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The sunlight effect on trace pollutants in wastewater

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Title of Thesis: The sunlight Effect on Trace Pollutants
                 in Wastewater
Alan R. Sheu, Master of Engineering, 1987
Thesis directed by: Dr. Richard Parker,
                     Professor of Chemistry

ABSTRACT

In order to study the sunlight effect on the
degradation rate of trace pollutants, ortho-cresol was
selected to serve as a model compound in our studies.
Solution of ortho-cresol alone, methylene blue alone,
and the mixture of ortho-cresol and methylene blue were
exposed to sunlight for more than four hours and
aliquots analyzed with a spectrophotometer in order to
follow the changes in absorption.   Rate data were
obtained for these three cases as a function of pH.

The results indicate that methylene blue does
catalyze the degradation of ortho-cresol in the presence
of sunlight with lower pH's affording higher reaction
rates.

The methylene Blue Test was carried out using
Merck's procedure on samples of natural putrescible
waters and artificially prepared putrescible waters. It
is observed that methylene blue catalyzes neither of
natural putrescible or artificial putrescible samples
under the conditions studied in this work.

THE SUNLIGHT EFFECT

ON TRACE POLLUTANTS IN WASTEWATER

BY

ALAN R. SHEU

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of Master
of Engineering in Environmental Science/Toxicology
Option.

1987

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in Wastewater

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Theory

The utilization of solar energy has been developed in various aspects, such as the conversion of solar radiation to electricity, direct conversion of solar energy into heat, etc. In principle, the attractiveness of solar energy is that it is an inexhaustible source with a minimum of adverse environmental consequences. The future development of solar utilization will depend on a number of serious constraints, including scientific and technological problems, marketing and financial limitations, and political and legislative actions.[1]

The quantum theory can be used to explain most of the photochemical processes: that light is made up of discrete particles called quanta or photons. Each quantum carries a certain amount of energy, e, determined by the wavelength of the light, λ.

$$e = \frac{h\,c}{\lambda}$$

In this equation h is Planck's constant and c is the speed of light in a vacuum. The equation can be expressed as

$$e = h \nu$$

where ν is the frequency of the light.

When the energy of a quantum is equal to the energy difference between ground state and excited state of a molecule, the molecule can absorb a quantum accompanied by transition of the molecule to the higher state. Such singular transition is described as the Stark-Einstein Law. Increasing the light density can only increase the number of molecules undergoing transition, but does not alter the nature of the transition. Only with extra-high light density, such as laser photochemistry, can the molecule then absorb two or three quanta simultaneously.

The radiation, which depends on the wavelength, can stimulate the molecule in several ways. Infrared light can vibrate or rotate a molecule to a higher level; ultraviolet light may remove an electron from the molecule causing ionization; intermediate light may promote the molecule from the ground state to an electronically excited state.

The energy equation of one mole of quanta (one einstein) can be expressed as

$$E = \frac{N h c}{\lambda}$$

where the N is Avogadro's number, and λ is in nanometers ($1*10^{-7}$cm).

So an einstein of 286 nm light has an energy about 100 kcal mole^{-1} which is near the energy of the carbon-carbon and carbon-hydrogen bond. For one einstein of 200 nm light, the energy is 143 kcal. And for the 700 nm light, the energy of one einstein is equal 40 kcal.

The ultraviolet and visible spectra of molecules are made up of broad bands in which a number of peaks are discernible. The band like absorption is due to the fact that molecules have closely spaced vibrational level between the ground state and excited state.[2]

Some organic dyes have been considered as catalysts in photoxidation processes for degradation of organic com-pounds. They are easily excited by UV light, and in turn transfer their energy to potentially reactive molecules, which subsequently undergo decomposition. Methylene blue [1] is an example of such an easily excitable dye. We have in this work explored the possibility of utilizing organic dyes to catalyze the degradation of refractory pollutants. We have chosen methylene blue to study the feasibility of using it to clarify waste water, and also

to react with compounds which serve as models for toxic pollutants.[3]

Ultraviolet waves are of sufficient energy to break molecular bonds with typical energies in the range of 70-100 kcal/mole[4]. The disruption creates free radicals which can attack otherwise stable species[5]. The photochemical evidence indicates that, as the incident wavelength increases to 254 nm, the yield of water decomposition through H-OH bond scission decreases rapidly. It is the $HO^{\cdot}$, produced by the homolytic bond cleavage, that cause the subsequent reactions.

The hydroxyl radical can initiate a chain reaction by any one of many pathways. A predominant route would be the abstraction of a labile hydrogen from an organic molecule (RH). the resulting organic radical ($R^{\cdot}$) in the presence of oxygen combines readily with the oxygen molecule to form a peroxyradical ($ROO^{\cdot}$). The ($ROO^{\cdot}$) radical is unstable and many possible radical-radical interactions can occur. When ($ROO^{\cdot}$) abstracts a hydrogen atom from another organic molecule, an organic free radical is generated with formation of an organic peroxide (ROOH). ROOH dissociates readily into oxyradicals ($RO^{\cdot}$) and hydroxy radicals. The oxyradical ($RO^{\cdot}$) usually fragments into a small organic acid or organic aldehyde and a amaller

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organic radical. This type of chain reaction can continue with the resultant oxidation of large organic molecules and production of small organic acids, carbon dioxide and water.

Many organic pollutants entering the state's water resources are not effectively removed by biological oxidation in municipal waste treatment facilities or in natural water courses. One common mode of treatment is chlorination, which can result in the formation of noxious chlorinated organics, which may be more toxic than the unchlorinated species.[6] A better degradative method must be found.

Methylene Blue has been used to secondarily clarify waste water. When exposed to sunlight the methylene blue catalyzes the decomposition of waste water to such an extent that the waste water becomes disinfected. Optimization of conditions of reaction could produce an economical method of purifying waste water. Low grade methylene blue is inexpensive and little is required for the process.[7]

Methylene Blue (Figure 1) is a substituted phenothiazine containing two dimethylamino substituents on

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the outer rings. Reduction of methylene blue by oxidizable materials such as waste water containing putrescibles leads to structure [2].
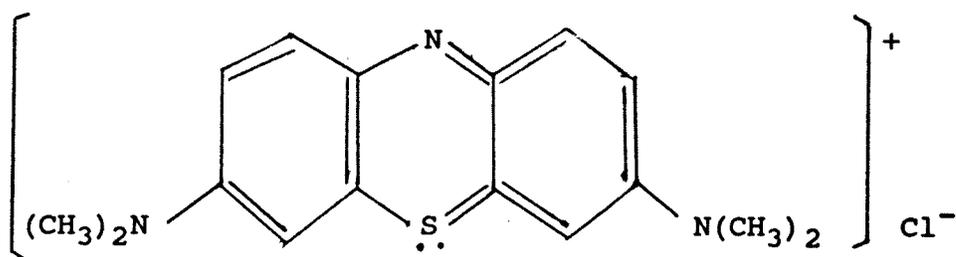
[1]

Methylene Blue
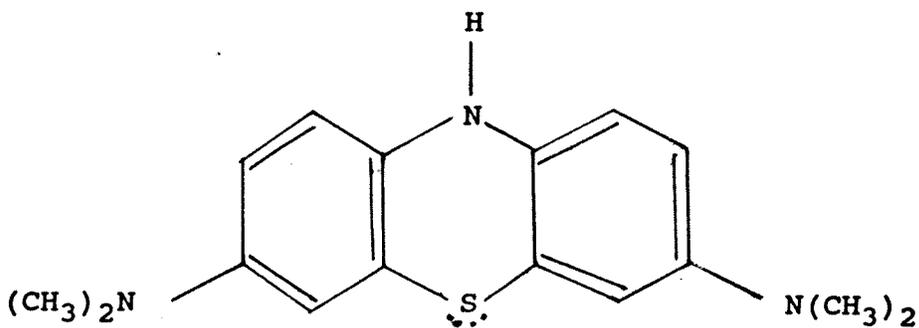
[2]

Figure 1. Structure of Methylene Blue Oxidized [1] and Reduced form [2]

Subsequent reoxidation of [2] can regenerate the original methylene blue.

In this study ortho-cresol has been selected as the model compound for toxic pollutants. Ortho-cresol is a typical phenol in that it is readily available and susceptible to oxidation. It has been identified as one of the most common components of waste water in the State of New Jersey. It is typical of those compounds which, when treated by chlorination techniques, yield products more toxic than themselves. Figure 2 shows the extremes of treatment by oxidations and chlorination. Complete oxidation would yield the harmless CO_2 and H_2O as products. This would be a desirable result. Chlorine treatment on the other hand, could result in the production of chlorinated molecules.
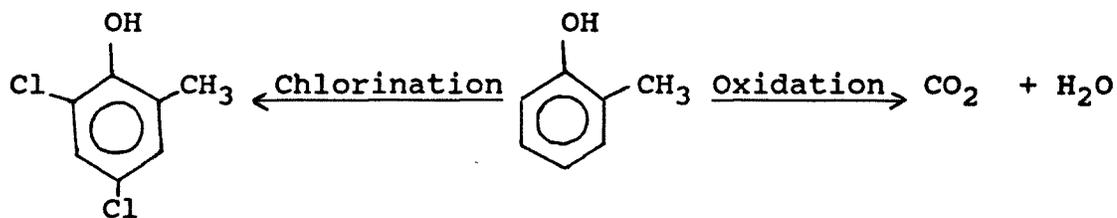
(one of many chlorination products)

Figure 2. Oxidation and chlorination of ortho-cresol

The object of this study is to enhance the degradation rate of toxic substances in wastewater using ortho-cresol as a model pollutant , by adding methylene blue as reagent and then exposing the test sample to the solar radiation. Determination of the sunlight effect was done by analyzing samples with a spectrophotometer. The reaction rate in terms of conc/time for each experiment has been calculated for comparison purposes. Before using methylene blue as a reagent for ortho-cresol, studies using Merck's analytical procedure were carried out on samples of prtrescible water.

Experimental

The reagents used were: 95.98% pure o-cresol which was obtained from Fisher Scientific Co., Fair Lawn, New Jersey; methylene blue which was obtained from Merck and Co., Inc., Rahway, New Jersey; and the sodium phosphate dibasic obtained from Matheson Coleman and Bell, East Rutherford, New Jersey.

All the chemicals used are listed with CAS number and hazards in Table I. Samples were prepared in a ventilating hood by wearing gloves and goggles to prevent skin and eye contact, and wearing a mask to eliminate any damage through inhalation.

The RESPONSE UV-VIS Spectrophotometer used for the analysis of samples was obtained from Gilford Instrument Laboratories, Oberlin, Ohio. The photometer and monochromator's wavelength range was from 200.0 nm to 900.0 nm with a deuterium light source for ultraviolet light and quartz-halogen light source for visible light. The ultrasonic waves were generated by the model 8845-40 Ultrasonic Cleaner which was obtained from Cole-Parmer Instrument Co., Chicago, Illinois. The model No. PT-9-C

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Ultraviolet Lamp was obtained from Sperti Sunlamp Division-Cooper Hewitt Electric Co., Erlanger, Kentucky. The samples were kept at $40^{\circ}C$ by the model 2095 Bath and Circulator which was obtained from Forma Scientific, Inc., Marietta, Ohio. The pH of the reaction mixtures was adjusted with a model 601A pH meter purchased from Orion Research, Inc., Cambridge, Massachusetts.

Table I. Chemical Properties and Hazards[8]

Ortho-cresol	Hazards
$CH_3C_6H_4OH$ CAS# 95-48-7 MW 108.14 MP $30^{\circ}C$	Poison,Combustible Causes skin and eye burns Harmful if inhaled May be fatal if absorbed through skin
Appearance: Colorless to light amber liquid	
Methylene Blue CAS# 61-73-4 MW 319.85 Appearance: Green crystals	Powdered material may form Explosive Dust-Air Mixtures.
Hydrochloric Acid HCl CAS# 7647-01-0 MW 36.46 Appearance: Clear solution	Causes skin and eyeburn
Sodium Hydroxide NaOH CAS# 1310-73-2 MW 40.00 Appearance: White Pellets	Causes severe skin and eye burns, Harmful if inhaled
Sodium Phosphate, Dibasic(anhydrous) Na_2HPO_4 CAS# 7558-79-4 MW 141.96 Appearance: White crystals	Low hazard for usual industrial handling

Determination of Water Contamination

The Methylene Blue Test was carried out by the Merck's procedure in order to determine the putrescibility of water.[9]

1. Preparation of Samples

Solutions of o-cresol ($1.000 * 10^{-3}$ M) and methylene blue ($1.338 * 10^{-3}$ M) were prepared. A 250 mL bottle was filled to overflowing with o-cresol solution. Methylene blue (1.5 mL) was added and the mixture stoppered immediately to prevent the formation of air bubbles. Samples of this stock solution were treated by one of the following procedures.

2. Reactions

A. The solution was stored at 25 °C for 7 days.

B. The solution was kept at 40 °C for 7 days.

C. Natural water from Branch Brook Park, Black Berry Bay, and Long Branch were collected as testing

samples in place of o-cresol, and were stored at 25^{0}C for 7 days.

D. Samples were prepared by adding maple leaves, magnolia leaves, and grass to distilled water and stored at room temperature for one week before performing the Methylene Blue Test.

Determination of Sunlight Effect on Trace Pollutants

The experimental procedure described below was used for determining the sunlight effect of the reactions of o-cresol with methylene blue.

Stock solutions of o-cresol (1.000 * 10^{-3}M), 0.200 M buffer solution (Na$_2$HPO$_4$), and methylene blue (7.98*10^{-6}M) were prepared. Three samples were prepared for investigation. Sample #1 was made by adding 280 mL o-cresol and 280 mL methylene blue to 280 mL buffer solution. Sample #2 was prepared by adding 280 mL distilled water in place of 280 mL methylene blue, and 280 mL o-cresol to 280 mL buffer solution. Sample #3 was prepared by mixing 280

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mL distilled water, 280 mL methylene blue , and 280 mL buffer solution. The final concentrations of methylene blue and ortho-cresol in the samples were $2.66 * 10^{-6}$ M and $0.333 * 10^{-3}$ M.

The pH of the samples was adjusted to 10.00. The samples were then exposed to sunlight on the roof for more than 4 hours. Aliquots were collected every hour, stored in a refrigerator for 8 hours and then taken out for spectrophotometer analysis after they were allowed to warm up to room temperature.

In a similar manner, all procedures were repeated at pH's 10.00, 10.25, 10.50, and 11.00.

Results and Discussion

1.Methylene Blue Tests

The decolorization of methylene blue is explained by
the reduction of the methylene blue by the putrescence and
decayed matter which has been produced by microorganisms.
The more putrescence the faster the methylene blue
decolorization occurs.

In the first series of experiments ortho-cresol was
used as a model for the organic pollutants produced by
microorganisms acting upon organic compounds present in
water.

The Methylene Blue Test, following Merck's procedure,
is used to measure the quantity of oxidized organic
material present in water. Methylene Blue has peaks of
maximum absorption of 245 nm, 291 nm, and 664 nm which can
be used as measures of the concentration of methylene blue
(vide infra). The results of the Methylene Blue Test
using o-cresol (1.0 * 10^{-3} M) showed no noticeable change

in color and little change in absorbance (Table II) over the seven day period. Even increasing the temperature from 23^0C to 40^0C had little effect on color or absorbance changes. Unfortunately, the Test appears not to be applicable to o-cresol.

Table II. Methylene Blue Test I

Sample	Temp (^{0}C)	λ_{nm}	T= 0	1	2	3	7 (days)	Color Change
				Absorbance				
H$_2$O	23	245.5	0.040	0.043	0.046	0.042	0.044	
+		291.5	0.150	0.172	0.182	0.177	0.173	none
MB		664.0	0.369	0.397	0.406	0.400	0.392	
OC+	23	270.5	2.342	2.144	2.141	2.104	2.044	
MB		664.0	0.387	0.456	0.436	0.436	0.416	none
H$_2$O	40	246.0	0.045	0.036	0.036	0.036	0.044	
+		291.5	0.176	0.163	0.169	0.177	0.169	none
MB		664.5	0.405	0.372	0.380	0.404	0.392	
OC+	40	270.5	1.965	1.945	1.905	1.905	1.717	
MB		664.5	0.218	0.218	0.194	0.211	0.198	none

Next we conducted experiments with samples collected from a lake in Branch Brook Park, a stream in Long Branch, and the creek called Black Berry Bay. None of these samples showed decolorization within 120 hours (see Table III). Again, there was little change in absorbances as a

function of time. Variations appear to be within experimental error. So it could be concluded that the natural water from these locations is nonputrescible.

Table III. Methylene Blue Test II

Sample	λ_{nm}	T= 0	1	2	3	7(days)	Color change
				Absorbance			
Branch	245.5	0.055	0.052	0.052	0.052	0.052	
Brook	291.5	0.242	0.247	0.251	0.233	0.238	none
Park	664.0	0.542	0.551	0.555	0.516	0.520	
Black	246.0	0.045	0.028	0.056	0.052	0.045	
Berry	291.5	0.274	0.262	0.265	0.264	0.231	none
Bay	664.5	0.602	0.571	0.583	0.585	0.549	
	246.0	0.042	0.043	0.043	0.047	0.043	
Long	291.5	0.254	0.239	0.236	0.235	0.215	none
Branch	664.5	0.563	0.521	0.530	0.532	0.485	
	246.0	0.038	0.043	0.045	0.041	0.040	
Grass	291.5	0.182	0.196	0.210	0.191	0.184	none
	664.5	0.412	0.439	0.478	0.435	0.411	
Maple	291.5	0.205	0.154	0.154	0.139	0.123	
Leaves	664.5	0.222	0.205	0.205	0.189	0.173	none
Cherry	291.5	0.341	0.131	0.131	0.132	0.111	
Leaves	664.5	0.182	0.177	0.185	0.183	0.193	none
	246.0	0.030	0.031	0.033	0.033	0.026	
Magnolia	291.5	0.202	0.205	0.212	0.206	0.174	none
Leaves	664.5	0.432	0.463	0.468	0.469	0.043	

Other samples were prepared by adding putrescible substances (maple leaves, magnolia leaves, and grass) to

distilled water and storing at room temperature for one week before performing the Methylene Blue Tests. The results again showed no decolorization taking place within 120 hours (see Table III). Therefore under the conditions employed in this test, no apparent oxidation of these organic materials was observed.

2. Sunlight Effect on Trace Pollutant

Perina[10] reported that methylene blue in the presence of sunlight facilitated the degradation of organic matter. Therefore, we attempted to reproduce these results with our model pollutant, ortho-cresol. To begin the analysis, spectra were obtained for buffered solutions of methylene blue, o-cresol, and the mixture of methylene blue and o-cresol. These are presented in Figures 3,4, and 5.

Upon examining them, it is observed that methylene blue has three peaks at wavelengths 246 nm, 291 nm, and 664 nm (Figure 3); o-cresol shows two peaks at wavelengths 236 nm and 270 nm (Figure 4). The mixture of methylene blue and o-cresol has three peaks at wavelengths 236 nm, 276 nm, and 664 nm (Figure 5).
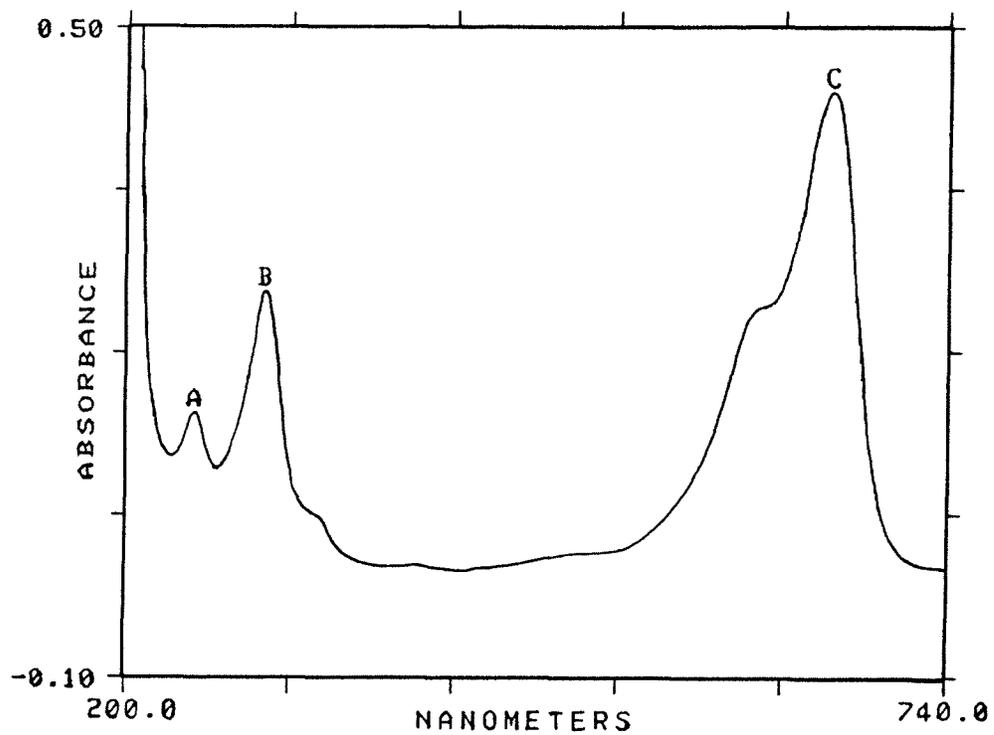
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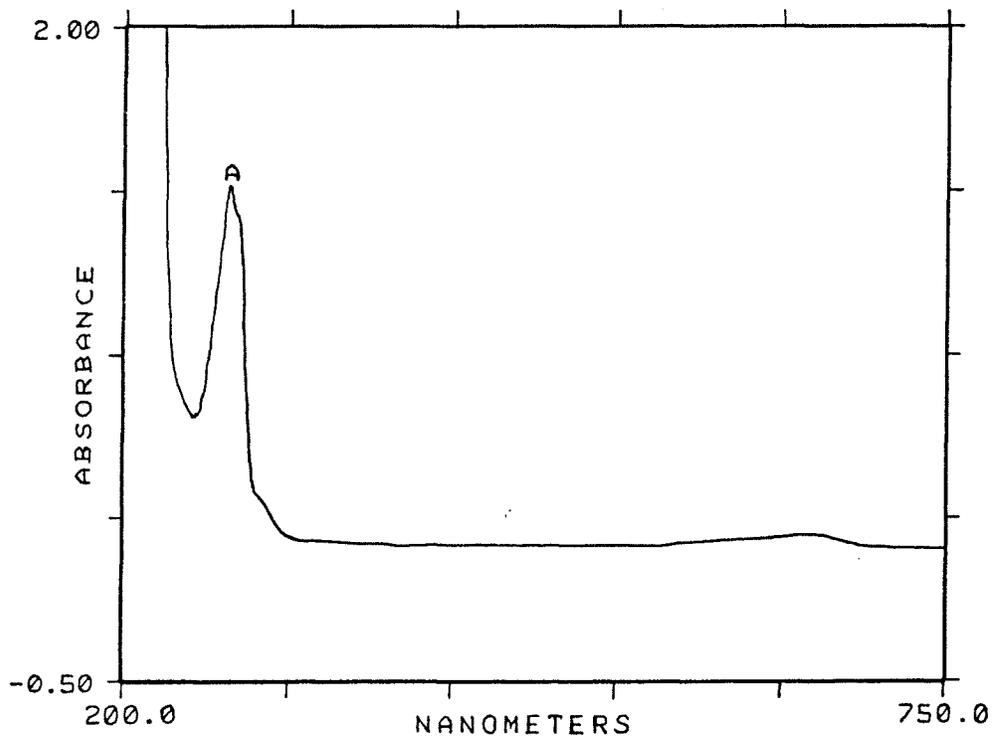Figure 3.   Spectrum of Methylene Blue

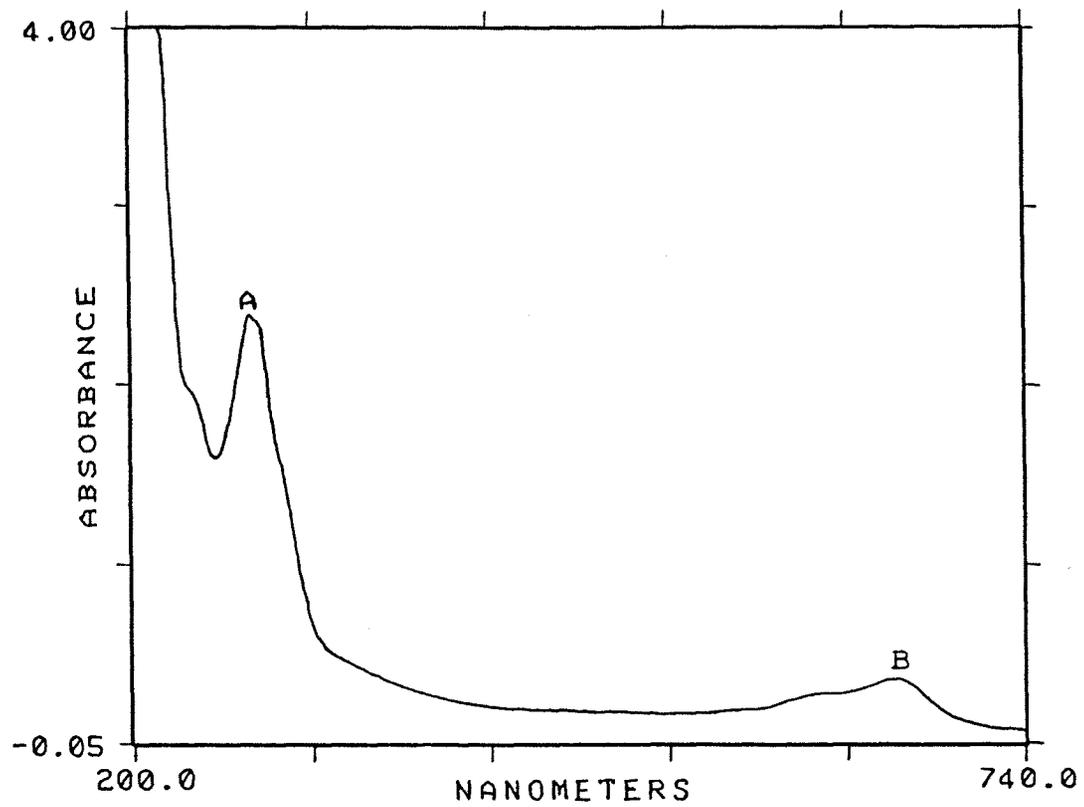Figure 4.   Spectrum of Ortho-cresol

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Figure 5. Spectrum of Mixture of Methylene Blue
and Ortho-cresol

It was decided to use the absorption at 236 nm as a measure of the concentration of o-cresol, and 664 nm as a measure of the concentration of methylene blue. The effect of sunlight on the two individual materials, as well as on the synergistic effect of the combination of the two materials could be measured at 236 nm and 664 nm.

Table IV presents the absorption as a function of time at the chosen wavelength for the reaction of methylene blue, o-cresol, and the mixture of methylene blue and o-cresol in the presence of sunlight at the different pH's. These data are in units of OD vs. time, in hours.

Figures 6,7, and 8 show the change in absorption with respect to time for the reaction of methylene blue, o-cresol, and the mixture of methylene blue and o-cresol in the presence of sunlight at a variety pH's. The data have been fit to a straight line equation using Sigmaplot. Sigmaplot is a software package for data analysis and plotting which is distributed by Jandel Corporation. The slopes obtained represent the reaction rate.

Table IV. Sunlight Effect on Methylene Blue, O-cresol,
and the Mixture of Methylene Blue and O-cresol.

				Absorbance		
pH	Sample	λ_{nm}	T= 0	1	2	3 (hr)
10.0	MB	246.0	0.0425	0.0404	0.0243	0.0182
		291.5	0.0182	0.1618	0.1112	0.0870
		664.0	0.4246	0.3802	0.2588	0.2123
	OC	236.0	0.1845	0.0461	0.0000	0.0369
		270.5	0.9043	1.0889	1.1074	1.1258
	MB+OC	236.0	0.3763	0.1881	0.1439	0.0664
		276.0	0.7746	1.1066	1.1730	1.2394
		664.0	0.3320	0.2656	0.2324	0.1771
10.5	MB	246.0	0.0148	0.0114	0.0091	0.0023
		291.5	0.0878	0.0832	0.0638	0.0388
		664.0	0.1983	0.1869	0.1436	0.0877
	OC	236.0	0.3548	0.2660	0.2660	0.1773
		270.5	0.9163	0.9311	0.9902	1.0346
	MB+OC	236.0	0.8846	0.7076	0.6487	0.3833
		276.0	0.7371	0.8551	0.8551	0.8551
		664.0	0.2359	0.2064	0.1917	0.1917
11.0	MB	246.0	0.0094	0.0024	0.0000	0.0024
		291.5	0.0706	0.0165	0.0071	0.0329
		664.0	0.1647	0.0400	0.0188	0.0753
	OC	236.0	0.9458	1.1232	0.9163	1.0050
		270.5	0.9902	1.0346	1.0641	1.0198
	MB+OC	236.0	0.3547	0.2956	0.2069	0.1774
		276.0	0.7094	0.6799	0.7094	0.7242
		664.0	0.1776	0.1482	0.1513	0.1328

Sunlight Effect of Methylene Blue at 246 nm
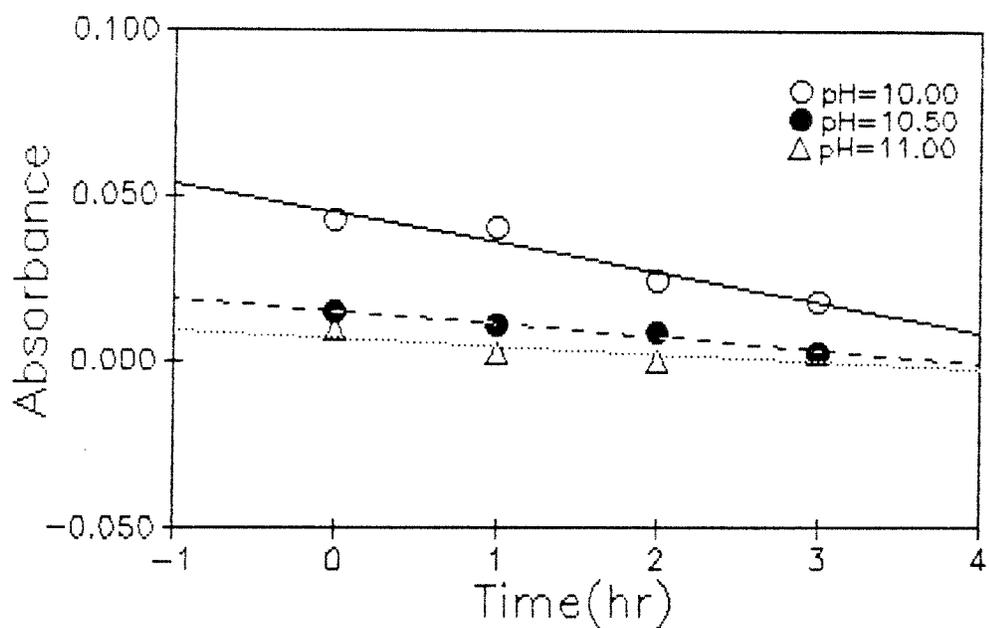
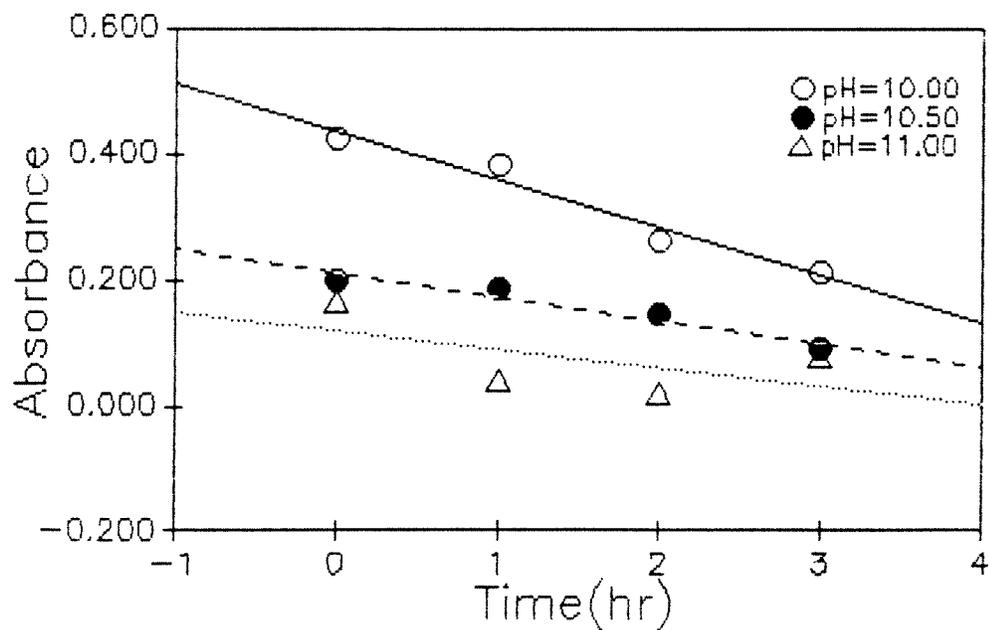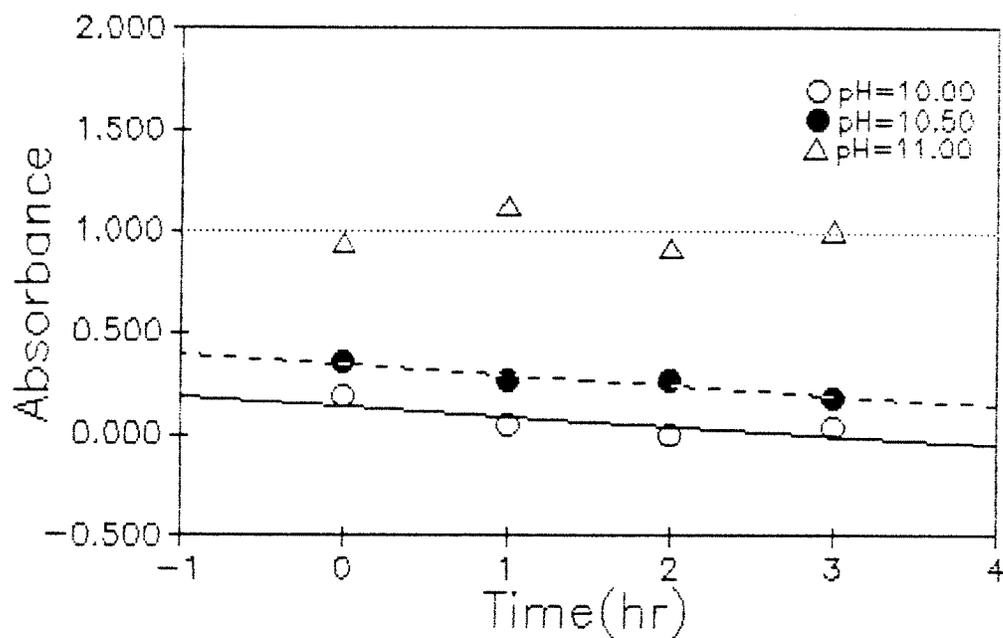# Sunlight Effect of Methylene Blue at 664 nm

Figure 6.   Sunlight Effect of Methylene Blue

Sunlight Effect of O-cresol at 236 nm
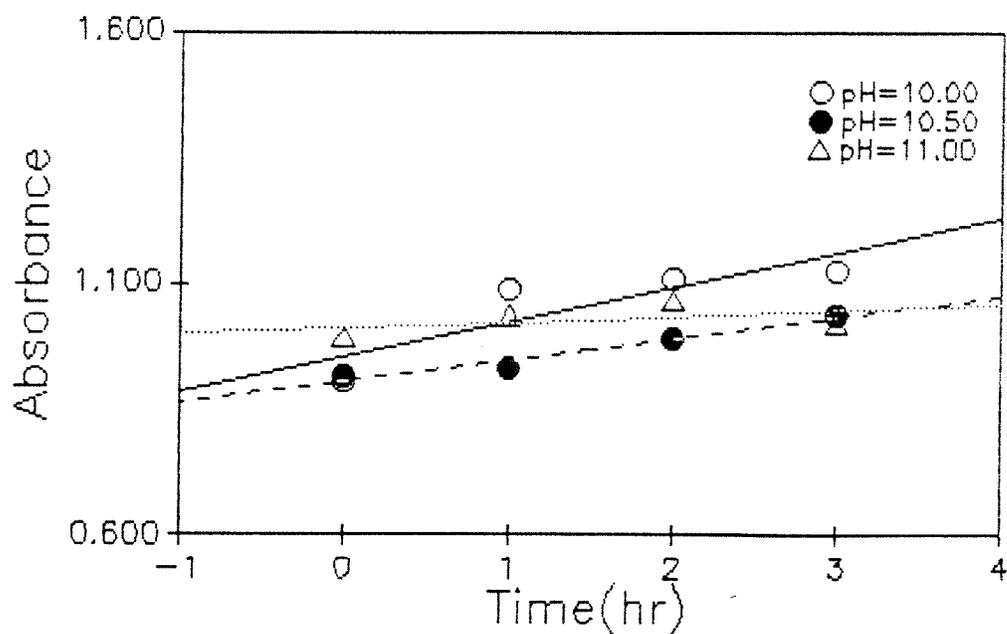

Sunlight Effect of O-cresol at 270 nm
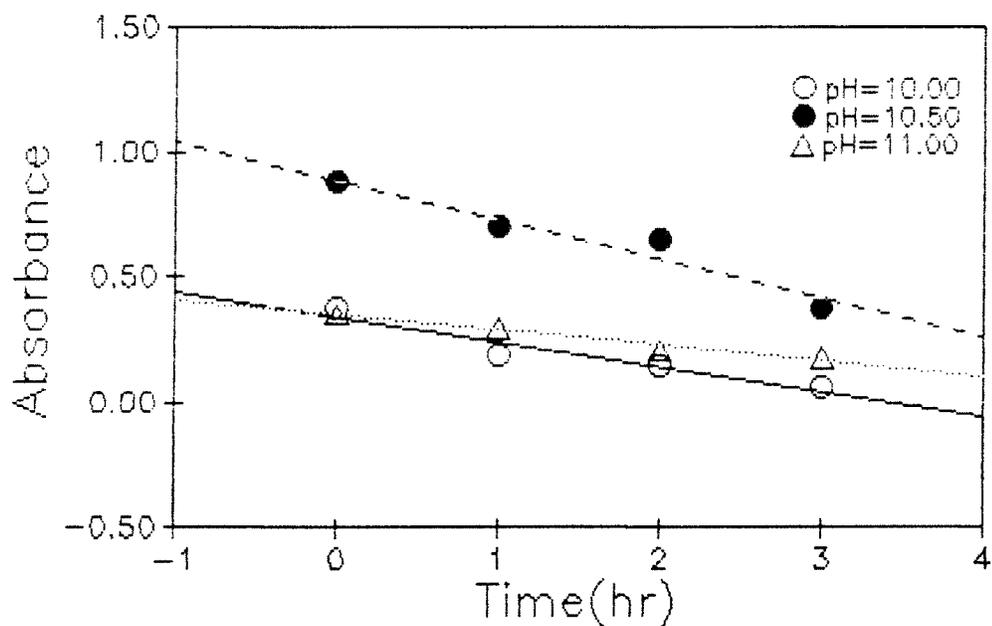

Figure 7. Sunlight Effect of Ortho-cresol

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Sunlight Effect of MB+OC at 236 nm
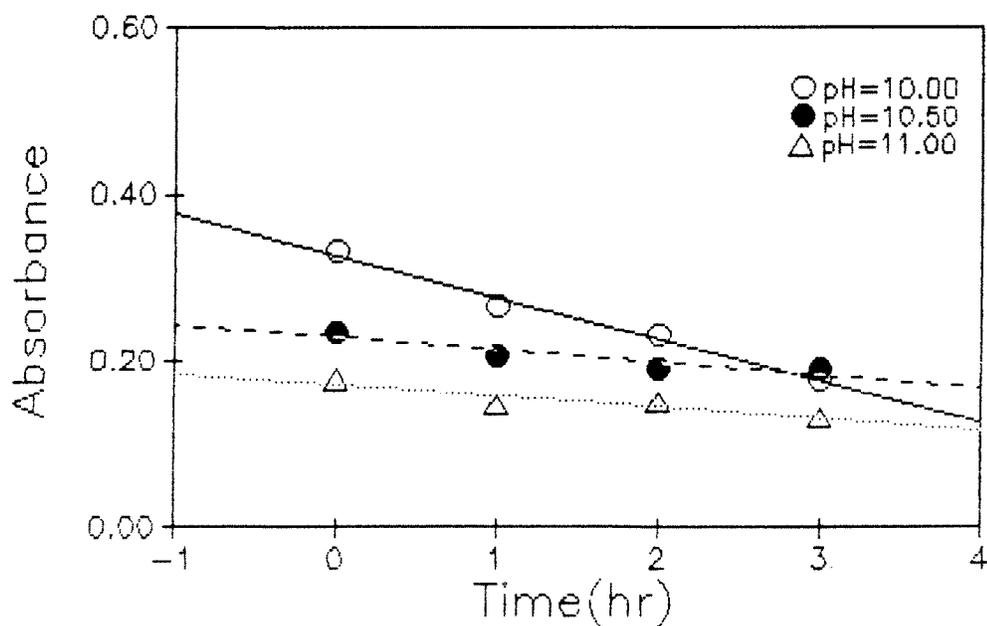

Sunlight Effect of MB+OC at 664 nm

Figure 8. Sunlight Effect of the Mixture of Methylene
Blue and Ortho-cresol

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Table V summarizes the effect of pH on the reaction rate for methylene blue by itself, o-cresol by itself, and the mixture of methylene blue and o-cresol. The results show that the rate is pH dependent.

Table V. Effect of pH on Reaction Rates(OD/hr) for Methylene Blue, O-cresol, and the Mixture of Methylene Blue and O-cresol.

			Reaction Rate (OD/hr)		
Sample	λ(nm)	pH=	10.0	10.5	11.0
MB	246		-0.0089	-0.0040	-0.0023
	664		-0.0760	-0.0375	-0.0290
OC	236		-0.0489	-0.0533	-0.0029
	270		+0.0683	+0.0414	+0.0118
MB+OC	236		-0.0974	-0.1562	-0.0621
	664		-0.0498	-0.0147	-0.0131

The rates in Table V, in OD/hr, do not represent the reaction on a molar basis. In order to convert OD/hr to (mole/L)/hr, which is a better measure of the rates of the reactions on a molecular basis it is necessary to correct for the molar absorption of each compound at each pH at

each wavelength studied. The rates of the reactions at
each pH, are therefore corrected for by dividing by the
extinction coefficient at that pH. The extinction
coefficent at each pH was obtained by dividing the
experimentally determined absorption by the known
concentration value (see Table VI). The results are
presented in Table VII and Figures 9,10, and 11. These
figures demonstrate the relationship between pH and
reaction rate.

Table VI. Extinction Coefficent at the Different Wavelengths for Ortho-cresol and Methylene Blue

|			Extinction Coefficent		
Sample	λ(nm)	pH=	10.0	10.5	11.0
MB	246		16000	5560	3530
	664		160000	74500	61900
OC	236		554	1070	2840
	270		2720	2750	2970
MB+OC	236		554	1070	2840
	664		160000	74500	61900

For the methylene blue, it is observed that the
reaction rate changes very little with pH. This is the

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methylene blue by itself and for the methylene blue in the mixture of ortho-cresol and methylene blue.   For ortho-cresol the rate is observed to increase as pH decrease for both the sample of ortho-cresol by itself and the mixture of methylene blue and ortho-cresol.   Presumably further reductions in pH would result in even more enhanced degradation of ortho-cresol in a system closer to neutrality.   There is one unmistakenable observation.   That is, ortho-cresol definitely degrades faster in the presence of methylene blue at each of the pH's studied.

Table VII. Reaction Rate (mole/L)/ hr (* 10^6)

			Reaction Rate (mole/L)/hr(*10^6)		
Sample	λ(nm)	pH=	10.0	10.5	11.0
MB	246		−0.56	−0.72	−0.65
	664		−0.48	−0.50	−0.47
OC	236		−88.30	−49.80	−1.02
	270		+25.10	+15.10	+3.97
MB+OC	236		−176.00	−146.00	−21.90
	664		−0.31	−0.20	−0.21

Reaction Rate of Methylene Blue at 246 nm
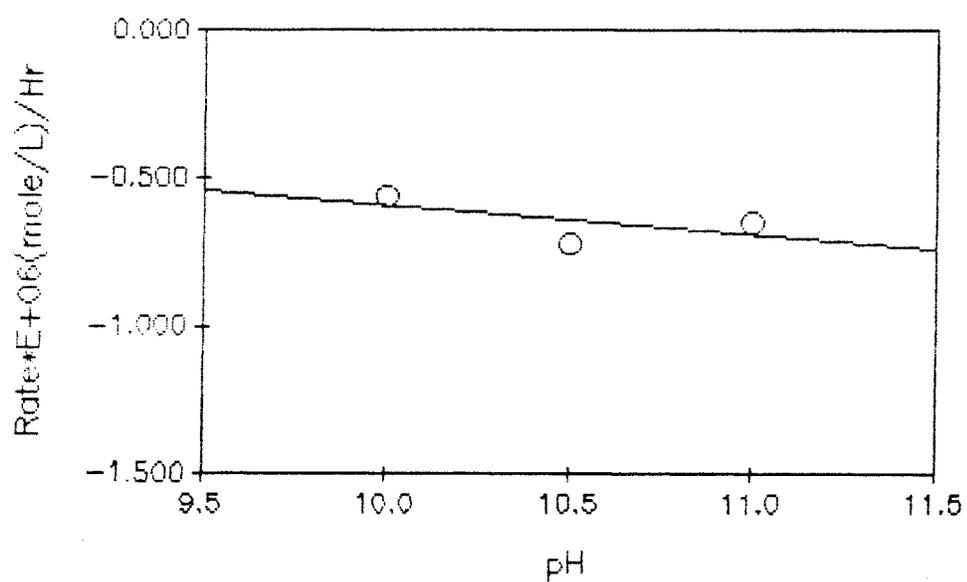
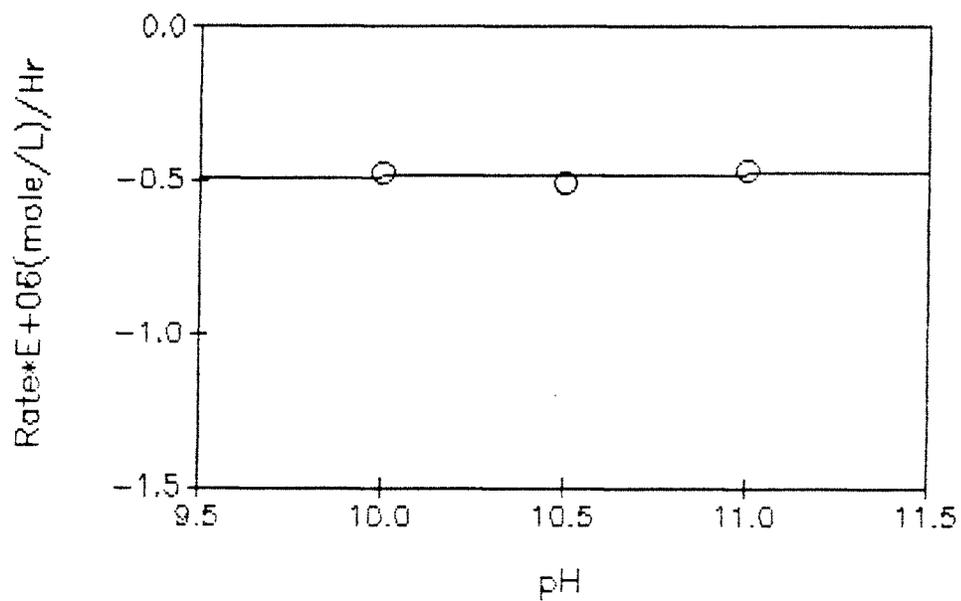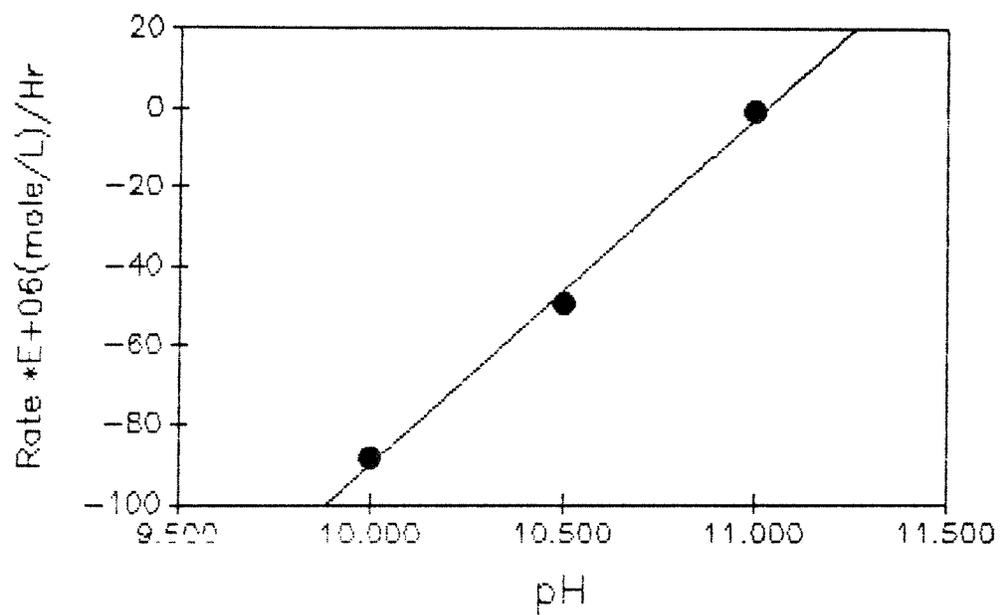## Reaction Rate of Methylene Blue at 664 nm

Figure 9.   Reaction Rate of Methylene Blue

Reaction rate of o-cresol at 236 nm
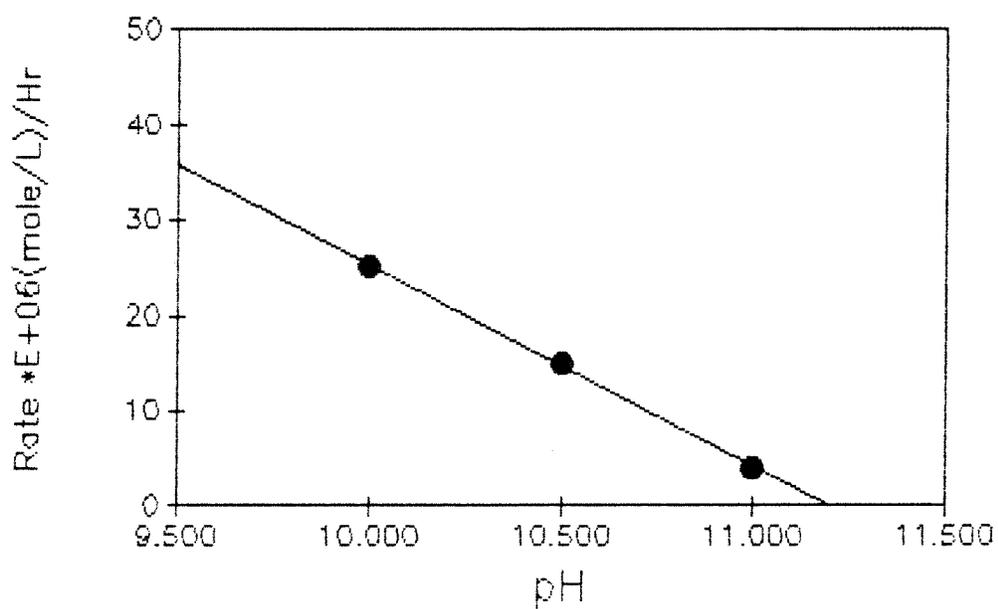

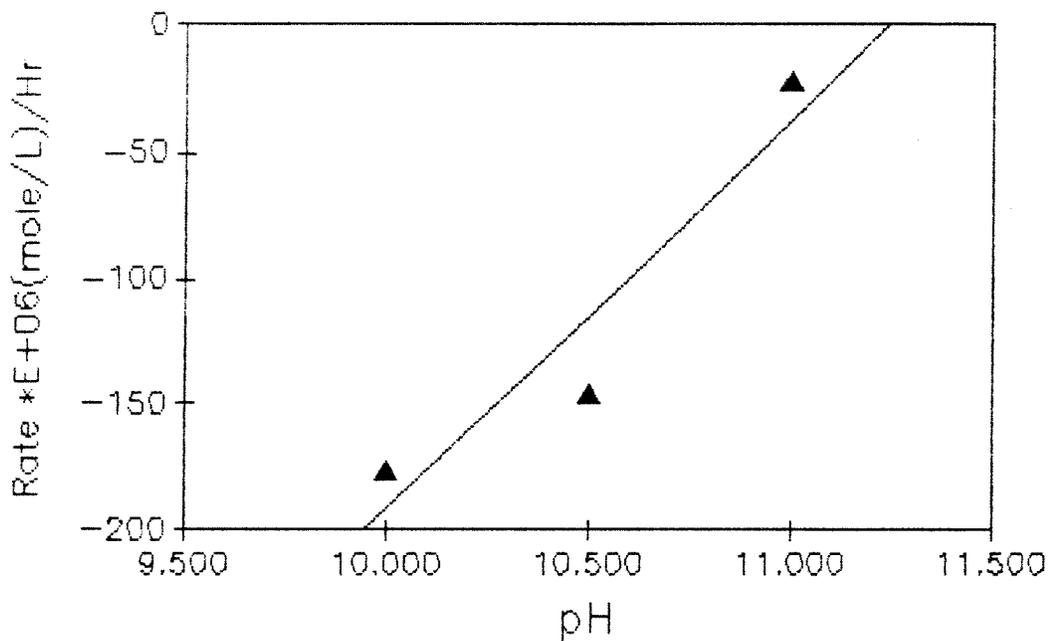# Reaction rate of o-cresol at 270 nm

Figure 10. Reaction Rate of Ortho-cresol

Reaction rate of MB+OC at 236nm
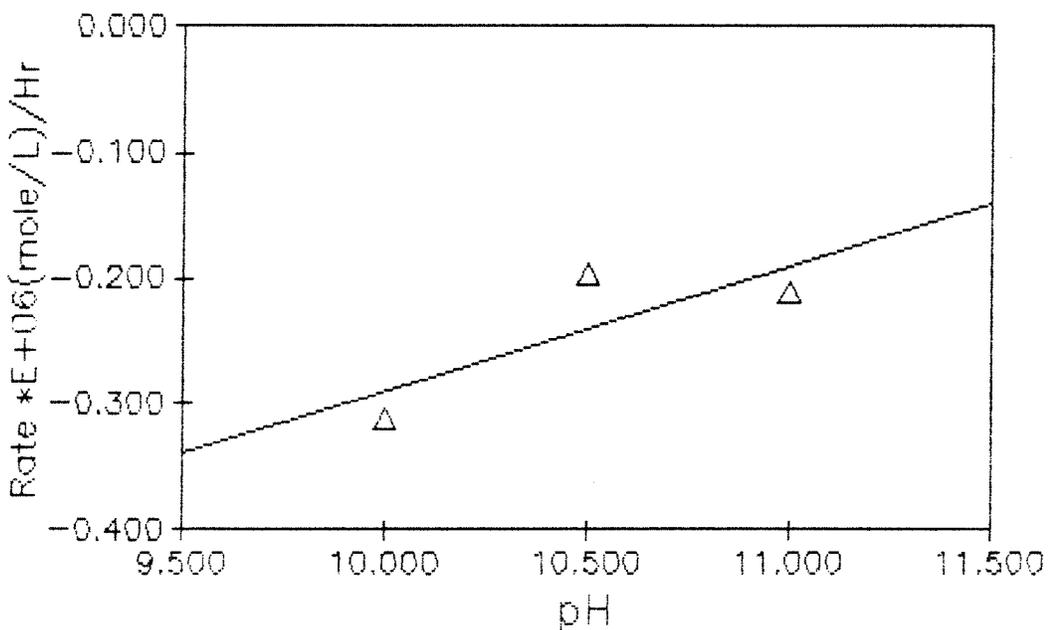

Reaction rate of MB+OC at 664nm

Figure 11. Reaction Rate of the Mixture of Methylene
Blue and Ortho-cresol

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To better compare the effect of pH on degradation rate for the three cases the data are fit to the empirical equation

$$Rate = k * pH + B$$

A regression analysis(of the rate vs pH) data yields the slope k which is a measure of the rate of change of the degradation rate with respect to pH.   These values are presented in Table VIII for comparison purposes.

Table VIII. Degradation Rate of MB+OC's synergistic effect

		k	
Wavelength(nm)	MB	OC	MB+OC
236		$8.73*10^{-5}$	$15.4*10^{-5}$
664	$0.70*10^{-8}$		$9.90*10^{-8}$

The pH dependence of the degradation rate of o-cresol is observed to be more in the mixture of methylene blue and o-cresol than for the o-cresol by itself.   Likewise, the pH dependence of the degradation of methylene blue is observed to be more in the mixture than for the methylene blue by itself.

The result of the enhancement of the degradation of ortho-cresol in the presence of methylene blue was not surprising. This is exactly what the research expected to accomplish from the beginning.

Conclusions and Recommendations

It appears that methylene blue does not appreciably catalyze the degradation of such natural products as leaves, grass, etc. under the conditions studied in this work.

Methylene blue catalyzes the degradation of ortho-cresol in the presence of sunlight. The reaction is pH dependent, with lower pH's (in the alkaline region studied) affording higher reaction rates.

It is recommended that (1) lower pH's than 10.0 be investigated in the methylene blue reaction, (2) other phenols be studied, (3) other redox dyes be investigated.

This exploratory work has demonstrated the possibility of utilizing redox dyes to decontaminate industrial waste waters at moderate conditions, at low cost, and ultimately on a large scale.

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