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Advanced Oxidation Processes and DDT Degradation Kinetics with H_2O_2/Sunlight

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Abstract: ***Advanced Oxidation Processes (AOPs) are a group of oxidation processes carried out to remove harmful persistent organic pollutants (POP) from water, which are otherwise very hard to remove. The last century saw a glut of chemical industries rising up to meet the needs of modern day commodity chemicals like detergents, dyes, pesticides and so on. Treatment of effluents of such industries has always been tenacious and cumbersome. Advanced oxidation process has now become the inevitable technology for the future to tackle the inexorable problems of pollution.***

Advanced oxidation process is a set of various methods by which dangerous organic pollutants are broken down to innocuous sub species and carbon dioxide. Normally this is done using a strong oxidizing agent such as H_2O_2 or O_3. These species are dissociated to form oxygen radicals either by irradiation of UV or by suitable catalysts such as Fenton`s reagent or TiO_2. Of all the POPs present, it is pesticides that the general public is most worried about. In our research, we have studied the advanced oxidation using H_2O_2/Sunlight system on two pesticides namely DDT and Dicofol. Time allowed for the process, the pH at which process is carried out, and the amount of H_2O_2 used for the process were found out to be the major parameters on the rate of reaction. The entire study was carried out using an Agilent Gas Chromatograph.

As the result, over 50% reduction in pesticide concentration over a period of 4 hours was found out. The decomposition of DDT, both of its o, p and p, p isomers, was found to follow first order kinetics. The effect of parameters on the reaction kinetics was also studied .This research study provides the kinetic data to design and develop an advanced oxidation treatment plant. It also provides an insight into the application of AOP in the pesticide industry effluent treatment. AOP when implemented along with current methods like solvent extraction, is an eco-friendly and economically feasible option.

Keywords – Advanced oxidation process, DDT, Dicofol

I. INTRODUCTION

The last century saw a glut of new chemical industries rising up to successfully meet the escalating requirements of commodity chemicals like detergents, dyes, pesticides and so on [1] . Treatment of effluents of such industries has always been tenacious and cumbersome. Currently these are centered on solvent extraction or adsorption rather than biological treatment of effluents which can be lethal to the microbes involved.

After its ban for agricultural purposes, the use of DDT has been in the field of malaria eradication. DDT is currently being produced in three countries, India, China and the Democratic People's Republic of Korea and totaled to about 11000 tons in 2007 [2]. Dicofol, a derivative of DDT is a popular acaricide . Both DDT and Dicofol can have detrimental effects on human health and nature.

Advanced Oxidation process is found out to be efficient in removing harmful pesticides from waste water [3]. Of the various methods available, this work focuses on DDT and Dicofol degradation kinetics using H_2O_2/Sunlight system.

II. ADVANCED OXIDATION PROCESS

Advanced Oxidation Processes (AOPs) are a group of oxidation processes carried out to remove harmful persistent organic pollutants (POPs) from water. AOP can be done in various ways namely using H_2O_2/UV, H_2O_2/TiO2, O3, H_2O_2/Fenton's and so on. H_2O_2/UV method used involves formation (1) and reaction (2,3) of hydroxyl radicals [4]. The unstable hydroxyl radicals initiate a chain reaction of oxidative degradation ultimately resulting in CO_2 and H_2O

$H_2O_2 + H_2O^- \rightarrow H_20 + O_2 + HO^*$ (1)

$HO^* + RH \rightarrow R^* + H_20$ (2)

$R^* + O_2 \rightarrow RO_2 \rightarrow$ further degradation (3)

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The process formation of hydroxyl radicals can be sped up by using a suitable catalyst such as TiO_2. Presence of ions such as bicarbonates or sulfates can also inhibit the formation [5].

III. EQUATIONS USED

The correlation between ln C/C0 and the time is linear for a first-order reaction plot. The kinetic expression can be presented as follows:

$$-\ln\left(\frac{C}{C_0}\right) = k.t \quad (4)\ [9]$$

C, C_0 - Concentrations at Time t and at initial conditions respectively.

IV. APPARATUS AND METHOD

A. *For optimizing the H_20_2 Concentration*

1000 ppb samples of DDT and Dicofol were prepared. The DDT and Dicofol used for making the solution was BIS Certified Technical samples with over 90% purity. To the sample solution, add 50% H_2O_2 to make the required concentrations (Volume %) .The time for treatment was fixed at 5 hours.

B. *For Kinetic study*

Using the optimum H_2O_2 concentration, sample industrial effluent was treated. From the initial effluent sample 100 ml was taken out at an interval of an hour and the pesticide was extracted with 10 ml HPLC Grade Hexane (99.9% purity, Merck Chemicals). Remaining amount of water was removed using anhydrous Sodium Sulfate. 1 ml of this solution was diluted to 10 ml using Hexane. The quantitative analysis was performed in an Agilent 7890 Gas Chromatograph with a DB-5 silica capillary column manufactured by Perkin-Elmer.

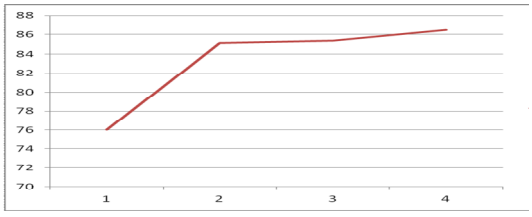
The source of UV was sunlight as artificial UV light when applied on an industrial scale is extremely costly. [7, 8]

V. RESULTS AND DISCUSSION

A. *Optimum Concentration of H_20_2*

The increase in concentration of H_2O_2 showed an appreciable variance in removal efficiency till the 2% concentration. After that the Removal of DDT and Dicofol remained almost unchanged. This stagnancy is due to the increased chances for the hydroxyl radical to react with the superfluous quantity of H_20_2 [6] (5).

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2 \quad (5)$$



Y axis – % removal of DDT X axis – volume% of H2O2

% H2O2	% Removal
1	76.05
2	85.116
3	85.35
4	86.45

Table 1: % Removal of DDT with varying H_2O_2 Conc.

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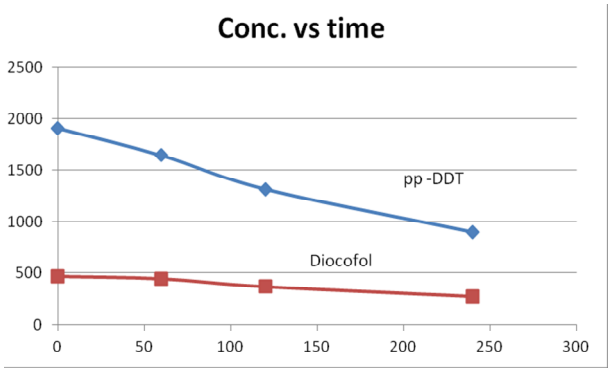
The optimum concentration was found out to be 2% by volume H_2O_2.

B. Concentration reduction

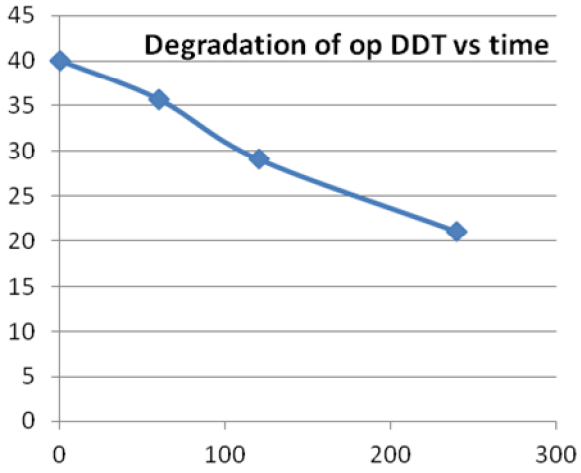
A reduction of 50% was found in both o,p and p,p DDT while Dicofol's reduction was about 42%.

Time(min)	p,p-DDT – (ppb)	o,p – DDT - (ppb)	Dicofol-(ppb)
0	1912	40	464.22
60	1648.67	35.67	441.01
120	1315	29.09	365.78
240	899.9	21.03	272.03

Table 2: Conc. Change with time



Y axis – Concentration in ppb, X axis – Time in minutes



Y axis – Concentration in ppb, X axis – Time in minutes

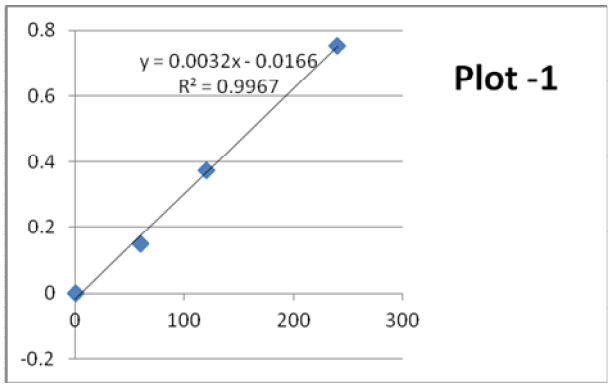
C. Kinetic Study of p,p DDT

As in eq(5), The plot between –ln(C/C0) and time is found to be linear. Hence the reaction follows first order kinetics (plot 1). The correlation coefficient that can explain the extent of fitness the function equation has to the experimental data and is presented by R^2.The high value of R^2 denotes the accuracy of the order approximation.

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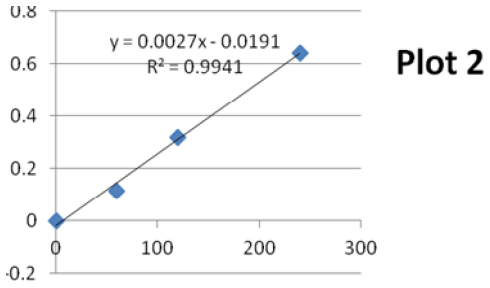
time - min	$\ln\left(\frac{C}{C_0}\right)$
0	-0
60	-0.114569
120	-0.318485
240	-0.642929



$-\ln(C/C_0)$ vs time

Similarly for o,p DDT (Plot 2),

Time Min	$\ln\left(\frac{C}{C_0}\right)$
0	-0
60	-0.114569
120	-0.318485
240	-0.642929



Since the convergence is high for both the cases, assumption of first order is justified.

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VI. CONCLUSION

AOP processes are highly effective for removal of harmful pesticides from water. Of many AOPs available a study using H_2O_2/Sunlight was studied. Sunlight was taken as the UV source as industrial implementation of artificial UV sources can be extremely costly. The study provided with the kinetic data required to build an advanced oxidation plant. Both the isomers of DDT were found to follow a pseudo first order degradation. Possible mechanisms for H_2O_2 action were also reviewed. Identifying the degradation intermediates of DDT requires further research. Making use of sunlight as the UV source limits the flexibility of runtime, but as the majority of pesticide industries are batch processes, solution to this is easy.

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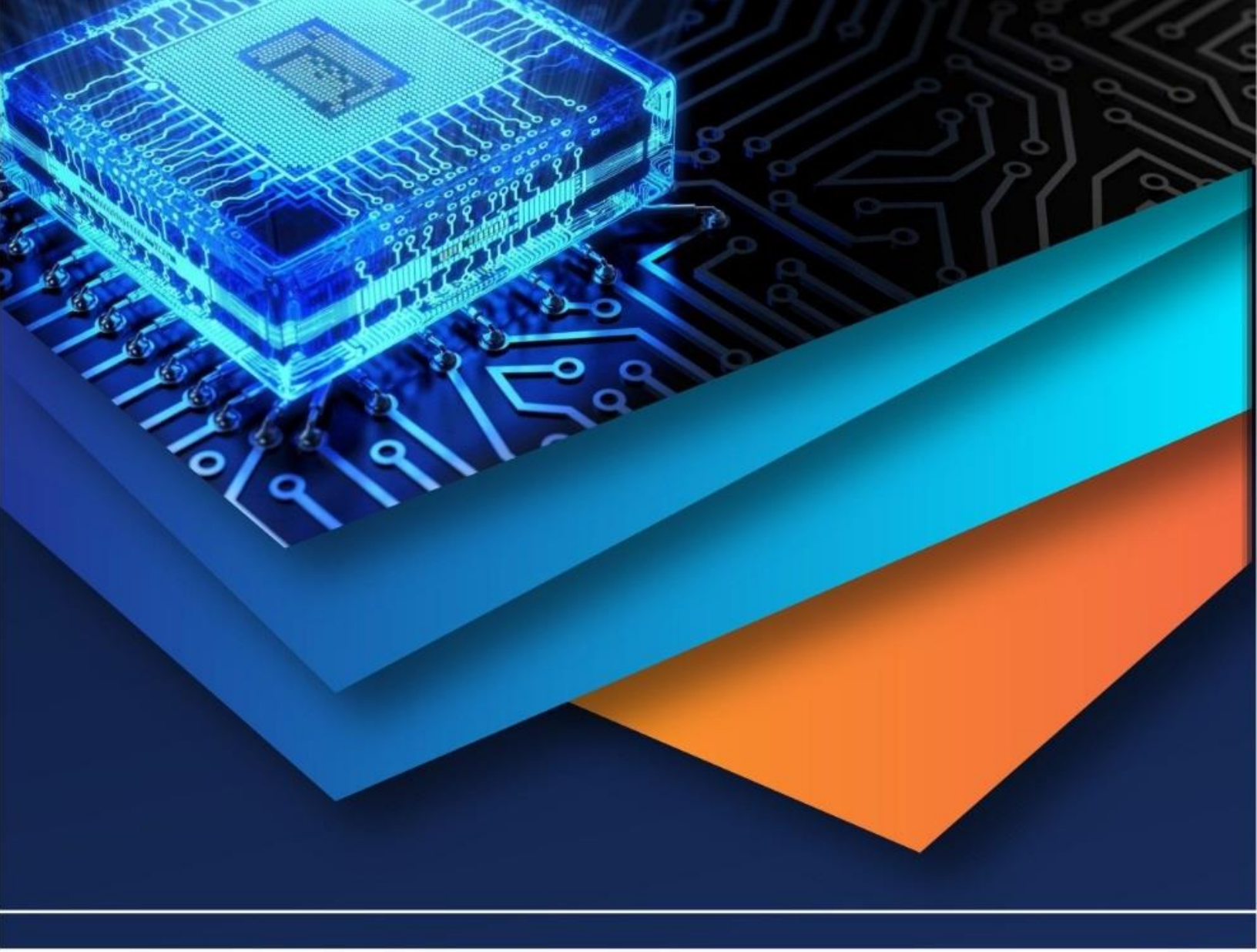
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