

Kinetics of Photodegradation of MCPA Herbicide in Aqueous TiO₂ Suspension

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Abstract

The direct and catalytic photodegradations of toxic and widely used herbicide, 2-methyl-4-chlorophenoxyacetic acid (MCPA) were investigated under the artificial (UV and Visible) and solar source of radiation, in aqueous suspensions of TiO₂ and ZnO. UV-Visible spectroscopy and High performance Liquid Chromatography (HPLC) were used to monitor changes of herbicides concentration. The degradation of MCPA in all experiments followed a pseudo-first order reaction. The reaction rate constants of the processes for UV/ TiO₂ system was 0.369 min⁻¹ and for UV/ZnO system was 0.0171 min⁻¹. The effect of the initial herbicide concentration was investigated and was concluded that the rate of herbicide degradation can be described in terms of Langmuir-Hinshelwood kinetic model.

الخلاصة

التجزئة الضوئية المباشرة و التجزئة الضوئية المحفزة للمبيد الزراعي (MCPA) السام و المستخدم بشكل واسع تم دراستها تحت ضوء المرئي و الضوء فوق البنفسجي و اشعة الشمس. تم دراسة التجزئة الضوئية المحفزة في وسط المائي باستخدام عوامل مساعدة TiO₂ و ZnO. استخدم جهاز المطياف الضوئي و كروماتوغرافيا السائل ذات الكفاءة العالية المقترن بمطياف الامتصاص لمتابعة التركيز المبيد خلال عملية التجزئة. و وجد بان كافة العمليات التجزئة الضوئية المحفزة للمبيد يتبع قانون المرتبة الاولى الكاذبة ، قيمة ثابت السرعة لتجزئة المبيد في النظام UV/ TiO₂ كانت مساوية الى 0.369 min⁻¹ و في النظام UV/ZnO كانت مساوية الى 0.0171 min⁻¹. تأثير التركيز الابتدائي للمبيد تم دراستها و وجدت بأنه يمكن تطبيق علاقة لانماير-هانشلود بنجاح و من خلال احتساب ثابت التوازن بين بأن الفعالية الضوئية للأنظمة المستخدمة يعتمد على قدرة امتزاز المبيد على العوامل المساعدة المستخدمة.

Introduction

Ground Water contamination is expected to be a primary source of human contact with a majority of the toxic pollutants in our environment, many of which are organic compounds, such as solvents, herbicide, chlorophenols, and volatile organics^[1].

Photodegradation is a process through which a direct photochemical transformation takes place where energy from light attacks the bonds within a molecular compound, thereby degrading the compound. Unfortunately, not all compounds can be degraded in this manner. Specifically, chlorophenol compounds cannot be degraded photolytically^[2]. For this reason, catalytic photodegradation becomes necessary. Catalytic photodegradation offers an advanced technology for the removal of toxic organics from water. In catalytic photodegradation the organic contaminants are oxidized ultimately to carbon dioxide and water leaving no waste dispose. Catalytic photodegradation oxidation uses light energy to react with a molecule leading to the formation of radicals in the solution. Several different molecules have been shown to be capable of promoting photodegradation, from methylene blue^[3], to ZnO^[4], to TiO₂^[5].

The radicals can be formed from the molecule itself or from constituents in the solution containing the molecule.

These radicals are then capable of oxidizing or reducing and thereby destroying the target contaminants. There are three known highly reactive intermediates formed by the process of catalytic photodegradation, oxygen singlet (1O_2), hydroxyl radicals ($\cdot OH$), and hydrogen peroxide (H_2O_2). Researchers suggested that the $\cdot OH$ is the prominent player in catalytic photodegradation. The hydroxyl radical's ability to degrade contaminants comes from its high level of oxidation power, which is more than twice as strong as chlorine^[6].

Pseudo-first order reaction rates are reported for the photodegradation via TiO₂ of Pentachlorophenol, 2,4 dichlorophenol, 3,5-dichlorophenol, 2,3,5-trichlorophenol, 2-chlorophenol, 4-chlorophenol, salicylic acid, and 2,4,6-trichlorophenol^[7-9]. Hsieh^[10] reported a pseudo-first order reaction for 2,4-dichlorophenoxyacetic acid degradation in system exposure to low-pressure UV-light and addition of 1.4 g.L⁻¹ of TiO₂ (anatase) to 2,4-D solution.

In the present work the comparison of MCPA catalytic photodegradation in distilled water under different sources of radiation have been carried out to estimate the efficiencies of these sources of radiation on the degradation process, as well as to compare the efficiencies of the studied catalysts on the degradation processes.

Experimental

Material

2-methyl-4-chlorophenoxyacetic acid (MCPA) is supplied by Fluka AG with the purity of 97.5% as a powder. TiO_2 Anatase and ZnO used through the present work were supplied by BDH chemicals with the purity of 96.85% and 97% respectively. Methanol was HPLC grade and purchased from Tedia Company-USA.

Instruments

Photodegradation experiments were performed with a laboratory constructed "illumination box" (Fig. 1). The sources of radiation are Tungsten-halogen lamp, 500W supplied by Philips and 100-Hg lamp (230V, 50Hz and 1 Am without wave length selector) from Osram- Germany. The lamps were placed at 10 cm apart from the photoreaction cell. Spectrophotometer model Cesil 3021, from England was used for measuring the absorbance of solution during the process.

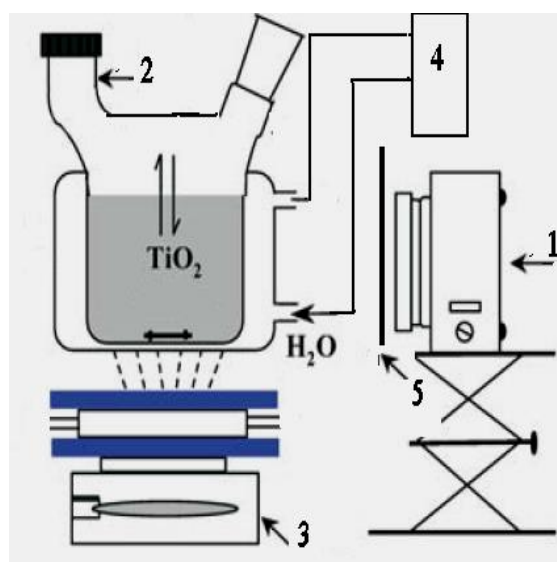


Fig.1 Block diagram of photodegradation reactor
1-Sources of light 2-Photochemical thermostat cell
3-Stirrer 4-Recycle water bath (water circulation)

5-Filter.

Hitachi L-4500 diode array HPLC connected with UV-visible spectrophotometer detector and analytical column (PRT 720041, ET2501814 Nucleosil 120-5 C18 Machereg) was used for the identification and determination of MCPA concentration under the following conditions; mobile phase: 40% Methanol 60% Water, flow rate: 1.2 mlmin^{-1} , detector wavelength: 280 nm and injection volume: $20 \mu\text{l}$.

Photodegradation procedure

The photodegradation experiments were carried out at 30°C in a laboratory-made photoreactor including a 35 ml cylindrical photochemical cell. Twenty milliliters of solution (50 mgL^{-1} of herbicide in distilled water) was added to the photochemical cell then irradiated immediately by the radiation source. For catalytic photodegradation 0.1 gL^{-1} of Semiconductor powder was added to an aqueous solution of herbicide mixture. The reaction mixture was stirred magnetically in the photoreaction cell.

Outdoor experiments were done in quartz cell during May to November (2006) in the presence of sunlight from 12 to 5 pm, so that the irradiation was as intense as possible.

The experiments of sunlight photodegradation were carried out under clear sky conditions. Incident solar radiation was measured within the wavelength of 285-2800 nm by (Solar 118-Haenni radio). The mean sunlight intensity was recorded from 590 to 706 Wm^{-2} .

Kinetic studies

The absorption spectra for MCPA solution were recorded in wavelength ranging from 190-350 nm. Concentration changes of MCPA were determined by monitoring the

absorption peak at a maximum wave length of 278 nm. A calibration curve was found to be linear in the range of 0.75 to 100 mg/L as shown in Fig. 2

Results and Discussion

The spectra of MCPA indicated that during the catalytic photodegradation, the intensities of the absorption bands exhibit sudden variation, after which their intensities tend to decrease gradually. Fig.3 shows the variation in absorption spectra of MCPA solution at various time interval of irradiation over 0.1 gL⁻¹ of (ZnO) catalyst

This figure declare that the absorption maxima at 278 and 229 nm

of MCPA spectra were decreased in intensity with irradiation time leading to practically no absorption bands in the UV-Visible spectra at longer time.

Several experiments were made in order to know the influence of direct irradiation on the degradation of MCPA solution without a catalyst. Fig 4 shows the effect of the different types of radiation (UV, Visible and sunlight) on direct photodegradation of 50 gL⁻¹ of MCPA. From Fig 4 clearly shown a very slow mineralization of MCPA under irradiation of all types of radiation.

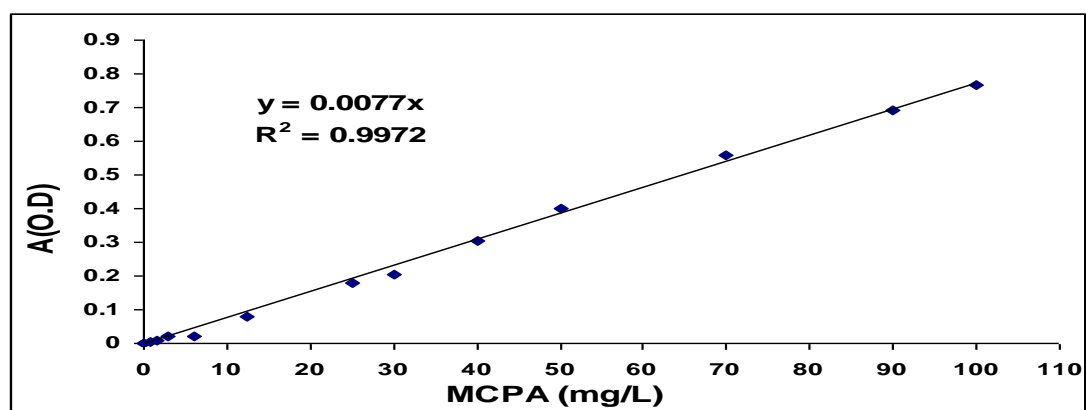


Fig. 2: Calibration curve between MCPA Concentrations (mg/L) and absorbance

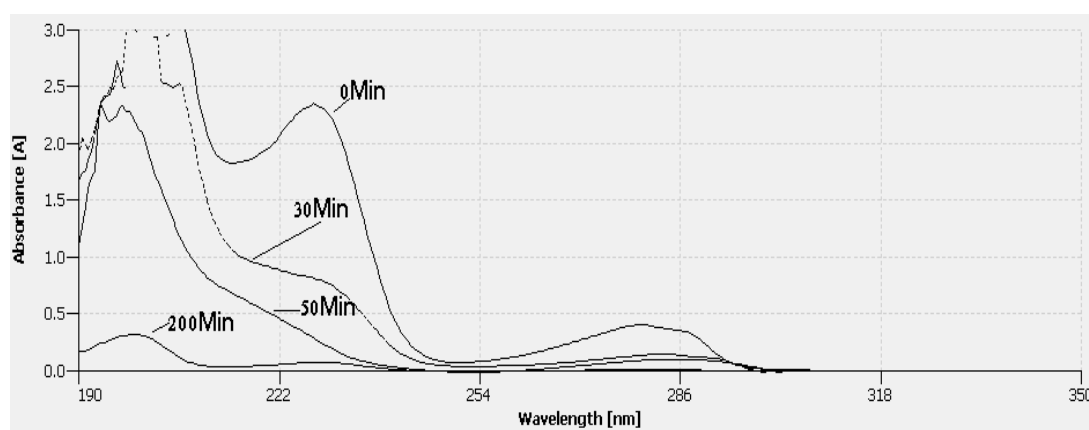


Fig. 3: UV-Visible absorption spectra of 50 mgL⁻¹ of MCPA over 0.1 gL⁻¹ ZnO at various irradiation times under UV radiation

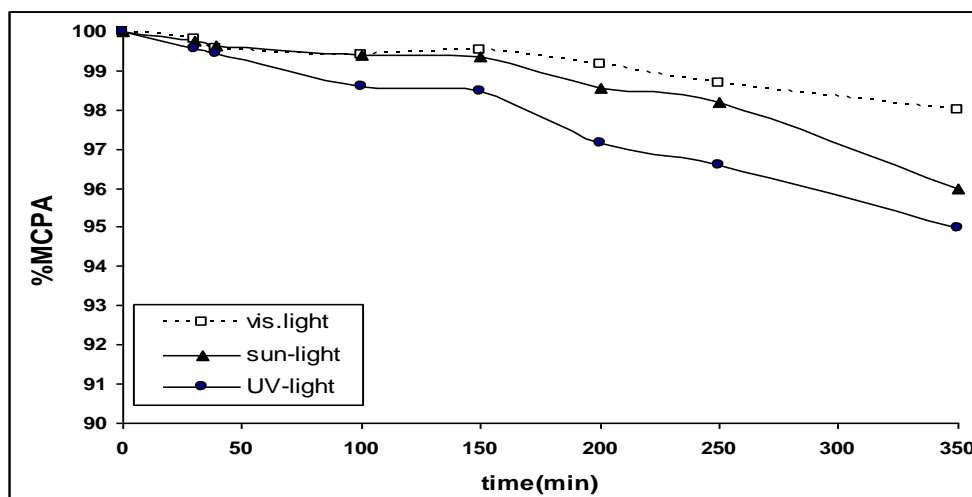


Fig. 4: Direct photodegradation of 50 mgL⁻¹, MCPA under different types of light

The best results were obtained with UV-irradiation. Since the emission spectra of UV- radiation mainly focus on the ultraviolet band having the advantageous of short-wave emission and high energy to initiate photodegradation of compounds. However, the spectrum of sunlight ranged from ultraviolet to near infrared and with the main flux concentrated on the visible light band [11].

The effect of the catalyst's concentrations (0.02-0.15 gL⁻¹) on the percentage of MCPA degraded was evaluated by using 50 mgL⁻¹ of the substrate under UV-illumination after 30 min at room temperature. The results in Table 1, verified the increase in the percentage of the pesticide degraded with increasing the catalyst's concentration up to 0.1gL⁻¹ approximately. This enhancement is due to increasing photon absorption by the photo catalyst. However, as the loading was increased beyond the optimum value (0.1gL⁻¹), the degradation percentage decreased due to the opacity of the suspension and light scattering [12].

Table 1: Effect of catalysts concentration on the catalytic photodegradation of 50 mgL⁻¹ MCPA under UV-illumination for 30 min.

TiO ₂ conc.(g/L)	%MCPA degr.	ZnO conc.(g/L)	%MCPA degr.
0	2.6	0	1.5
0.025	28	0.025	12.2
0.05	52	0.05	29
0.075	67	0.075	48.8
0.1	79	0.1	58
0.125	75	0.125	65.7
0.15	86	0.15	65.3

Therefore, a catalyst loading of 0.1 gL⁻¹ corresponding to the highest absorption of incident photons by the catalytic photodegradation was used for all the experiments in this study.

The catalytic photodegradation of MCPA was studied at four different experimental conditions: (1) under UV radiation with the presence of TiO₂, (2) under sunlight with the presence of TiO₂, (3) under visible-radiation with

TiO₂, (4) over TiO₂ with protection from light (in dark). The results of MCPA degradation under these conditions are shown in Fig. 5, which indicates the role of TiO₂ particles as effective catalyst in the presence of radiation source, and a good photodegradation results were obtained by TiO₂/UV system rather than other systems. This is because the wavelength and energy of UV light are shorter and higher than those of the sunlight or visible light^[11].

Since, the spectrum of natural sunlight ranged from ultraviolet (3-5%) to near infrared and with the main flux concentrated on visible light band^[13] and The utilization of TiO₂ photocatalysts requires UV irradiation, therefore only makes use of 3-5% of the sunlight that reach earth^[14]. The similar behavior has been reported for

the catalytic photodegradation of phenol and 2,4-dichlorophenol, which showed that these two compounds were degraded by TiO₂/UV system more than by other systems (TiO₂/dark, TiO₂/Sun light or TiO₂/Vis)^[15].

In order to compare the efficiency of TiO₂ and ZnO, the catalytic photodegradation experiments have been carried out with the same sources of light in addition to experiments under dark conditions on ZnO suspension. The results of these experiments showed that the photocatalytic degradation of the herbicide in the presence of ZnO is much more efficient than the direct photodegradation and less efficient than the corresponding catalytic photodegradation in the presence of TiO₂ as observed in Fig.6.

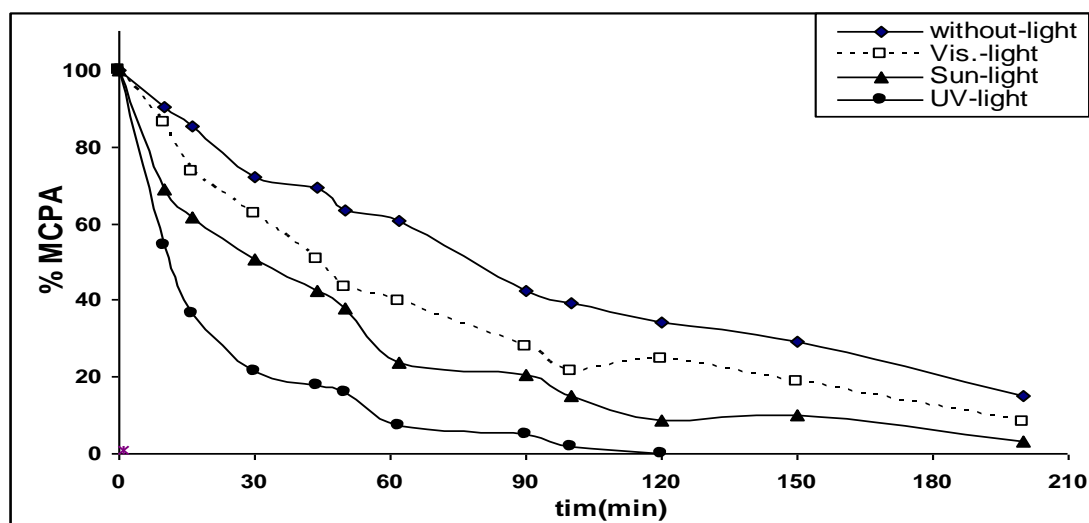


Fig. 5: Catalytic photodegradation of 50 mgL⁻¹, MCPA over 0.1gL⁻¹ TiO₂, under UV, Visible and natural Sunlight

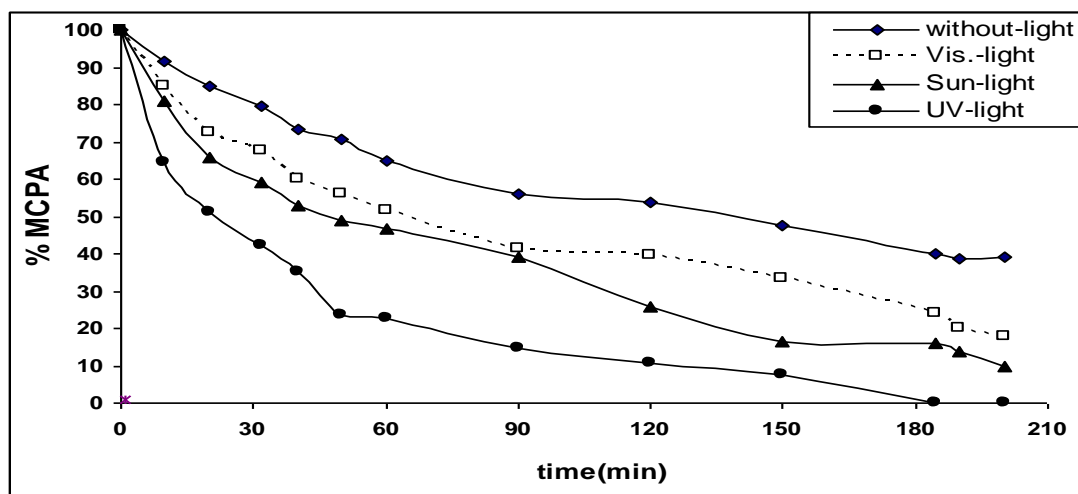


Fig. 6: Catalytic photodegradation of 50 mgL^{-1} MCPA over 0.1 gL^{-1} ZnO With and without different sources of radiation at room temperature.

Generally, it has been found that processes, direct and catalytic photodegradation reactions, followed first order kinetics but this might change usually to zero order at higher initial concentrations of substrate ^[16].

The kinetic studies of the experiments were monitored spectrophotometrically (at the wavelength 278 nm) and by HPLC analysis. In the case of HPLC analyses, the concentration of MCPA during the degradation process were monitored by observing the peak intensity at retention time 10.93 min (see Fig.7). which shown decreasing of the of the peak intensity gradually during the degradation process.

The graphical method was employed to predict the order of the reaction. The plot of $\ln [\text{MCPA}]/[\text{MCPA}]^{\circ}$ versus irradiant time, (where, $[\text{MCPA}]$ is the concentration of herbicide at time t , $[\text{pes}]^{\circ}$ is the initial concentration of herbicide), give a straight line behavior ,which suggests the first-order kinetics of the catalytic photodegradation(see Fig . 8)

The reaction rate constant(k) which was determined from the slope of the straight line and the reaction half time ($t_{1/2}$) are shown in Table 2. The similarity between HPLC and spectroscopic results of the concentration changing during the photodegradation process are also reported by other workers. ^[17, 18]

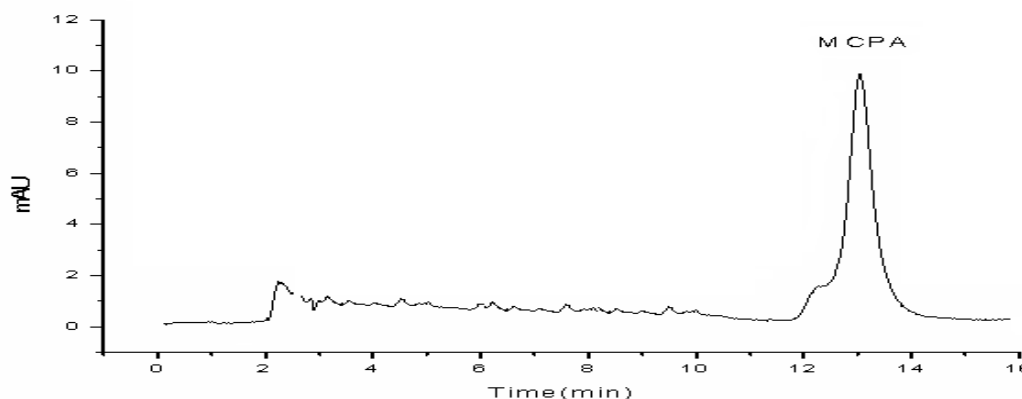


Fig.7: HPLC Chromatogram of stander MCPA in distilled water

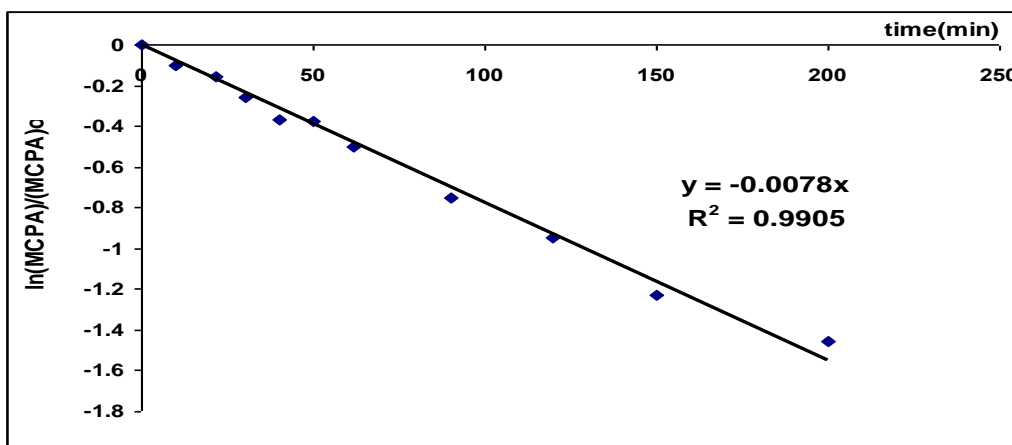


Fig.8: Plotting of $\ln [MCPA]/[MCPA]_0$ versus time of catalytic photodegradation over TiO_2 /dark.

Table 2: Kinetic parameters determined by HPLC and spectroscopy for catalytic photodegradation of MCPA.

Systems		Determined spectroscopically			determined by HPLC		
		$k(\text{min}^{-1})$	R^2	$t_{1/2}(\text{min})$	$k(\text{min}^{-1})$	R^2	$t_{1/2}(\text{min})$
TiO_2	Dark	0.0074	0.99	93.64	0.0079	0.978	87.72
	Visible	0.0103	0.9	67.28	0.0109	0.89	63.57
	Sunlight	0.0149	0.862	46.51	0.0153	0.882	45.29
	UV	0.0369	0.94	18.78	0.0374	0.925	18.52
ZnO	Dark	0.0053	0.98	130.75	0.0052	0.895	133.26
	Visible	0.0083	0.91	83.49	0.0079	0.939	87.72
	Sunlight	0.0113	0.97	61.32	0.0116	0.885	59.74
	UV	0.0171	0.87	40.52	0.017	0.847	40.76

The results were described successfully by Langmuir-Hinshelwood (L-H) model. This model assumes that the reactions take place at the surface of the catalyst, and the reaction rate is proportional to the fraction of the surface covered by the reactant according to following equations^[19, 20].

$$r = \frac{-dc}{dt} = k'\theta = \frac{k'KC_0}{1 + KC_0} \dots\dots\dots(1)$$

$$\frac{1}{r} = \frac{1}{k'} + \frac{1}{Kk'C_0} \dots\dots\dots(2)$$

Where r is the rate of reaction, C^0 is the initial concentration of the pesticide, t is time, k' is the L-H

specific reaction rate constant, θ is the fraction of the surface covered by the reactant, and K is the adsorption equilibrium constant. For diluted solutions ($C^0 < 10^{-3}$ M), the reaction is of the apparent first order, whereas for concentrations $C^0 > 5 \times 10^{-3}$ M, the reaction rate is apparent zero order^[21].

Then according to equation 2, the representation of inverse of r as a function of the initial MCPA concentration (C^0) gives a straight line^[22] as shown in Fig.9.

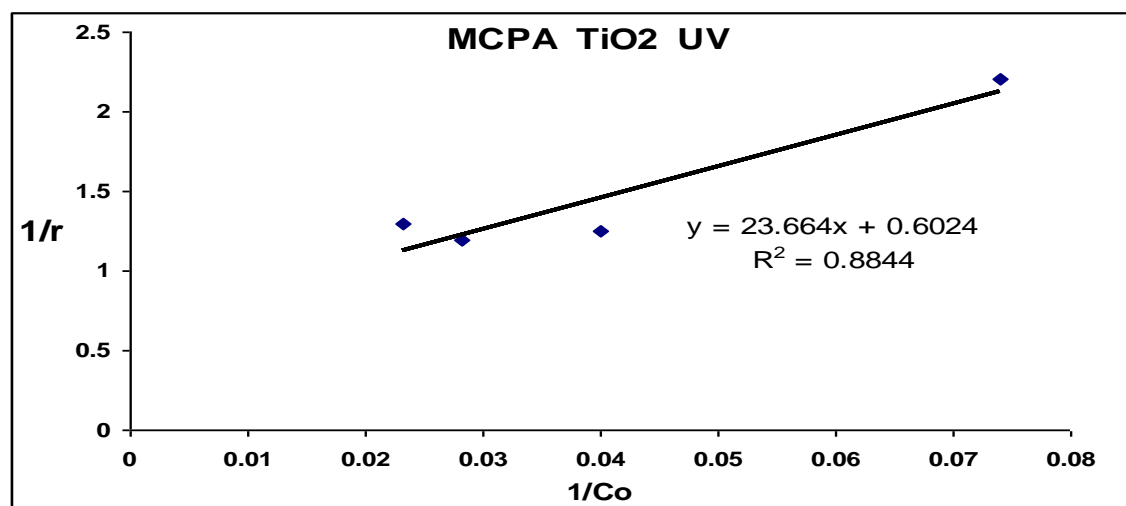


Fig. 9 : 1/r versus 1/C₀ for MCPA catalytic photodegradation over TiO₂/UV system.

Values of k' and K were calculated by linear regression analysis of the experimental data from slope and intercept. Values of k' ($\text{mgL}^{-1}\text{min}^{-1}$) and K (Lmg^{-1}) of MCPA degradation over TiO₂ and ZnO catalysts were tabulated in Table 3.

Table 3: Values of k' and K obtained from the degradation of MCPA over TiO₂ and ZnO under UV-irradiation

ZnO		TiO ₂	
$K, \text{mg}^{-1}\text{L}$	$k', \text{mg.L}^{-1} \text{min}^{-1}$	$K, \text{mg}^{-1}\text{L}$	$k', \text{mg.L}^{-1} \text{min}^{-1}$
0.074	0.72	0.025	1.66

As shown in Figure 8, the rate of reaction changed with changing the initial concentration of MCPA. This indicates that the degradation kinetics are not of simple first-order but pseudo-first order^[23]. At high substrate concentration, the adsorbed reactant molecules may occupy all the catalytic sites on catalyst surface and this leads to zero order kinetics. At low concentration, the number of catalytic

sites will not be a limiting factor and the rate of degradation is proportional

to the substrate concentration, according to apparent first order kinetics^[22].

The high values of adsorption constant (K) indicates that the higher electron density of aromatic ring of MCPA molecule leads to a stronger adsorption on the electrophilic sites at the catalysts surface^[24,25].

Therefore, one might conclude that the relatively high value of adsorption constant reflects the importance of the catalytic photodegradation reaction of the adsorbed MCPA molecules on the surface of catalysts beside the oxidation of this molecule by hydroxyl radicals in bulk solution^[26]. This behaviour has also been reported for Metobromuron, Isoproturon and chlobromuron on TiO₂ degradation^[23].

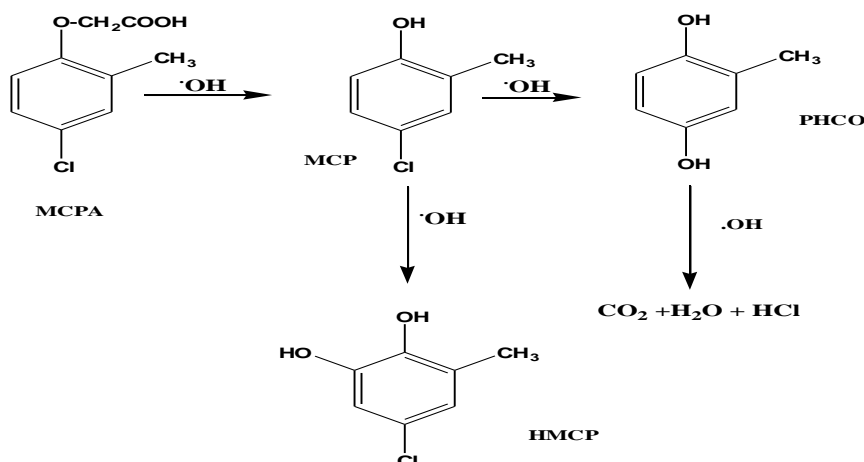
The results for the catalytic photodegradation of MCPA in a present work were compared with the catalytic photodegradation results of the same pesticide by other advanced oxidation process (AOP) systems. This

comparison is tabulated in Table 4, which declare that, the efficiency of TiO_2/UV system used in this work is higher than that of $\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ systems, which were used by other workers for the same herbicide and their efficiency is lower

than that of Photo-Fenton system. But ZnO/UV system used in this work has lower efficiency than that of other systems. The previous papers suggest the mechanism of MCPA degradation as shown in a follows mechanism^[30-32]

Table 4 The efficiency comparison of MCPA degradation by the systems used in this work and the other advanced oxidation process systems.

System	Herbicide	Conditions	k (min ⁻¹)	Ref.
TiO_2/UV	MCPA	50 mgL ⁻¹ of MCPA, 0.1 gL ⁻¹ catalyst and under low pressure Hg lamp	0.0374	This work
ZnO/UV	MCPA		0.017	
Photo-Fenton reaction	MCPA	70 mgL ⁻¹ of MCPA, 445 mM H_2O_2 , 2.5 mM Fe(III) and under low pressure Hg lamp	0.053	27
$\text{H}_2\text{O}_2/\text{UV}$	MCPA	0.08×10^{-3} M of MCPA, 1×10^{-3} M O_3 , 0.05 M of H_2O_2 and under high pressure Hg lamp	0.0346	28
$\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$	MCPA	0.08×10^{-3} M of MCPA, 1×10^{-3} M O_3 , 0.05 M of H_2O_2 and under high pressure Hg lamp	0.0361	29



The probable mechanism of MCPA degradation

Conclusions

Direct photodegradation indicated to be not efficient systems for the degradation of MCPA. Therefore the catalytic photodegradation becomes necessary. The catalytic photodegradation over TiO_2 and ZnO exhibited different reaction rate and followed a pseudo-first order reaction. It appears that TiO_2 has a higher

degradation efficiency of than ZnO . The photocatalytic activity increases with an increase in catalyst's concentration, then it reaches an optimum value. At a concentration greater than the optimum, the activity decreased. UV-radiation used in this work was more efficient than Sun or Visible light as a source of radiation.

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