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Degradation of Organophosphorus Pesticides in Water during UV/H₂O₂ Treatment: Role of Sulphate and Bicarbonate Ions

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Abstract: The photodegradation of two organophosphorus pesticides, malathion and diazinon, by sulfate radicals and bicarbonate radicals in aqueous solution were studied. The effect of the operational parameters such as pH, salt concentration, water type, H₂O₂ concentration and initial concentration of pesticides was studied. Gas chromatography mass spectroscopy (GC-MS) was used for analyses of pesticides. When salt effect was studied, it was found that sodium bicarbonate was the most powerful inhibitor used, while sodium sulfate was the weakest one. The highest degradation in UV/H₂O₂ process for malathion was found in alkaline condition and for diazinon in acidic condition. The photodegradation in all waters used in this work exhibited first order kinetics. Photodegradation rate in distilled water was higher than real water. The degradation of pesticides increased with increasing of H₂O₂ concentration.

Keywords: Advanced oxidation process; Bicarbonate; Hydrogen peroxide; Sulphate; Ultraviolet light.

Introduction

Advanced oxidation processes (AOP_s) can be used for the treatment of polluted waters^{1,2}. These alternative processes involve hydroxyl radicals as common oxidant. AOP_s May be used for either the complete mineralization of organic pollutants or the selective removal of bioresistant compounds and their conversion to biodegradable intermediates. AOP_s involves various combinations of ozone, hydrogen peroxide, sonolysis, ultraviolet (UV) radiation, and photocatalytic treatments that are capable of oxidizing a wide range of contaminants in

water, air and contaminated soil. Over the last few decades, selected AOP_s have been developed and shown to have industrial applications³.

Formation of hydroxyl radical in engineered water treatment systems can be achieved using advanced oxidation processes (AOP_s) such as UV/ H₂O₂, ozone/H₂O₂, and ozone⁴. The role of hydroxyl radicals in the treatment of pesticides utilizing the AOP processes has been investigated⁵. The °OH concentration level in turn is affected by the background impurities present in water of the impurities, inorganic anions such as bicarbonate and sulphate ions are very common in most of aqueous solution⁶.

Malathion and diazinon are commonly used organophosphorus pesticides in industry, agriculture sector for plant protection by controlling a variety of sucking and leaf eating insects because of its inhibition of the acetylcho linesterases of the vast majority of insects^{7,8}.

Wu et al⁹., reported that the presence of bicarbonate ions reduced the pesticides (parathion and chlorpyrifos) degradation rates via scavenging of hydroxyl radicals.

Liao et al¹⁰., demonstrated that the role played by the chloride and bicarbonate ions in the °OH scavenging at different pH and concentration.

The aim of this study were to investigate the photodegradation of malathion and diazinon in the presence of bicarbonate and sulphate under UV/H₂O₂ process.

Experimental

The reaction solutions were sodium bicarbonate (NaHCO₃) and sodium sulphate (Na₂SO₄). The initial concentration of H₂O₂ was obtained by adding a pre-determined amount of stock solution prepared from 30% H₂O₂ solution which was purchased from Merck Co. (Darmstadt, Germany).

The dimension of this reactor was 5 cm inside diameter and 30 cm in height and has the volume of the batch reactor 0.85 L. Hydrogen peroxide assisted the degradation was conducted using 10 , 30 mgL⁻¹ H₂O₂, from a 30% stock solution. The tested compounds in this study diazinon and malathion, which was from Supelco Inc. (Bellefonte, PA, USA), NaOH and HNO₃ were obtained Merck Co. (Darmstadt, Germany).

The concentration of malathion in the samples was 200, 400 and 600 µgL⁻¹. The concentration of diazinon in samples was 100, 300 and 500 µgL⁻¹ and used the 30% insecticides. The samples were adjusted in reactor in 5 time of remaining (60, 90, 120, 150, 180 s). The pH of the samples solution malathion and diazinon were 3,7,9 and reaction temperature in 25 ± 1°C . Samples of this study are synthetic from deionized water.

For the photolysis of diazinon and malathion , a solution containing pesticide and double distilled water was used. There after, 850 ml of prepared suspension was transferred to a 1000 ml Pyrex reactor. Irradiation was carried out with a 150 w medium pressure mercury lamp (philiph, Holland), which was above the batch photo reactor. The distance between solution and UV source was constant, 3.75 cm. In all experiments the pH was adjusted by HNO₃ or NaOH and then the pH values were measured with pH meter (Sartorius, Germany) After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by magnetic stirrer to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time.

Table 1. Characteristics of real water.

Characteristics	Unit	Value	
		Tap water	River water
pH		7.44	7.46
Turbidity	N.T.U	1	12.5
Specific conductivity	m scm^{-1}	638	725
Total hardness	mgL $^{-1}$ CaCO $_3$	230.35	258.1
Total alkalinity	mgL $^{-1}$ CaCO $_3$	210	290
Bicarbonate concentration	mgL $^{-1}$ HCO $_3^-$	256.2	353.8
Sulphate concentration	mgL $^{-1}$ SO $_4^{-2}$	79.4	67.98

Analyses were performed by gas chromatography mass spectroscopy (GC-MS). For identification, 1ml of samples was injected into the GC-MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was 270oC and analysis was done using a capillary column (varian DB-5 column; 30m 250 μm I.D. , film thickness 0.25 μm). The method started at 150oC , which was held for 2 min, then ramped to 120oC at a rate of 25oC/ min, followed by an increase to 270oC (held for 2 min) the method used a split, split ratio 1:10 Helium (99.999%) was used as carrier gas at 1 ml/min . Data were analyzed using T – test, ANOVA one way test using SPSS software.

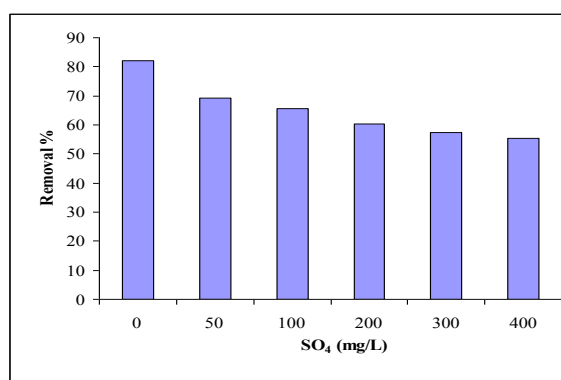


Figure 1. Comparison of removal percentage for degradation of malathion in the presence of sulfate pH=9; Time=180 S;H $_2$ O $_2$ =30mg/L.

Results and Discussion

Salt Effect

The salt effect on the photodegradation of pesticides (malathion and diazinon) was studied using sodium bicarbonate and sodium sulfate. The influence of different concentration of

salts (50 – 400 mgL⁻¹) on the photodegradation of pesticides (malathion and diazinon) are presented in Figures 1, 2, 3, and 4.

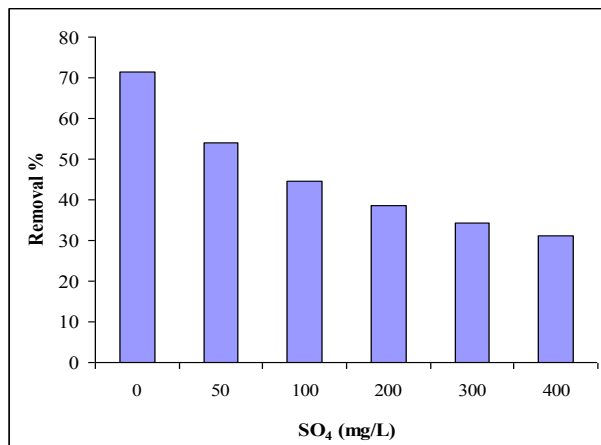


Figure 2. Comparison of removal percentage for degradation of diazinon in the presence of sulfate pH=3;Time=180 S;H₂O₂=30mg/L.

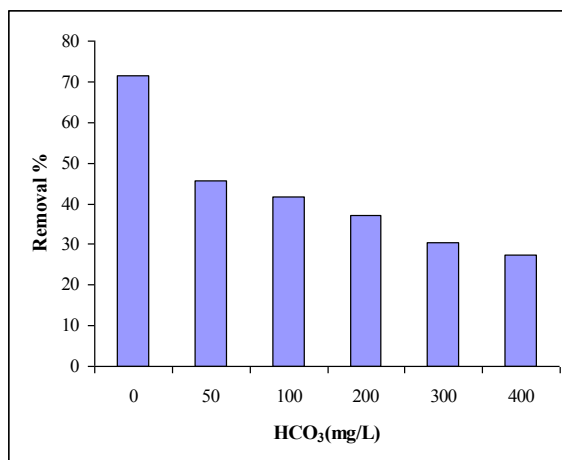


Figure 3. Comparison of removal percentage for degradation of diazinon in the presence of sulfate pH=3;Time=180 S;H₂O₂=30mg/L.

Photodegradation in the presence of sodium bicarbonate and sodium sulfate was slower in comparison to the reaction without salts. The decrease in the reaction in the presence of salts is due to the hydroxyl scavenger property of sulfate and bicarbonate ions.

When the salts effects are compared in Figures 1, 2, 3, and 4 it can be seen that sodium bicarbonate was the most powerful inhibitor studied while sodium sulfate was the weakest one.

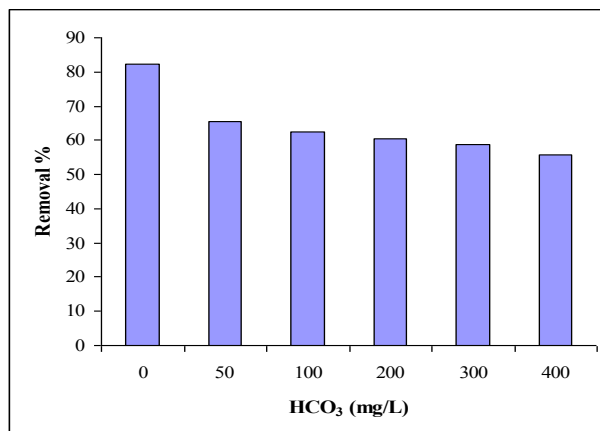


Figure 4. Comparison of removal percentage for degradation of malathion in the presence of sulfate pH=9; Time=180 S; H₂O₂=30mg/L.

Effect of pH

It was observed that both pesticides were significantly influenced by pH value of the solution, and the highest removal efficiency was achieved at pH 9 for malathion and pH 3 for diazinon, as shown in Figure 5. The results indicated that degree of photolysis increased with increasing of pH for malathion but for diazinon with increasing of pH the degree of photolysis decreases. The reason for the first phenomenon was that OH^- ions with elevated concentration would increasingly scavenge yielded highly oxidative $^{\circ}OH$ species.¹¹ The reason for the second phenomena was that breakdown rate of diazinon of acidic waters is quicker than that in another solution, also the fraction in the molecular state of diazinon was larger when the pH was smaller.

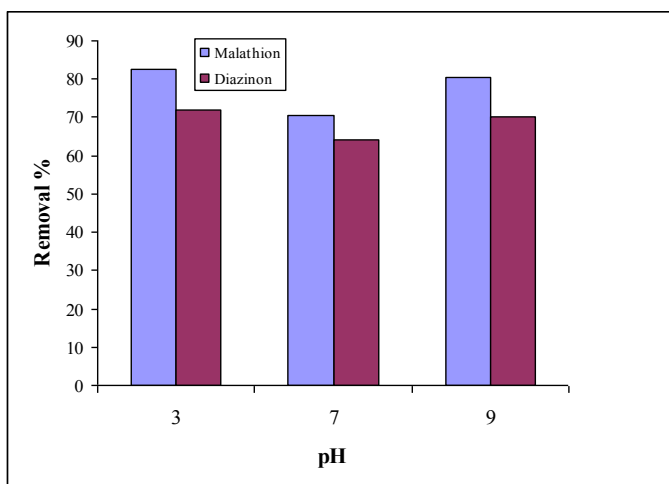


Figure 5. Pesticide degradation percentages at different pH after treatment with UV/H₂O₂ process.

Effect of H₂O₂ Concentration

The results in Table 3 show that removal mean percentage of both pesticides in 30 mgL⁻¹ of H₂O₂ concentration was higher than in 10 mgL⁻¹. Also, the removal mean percentage of the malathion was more than diazinon.

Table 3. Comparison of decomposition mean percentage pesticides with UV/ H₂O₂ process at different hydrogen peroxide concentration.

H ₂ O ₂ concentration	Malathion	Diazinon
mgL ⁻¹	Mean±S D	Mean±S D
10	77.88±23.96	68.72±18.25
30	82.17±24.24	71.43±22.86
P.value > 0.05		

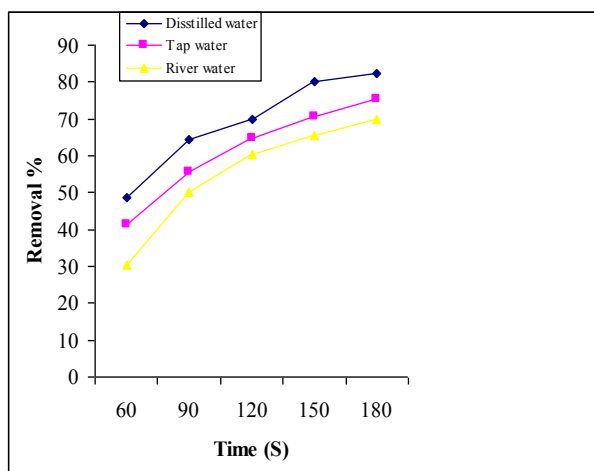


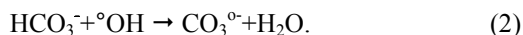
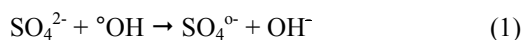
Figure 6. Investigation the efficiency of UV/H₂O₂ process in removal of malathion from real water. [malathion]₀ =200 µg/L;H₂O₂ =30 mg/L.

Addition of hydrogen peroxide increased the UV degradation rates of both pesticides mainly due to the formation of hydroxyl radicals through the photolysis of H₂O₂¹².

Degradation of Pesticides in Different Type of Water

The real water samples that were obtained from drinking water in Tehran and Babol-Rood River in Mazandaran , Iran. The characteristics of the real water are presented in the Table 1.

The photodegradation data of pesticides shows the first – order reaction rate carrier in all type of water. The results in Table 2 and Figure 6, and 7 show that photodegradation rate in distilled water higher than in natural water (tap, river waters), and photodegradation rate followed the following order: distilled water> tap water> river water. This inhibition is undoubtedly due to their ability to act as hydroxyl radicals scavengers by the following reaction:^{13,14}



This may be due to the presence of organic carbon in natural water which inhibits the degradation rate of pesticides (malathion and diazinon). These organic matters absorb most of the photons emitted there by slowing down the degradation reaction of pesticides.¹⁵

Table 2. Comparison of degradation kinetic rate constant of pesticides with UV/ H₂O₂ in process at various waters.

Pesticide	Distilled water		Tap water		River water	
	$k\left(\frac{1}{s}\right)$	R ²	$k\left(\frac{1}{s}\right)$	R ²	$k\left(\frac{1}{s}\right)$	R ²
Malathion	0.0083	0.92	0.008	0.97	0.0066	0.95
Diazinon	0.012	0.94	0.0405	0.93	0.0077	0.98

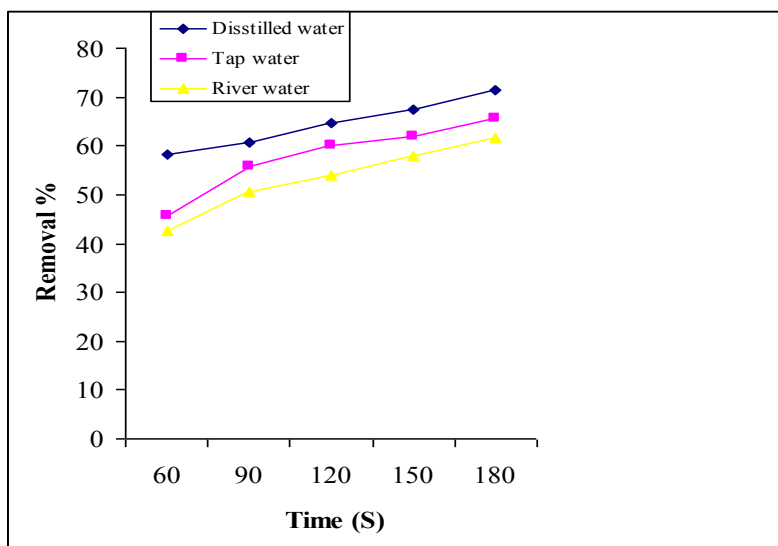


Figure 7. Investigation the efficiency of UV/H₂O₂ process in removal of diazinon from real water. [diazinon]₀ =100 µg/L;H₂O₂ =30 mg/L.

Conclusion

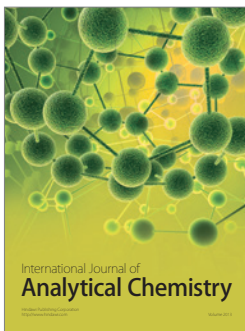
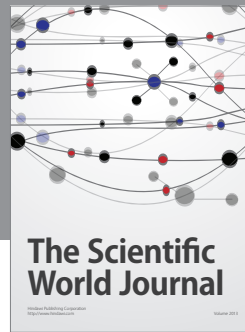
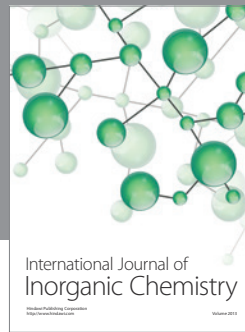
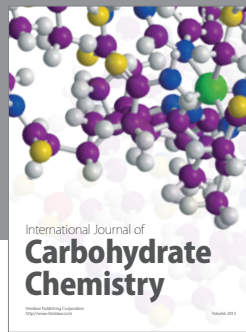
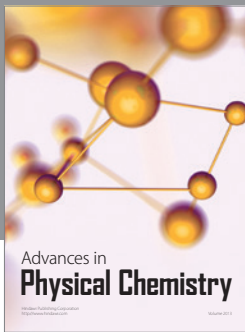
This study reveals the role played by the sulphate and bicarbonate ions in the °OH scavenging at different condition (pH, salt type, salt concentration, water type , H₂O₂ concentration).It was found that sodium bicarbonate was the most powerful inhibitor. Photodegradation rate in distilled water was higher than in natural water.

Acknowledgments

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