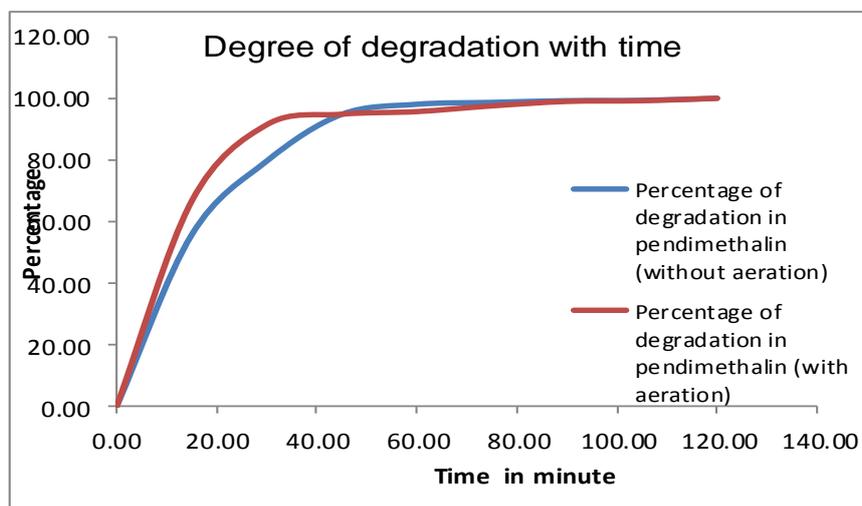


Figure 10: Degree of degradation of Pendimethalin with time

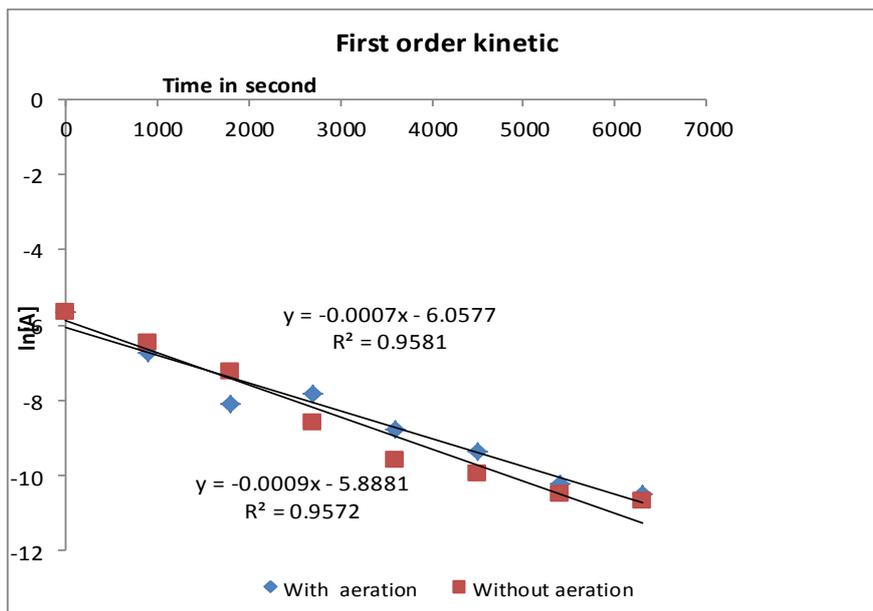


Figure 11: First order kinetics of electro generated Fenton’s oxidation

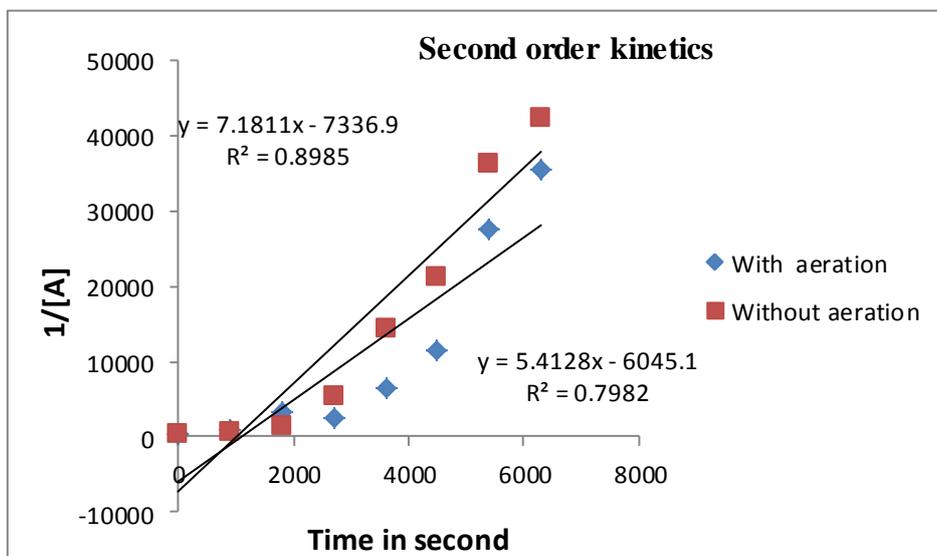


Figure 12: Second order kinetic of electro generated Fenton’s oxidation

Table 5
Amount of Pendimethalin remains in the solution with time

Initial concentration of pendimethalin in ppb	Contact time in Min	Pendimethalin remaining in solution ppb (without aeration)	Pendimethalin remaining in solution ppb (During Aeration)
1000	0	1000.00	1000.00
1000	15	443.05	333.81
1000	30	203.72	85.78
1000	45	52.03	52.10
1000	60	19.42	43.18
1000	75	13.27	24.61
1000	90	7.75	10.18
1000	105	6.61	7.92
1000	120	0.00	0.00

Table 6
Comparison of correlation coefficients obtained in electro generated Fenton's reaction

Experiment	Order of reaction	Regression coefficients (R ²)
With aeration	First order kinetics	0.9581
	Second order kinetics	0.7982
/Without aeration	First order kinetics	0.9572
	Second order	0.8985

From figure 10 it was observed that up to 30 minutes degradation reaction was vigorous and there onwards the reaction was found to be steady in both experiments. It was also observed that in experiments with aeration, the initial reaction up to 30 minutes was found to be faster (91 %) than without aeration (79.6%). Figures 11 and 12 represent the first order and second order kinetic graphs respectively. Regression coefficients (R²) values obtained from figures 11 and 12 are tabulated in table 6. It was observed that electro-generated Fenton's reaction with and without supply of air follows first order kinetics (Table 6) with Regression coefficients (R²) value 0.96.

Conclusion

Optimum pH in classical Fenton's reaction was found to be 3. At this pH 100% degradation of Pendimethalin 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 88.4% degradation of Pendimethalin was achieved even in the absence of externally added hydrogen peroxide and complete degradation was attained with dosage of 0.0029g of H₂O₂/ml in 120 minutes of contact time. Kinetic study reveals that during classical Fenton's reaction, Pendimethalin degradation does not follow either first order or second order kinetics and is found to obey pseudo first order kinetics. In the case of electro-generated Fenton reaction, degradation of Pendimethalin fitted with the first order reaction kinetics.

In Electro generated Fenton's reaction supply of Fe²⁺ is rendered by sacrificial iron anode. Electro generated Fenton's oxidation study leads to the complete destruction of Pendimethalin in effluent water system with minimum hydrogen peroxide and *in situ* generated Fe²⁺ and it was observed that reasonable treatment process time of 120 min is required whereas in classical Fenton's reaction degradation happened only in the presence of externally added Fe²⁺(FeSO₄) and higher amount of Hydrogen peroxide.

The study reveals that the process of oxidizing, Pendimethalin by electro generated Fenton's oxidation can be successfully employed for efficient mineralization of Pendimethalin and this process leads to the complete destruction of Pendimethalin. Electro generated Fenton's oxidation can be used as a green technology for the degradation of Pendimethalin from industrial effluent water.

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