Herbicide propanil degradation in aqueous solutions by Fenton's reagent and photo-Fenton system

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Abstract

The chemical degradation of pesticide propanil in water by Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (H_2O_2/Fe^{2+}/UV) processes was investigated. A laboratory set-up was designed to evaluate and select the optimal oxidation process. The degradation rate is strongly dependent on the pH, initial concentrations of the pesticide, H_2O_2 and temperature. The effect of these parameters has been studied and the optimum operational conditions of these two processes were found. The optimum conditions were obtained at pH 7 for the H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV. The kinetics of degradation was found to follow first-order reaction rules. The photo-Fenton system proved to be the most efficient and occurs at a much higher oxidation rate than Fenton system and allows achieving 100% degradation of propanil in 180 min of reaction time. The results of the study showed that photo-Fenton process was an effective and economic treatment process for propanil under neutral conditions by producing higher mineralization efficiency in a relatively short radiation time compared to Fenton process.

Keywords: Propanil ; Advanced oxidation processes (AOPs); Fenton; Photo-Fenton.

Introduction

The pesticide and chemical industries are considered togenerate wastewaters containing toxic and sometimes no biodegradablecompounds that remain in the environment evenafter their wastewaters have been subjected to conventional processing[1]. propanil (3,4-dichloropropioanilide) is extensively used in Greece and other Europeancountries for the control of some annual grasses andbroadleaf weeds in several different crops and especiallyin rice. Consequently, their residues havebeen detected in various natural waters of Europeancountries [2]. Therefore, the investigation of remediationtreatments of polluted waters containing traceamounts of herbicides is of environmental interest.In the last few years, research on new methods forwater purification has moved from processes involvingphase transfer of a contaminant (e.g. from liquid tosolid, such as activated carbon, or from liquid togas such as air-stripping of volatile contaminants)towards processes involving chemical or biochemicaldestruction of the contaminant [3–5].

In recent years, advanced oxidation processes (AOPs) have been intensively investigated for the treatment of waters and wastewaters. AOPs, defined as processes generating hydroxylradicals ($OH^•$), are considered to be promising alternatives to conventional processes due to their efficiency in oxidizing a great variety of organic contaminants [6]. The Fenton and photo-Fenton systems have been widely applied in the treatment of non-biodegradable wastewater in the field of AOPs [7, 8].Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide, and exploits the reactivity of the hydroxy lradicals produced in acidic solution by the catalytic decompositionof H_2O_2 [9]:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^•$ (1)

Hydroxyl radicals may be scavenged by reaction with anotherFe^{2+}:

$OH^• + Fe^{2+} \rightarrow OH^- + Fe^{3+}$(2)

Fenton reagent appears to be a very powerful oxidizing agent.Besides, the process is simple and non-expensive, it taking place atlow temperatures and at atmospheric pressure [10]. The chemicalsare readily available at moderate cost and there is no needfor special equipment.In photo-Fenton process in addition to the above reactions

the formation of hydroxyl radical also occurs by the followingreactions (Eq. (3))[11]:

$Fe^{3+} + H_2O + h\nu \rightarrow OH^• + Fe^{2+} + H^+$(3)

The rate of organic pollutant degradation could be increasedby irradiation of Fenton with UV or visible light (photo-Fentonprocess). The illumination leads not only to the formation ofadditional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+}. In this way, the concentration of $Fe^{2+}$is increased and the overall reaction is accelerated. Among theAOPs, the oxidation using Fenton's reagent and photo-Fenton'sreagent has been found to be a promising and attractive treatmentmethod for the effective degradation of pesticides.The main objective of this study is to analyses the feasibilityof degradation of propanil by Fenton and photo-Fentonprocesses. The influence of different operational parameters(pH, H_2O_2,propanil concentration) which affect the efficiency of Fentonand photo-Fenton reactions, in propanildegradation was alsoinvestigated.

MATERIALS AND METHOS

Reagents:

propanil (3,4-dichloropropioanilide, $C_9H_9NOCl_2$) supplied by Iraqi company (Stam F- 34,360g/L active ingredient) with purity of 98%.De-ionized water was used throughout this study. H_2O_2 (30 wt%), $Fe(NO_3)_3{\cdot}9H_2O$, H_2SO_4, NaOH and Na_2CO_3, HCl (36.5- 38.0%) from Sigma while bentonite clay was obtained from the General Company for Geological Survey and Mining, Ministry of Industry and Mineral Baghdad, Iraq.

Preparation of catalyst:

The Fe- bentonitenanocomposite was prepared through the following steps[12]. Firstly, an aqueous dispersion of bentonite clay was prepared by adding 10g bentonite clay to 500 mL H_2O under vigorous stirring for 3 h at room temperature. Secondly, sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate for 3h such that a molar ratio of 1:1 for $[Na^+]/[Fe^{3+}]$ was established. Thirdly, 500 mL solution obtained from the second step was added drop by drop intothe dispersion of bentonite clay prepared in the first step under vigorous stirring. Fourthly, the suspension was stirred for 3h followed by ageing at 100°C in an autoclave for 48h. Finally 1000 mL solution containing Fe-B nanocomposite was obtained for the coating of the Fe-Bnanocomposite on the stainless steel plate substrate. The coating of Fe-B nanocomposite on the inner wall surface of photo-reactor was conducted by thermal spray method[12]. The photo- reactor is made of stainless steel pipe with diameter of 4 cm and length 15cm, as shown in fig (1).

Results and discussion

Characterization of the catalyst:

1XRD:

X- ray diffraction(SHIMADZU 6000 X-Ray) in fig (3)exhibited strong diffraction peaks at 2ϴ of (25.5°, 26.2°) indicates that the Fe-B nanocomposite mainly consists of SiO_2 (quartz) and (33.15°,39.28°) indicates consists Fe_2O_3 (hematite). If there is increase in particle size then the peak intensity of diffraction pattern will increase proportionally [13].

AFM analysis:

Atomic force microscope (AFM, AA3000 of Angstrom Advanced Inc. USA), was used to investigation Fe- B nanoparticles. AFM analysis represent data in three dimensions, so that it is possible to measure the height of the nanoparticles quantitatively. Figs (4) explain the particle size is less than 100nm and show the morphology of nanoparticle and the average particle size of Fe-B nanocomposite is around 80 nm.

Photo reactor

All experiments were performed in cylindrical photo reactor with a total volume of 50 ml. Fig (5) show the structure of propanil and its UV- spectrum.

Degradation of herbicide propanil

In the Fenton and photo-Fenton processes, theH_2O_2 was oxidized and$OH^{\bullet}$was produced. The formation of$OH^{\bullet}$depends on several factors such as pH, H_2O_2, initial and concentration ofpropanil . Therefore, the effects of the previous factors were investigated.

Figure (6) show the calibration curve for propanil which was determined in λ max= 248 nm that obeys the (Lambert beer's law) at specific concentrations prepared for each compound. After that, the absorption has been recorded and a calibration curve plotted between adsorption and concentration, the best line between points has been drawn.

To study discoloration of propanil, the UV-visible absorption spectra of (10 ppm) propanil solution at a pH=7.0 before and after treatment with photo-Fenton catalyst in the presence of 6W UVC were measured and are presented in Fig. 7.

To evaluate the efficiency and the benefit of each condition on the pesticide degradation experiments were carried out under the following conditions: (1) pesticide +H_2O_2, (2) pesticide + Fenton reagent, (3) pesticide + Fenton reagent + UV.

Fig (8) show it is possible to observe that pesticide isable to beoxidizedby H_2O_2 alone but in less efficiency. In Fenton process propanil(100ppm) percentage R% removal was 99.4% after180 min but propanil (10ppm) removal was 100%. For photo-Fenton process 99.6% degradation of propanil (100ppm) wasobtained at 180 min and propanil (10ppm) 100% degradation. Therefore, photo-Fenton process alone ismore efficient than other experimental conditions. The relativeefficiencies of the above processes are in the followingorder: Fe^{2+} +H_2O_2 +UV (photo-Fenton) > Fe^{2+} +H_2O_2 (Fenton)>>H_2O_2. The high efficiencyof photo-Fenton process is due to the formation ofmore hydroxyl radical than the other processes. In combinationof thermal process and UV light, the oxidation powerof Fenton reagent was significantly increased due mainly tothe photo-reduction of Fe^{3+} to Fe^{2+}, which could react withH_2O_2establishing a cycle mechanism of generating additionalhydroxyl radicals (Eq. (3)). Furthermore, the effect of UV lightwas also attributed to the direct hydroxyl radical formationand regeneration of Fe^{2+} from the photolysis of the complex$Fe(OH)^{2+}$ in solution. It was known that the existing form offerrous iron was connected with the acidity of solution. At aboutpH 3, a part of ferrous iron would exist as the form of $Fe(OH)^{2+}$,whose photolysis under UV illumination could directly produce$OH^{\bullet}$ radical and Fe^{2+}, as indicated below [12]:

$Fe(OH)^{2+} + h\nu \rightarrow OH^{\bullet} + Fe^{2+}$(4)

Therefore, higher degradation rate and percentage of propanilcame out in the photo-Fenton system.

Fig(9) shows the relationship between rate constant for the degradation of propanil and initial concentration of H_2O_2 for Fenton and photo-Fenton processes. This basically implies a better control of H_2O_2 concentration. The objective of this evaluation is to select the best operational concentration of H_2O_2 in photo-Fenton processes. In these experiments, the original amount of H_2O_2 was changed from 0.8ml to 5ml. The results indicate that the degradation of propanil was increased by increasing the volume H_2O_2. This can be explained by the effect of the additionally produced of hydroxyl radicals,with increasing H_2O_2volume from 0.8ml to5ml for photo-Fenton processes. This may be due to recombination of hydroxyl radicalsand also hydroxyl radicals reaction with H_2O_2, contributing to the $OH^{\bullet}$ scavenging capacity (Eqs. (6)– (8)) [13].

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad (6)$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad (7)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 (8)$$

It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation.It is important from an application point of view to study thedependence of removal efficiency on the initial concentrationof the pesticide. Therefore, the effect of pesticide concentrationon the degradation efficiency was investigated at differentconcentration of propanil and presented in Fig(10)for photo-Fenton processes.It was observed thatthe degradation decreases with increasing theinitial concentration of the pollutant. At low concentration ofsubstrate, the rate constant is higher compared with that at higherconcentration, whereas the rate of degradation increases with anincrease in the initial concentration of substrate. The presumedreason is that when the initial concentration of the pesticideincreased, the hydroxyl radical concentrations remain constantfor all pesticide molecules and hence the removal rate constantdecreases [14, 16].

The pH value affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency.

The effect of pH on the degradation of propanil by photo-Fenton processes is shown in Fig(11). This figure shows that pH significantly influences the degradationof propanil. The experiments were carried out at pHwithin the range 2–14. At low pH (2) low degradation was obtainedin photo-Fentonprocesses. The optimumpH was found to be about 7. The degradation decreased at pHvalues higher than 7, because iron precipitated as hydroxide,which resulted in a reduction in the transmission of the radiation(photo-Fenton) [17]. Additionally, the oxidation potentialof hydroxyl radical was known to decrease with increasing pH[16]. The low degradation at pH =2 is also due to thehydroxyl radical scavenging of H^+ ions (Eq. (5)) [18].

$$OH^{\bullet} + H^+ + e^- \rightarrow H2O \qquad (5)$$

Effect of temperature on the degradation of propanil was investigated in three different temperature (298.15, 308.15, 318.15) K at the following condition pH= 7, with different initial concentration(10, 20, 60,) ppm of propanil. The results in fig (12) show that, the degradation of propanil decreases as temperature increases that indicated an anti- Arrhenius relation. The disappearance of propanil during the first 180 min of oxidation could be described as a first-order reaction kinetics with regard to pesticide concentration as it may be seen from the data in Fig(13). Degradation rate constants, k (in min−1), were determined from the slope of $-\ln(C/C_0) = f(t\ (\text{min}))$ plots, where $C0$ and C are the concentration of propanil at times 0 and t. The apparent rate constant has been chosen as the basic kinetic parameter, since it on independent on the concentration and, therefore, enables one to determine the catalytic activity. Also, to have a better knowledge on the degradation process is presented the time necessary to reduce to 50% the initial concentration of propanil, the half-life time ($t_{1/2}$). The experimental data in Fig. 13 show that photo-Fenton processes had a significant accelerating effect on the rate of oxidation of propanil.

4. Conclusions

The results showed that Fenton and photo-Fenton processesare powerful methods for degradation of propanil, but photo-Fenton process is more efficient. The degradation rate andpercentage were influenced by the initial concentration of thepropanil, the pH of solution, and the amount of hydrogenperoxide. Propanildegradation follows, evenfor Fenton and photo-Fenton, a first-order kinetic law. The optimum conditions for the degradation of propanil in Fenton and photo-Fenton processes were observedat pH 7 with a pesticide concentration of 10ppm. Photo-Fenton was more efficientthan Fenton. The advantages of the photo-Fenton processas an oxidative treatment are low cost, rapid degradation,and simple handling. Therefore, H_2O_2/Fe^{2+}/UV system wouldbe applied to wastewater treatment works as a new developingmethodology for reducing levels of other pesticides, especiallyin countries with abundant solar light.

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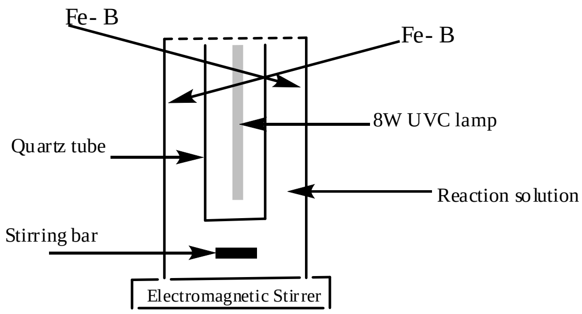


Fig (1): Experimental set- up of the photo- reactor coated with a Fe- B.

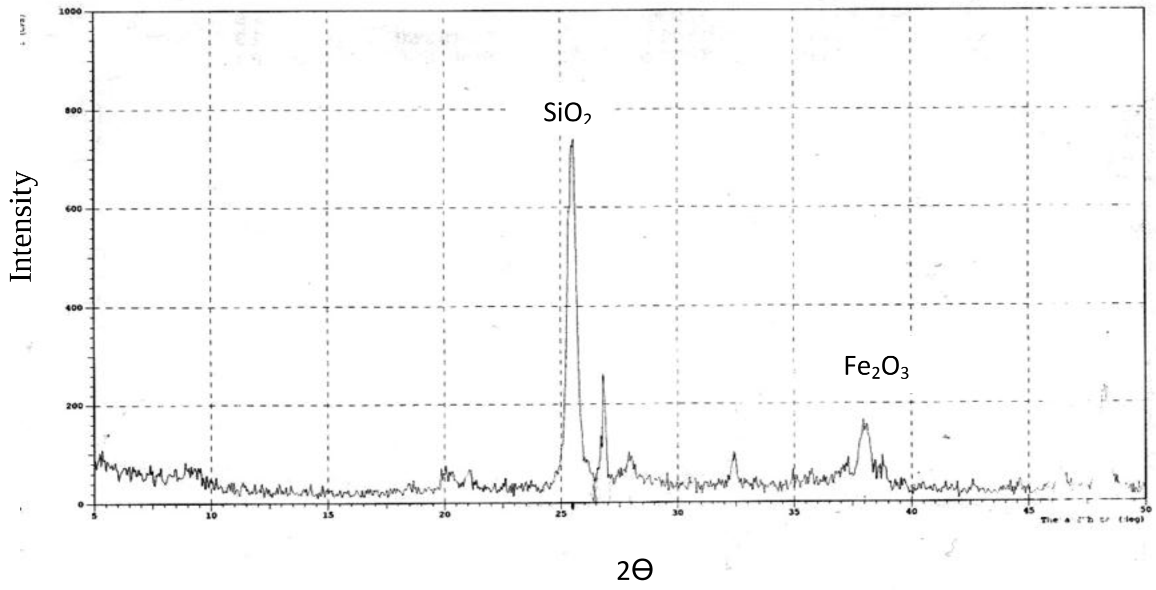


Fig (3): XRD for: Fe-B nanocomposite

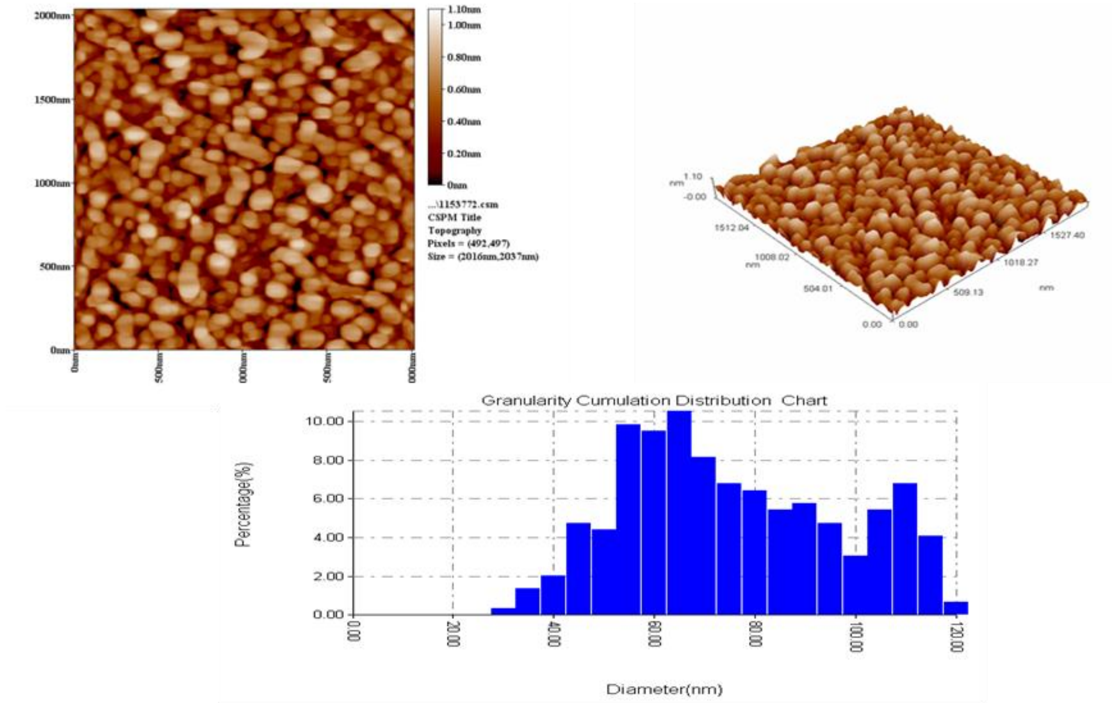
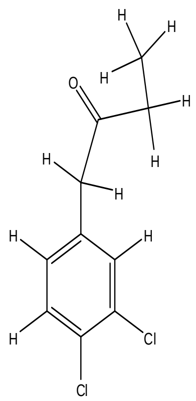
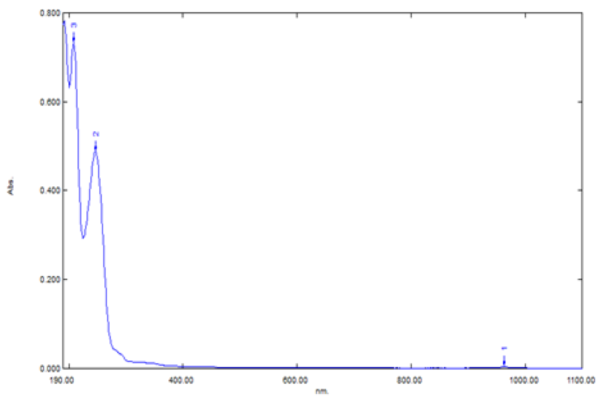


Fig (4): AFM of Fe- bentonit nanocomposite



1-(3, 4-dichlorophenyl)butan-2-one



Fig(5) : Chemical structure and UV spectrum of propanil (λ max = 248 nm).

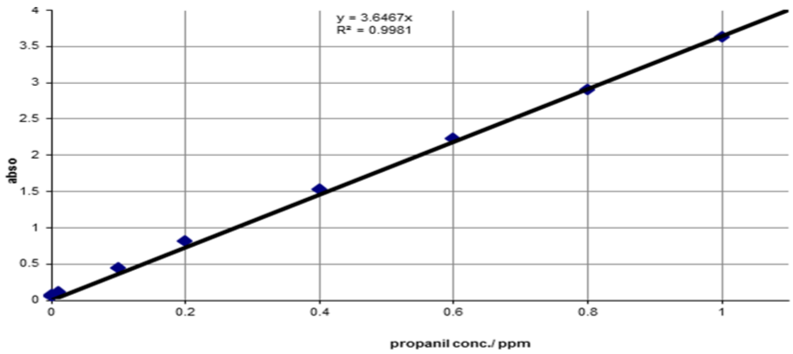


Fig (6) calibration curve for propanil at λ max= 248 nm

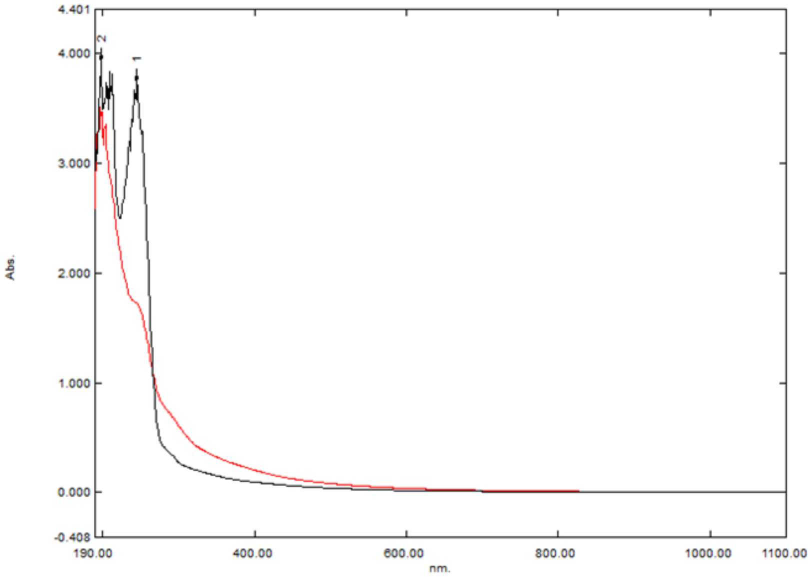


Fig (7): UV-visible spectra of the 10 ppm of propanil solution before and after treatment with photo- Fenton catalyst at pH=7.0 and 298.15K for 180 min.

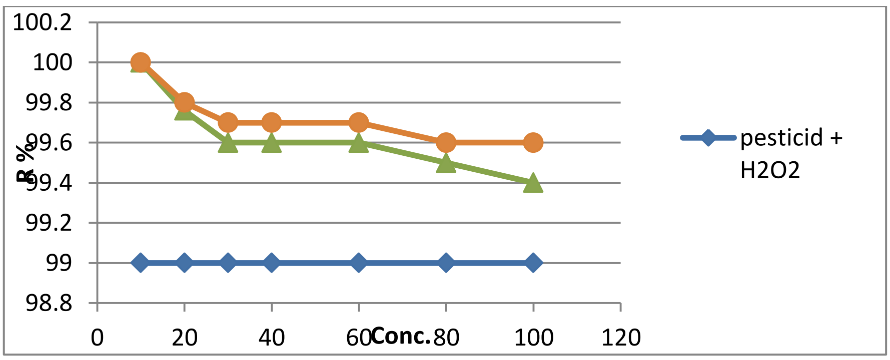


Fig (8): Chemical degradability of propanil with different process.

pH = 7,concentration in(ppm) and Temp 298.15 K

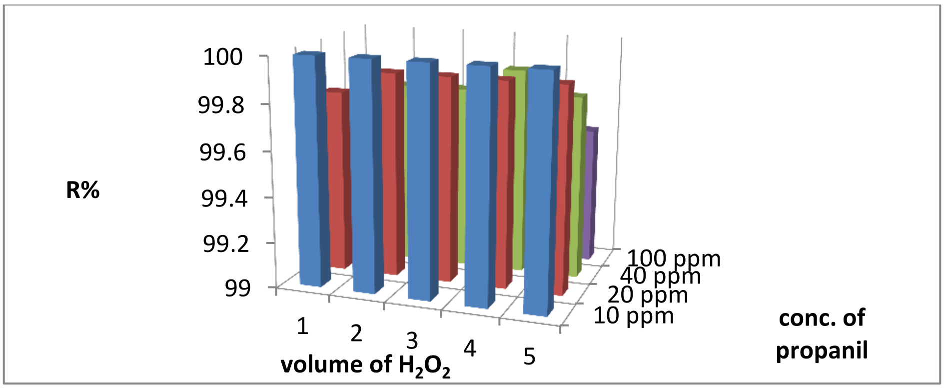


Fig (9): variation of R% with H_2O_2 volume for different propanil concentration in presence of UV- light and catalyst at 298.15K and pH= 7

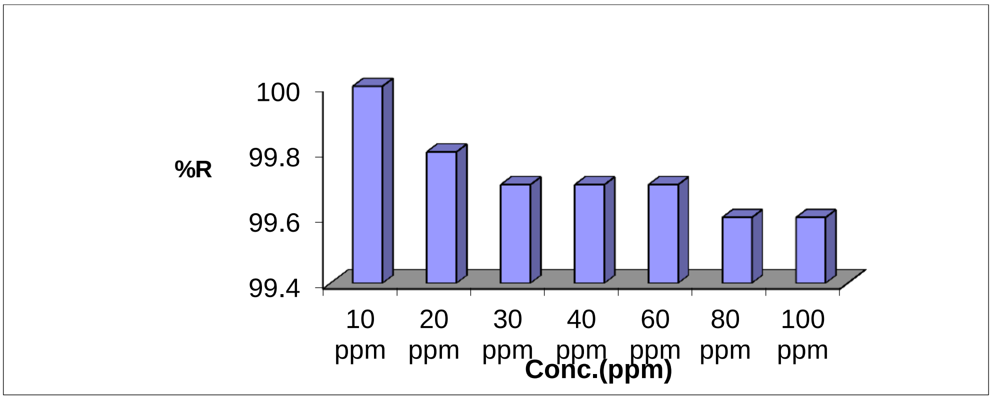


Fig (10): Effect of initial propanil concentration on its degradation; at temperature 298.15K, pH= 7, and (0.8ml H_2O_2 + catalyst+ 8W UVA).

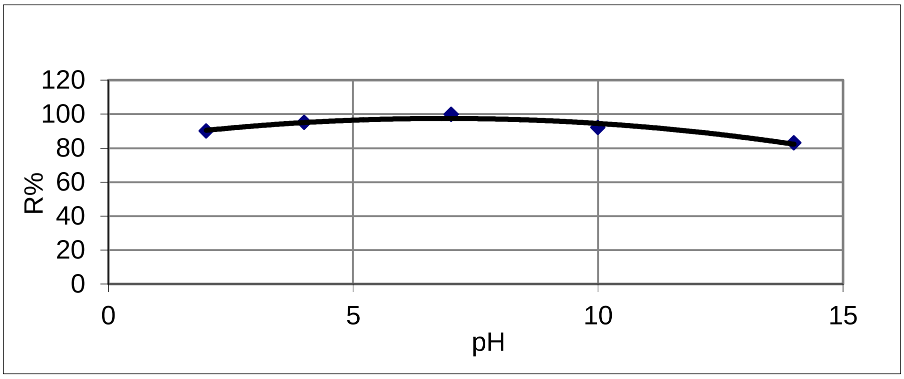


Fig (11): pH value and the R%

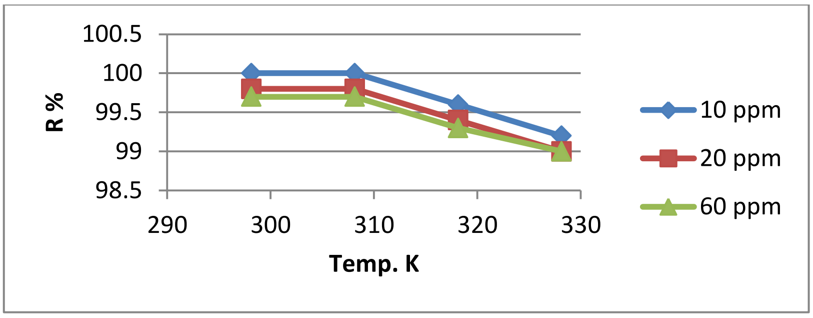


Fig (12): %R against temp. for different propanil concentration after 180 min.

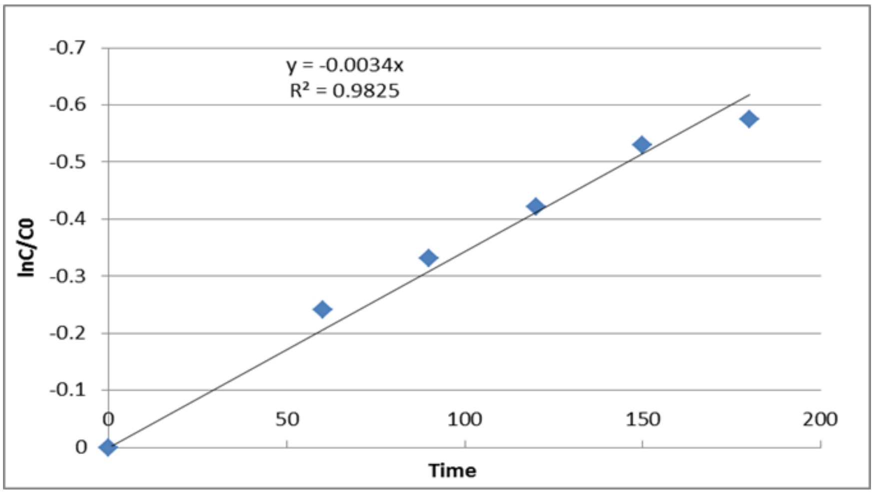


Fig (13): The relation between $\ln C/C_0$and Time (min)at temp. 298.15