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REMOVAL OF PHTHALATES FROM CONTAMINATED WATER USING DIRECT PHOTOLYSIS AND UV/H_2O_2 PROCESSES

B. Tawabini[1], M. Al-Suwaiyan[2], R. Allayla[3], M. Al-Malack[4], A. Abulikbash[5] and A. Al-Arfaj[5]

1: Research Engineer III, Research Institute, KFUPM
2: Associate Professor, Civil Engineering Department, KFUPM
3: Professor, Civil Engineering Department, KFUPM
4: Associate Professor, Civil Engineering Department, KFUPM
5: Professor, Chemistry Department, KFUPM

KFUPM # 952, Dhahran 31261. Email: bassamst@kfupm.edu.sa

ABSTRACT

This study was conducted to evaluate the removal efficiency of phthalate from contaminated water using the direct photolysis and the ultraviolet / hydrogen peroxide (UV/H_2O_2) process. Dimethyl phthalate (DMP) with an initial concentration of 20 ppm was used as a model compound. A low-pressure mercury UV lamp of 100 mWatt intensity was used to provide the radiation. The effects of initial concentration of H_2O_2, UV exposure time, pH and temperature were assessed. The results showed that about 60 % of DMP were removed directly by activation caused by UV light after an exposure time of one hour. However, the removal efficiency increased when the DMP-spiked water was first dosed with H_2O_2 prior to irradiating with UV light (i.e. UV/H_2O_2). More than 98% of DMP was removed after 45 minutes when the UV-irradiated solution was dosed with 136 ppm of H_2O_2. The results also showed that lowering the pH and increasing the temperature enhanced the removal of DMP by UV/H_2O_2 process.

Keywords: *Ultraviolet light, hydrogen peroxide, hydroxyl radical, phthalates, UV/H_2O_2 process, advanced oxidation processes, industrial waste treatment.*

الملخص

تم عمل هذه الدراسة من أجل تقييم فعالية معالجة مياه ملوثة بمادة phthalate Dimethyl باستخدام طريقة أكسدة متطورة تعتمد على إنتاج كمية من جذر الهيدروكسيل الحر (OH^o) بواسطة تسليط الأشعة الفوق بنفسجية على الوسط الذي يحتوي على مادة بروكسيد الهيدروجين (H_2O_2) . يقوم جذر الهيدروكسيل في بعض الحالات بتكسير المادة العضوية إلى ثاني أكسيد الكربون وماء . وتم في هذه الدراسة أيضا تقييم مفعول بعض العوامل مثل جرعة الأشعة فوق البنفسجية وتركيز مادة بروكسيد الهيدروجين، والرقم الهيدروجيني والحرارة على أداء هذه الطريقة على إزالة المادة العضوية الملوثة من المياه . ولقد أثبتت الدراسة أن حوالي ٦٠% من المادة الملوثة قد تم معالجتها بواسطة تسليط الأشعة فوق البنفسجية فقط ,وان هذه النسبة زادت إلى أكثر من ٩٨% عند إضافة مادة بروكسيد الهيدروجين بتركيز ١٣٦ جزء في المليون . ,لقد دلت النتائج أيضا على أن الرقم الهيدروجيني والحرارة يلعبان دورا هاما في تحديد فعالية الطريقة المستخدمة في هذه الدراسة.

1. INTRODUCTION

Esters of Phthalic acids (PAEs), also called phthalates, are formed by linkage of an alkyl group to the carboxylic group. They are environmentally ubiquitous pollutants with a variety of industrial uses including carrier for pesticides and insecticides and insect repellent, and are used in cosmetics fragrances, lubricants, de-foaming agents and as plasticizers added to the polyvinyl chloride (PVC) and plastics to improve their flexibility [Staples et al, 1997]. These chemicals are suspected to cause health problems. In fact, due to their carcinogenic properties, six (6) phthalates have been included in the priority pollutant list set by the U.S. Environmental Protection Agency [Cartwright et al, 2000]. In this study, DMP (Figure 1) was used as a target compound.

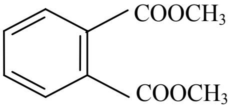

Figure1: Di Methyl Phthalate (DMP)

The interest in developing Advanced Oxidation Processes (AOPs) in chemical water treatment has grown recently [Tedder et al, 1997]. These processes generate highly reactive hydroxyl radicals (OH^o) to oxidize various compounds in the water. These radicals are characterized by having a high oxidation potential (2.8 V) that can, in some cases, completely mineralize contaminants by converting them into CO_2 and H_2O [Ruppert et al, 1994]. Several AOPs processes can generate the hydroxyl radicals including: UV/H_2O_2, Fenton's reagent (Fe^{2+} / H_2O_2), peroxone (ozone / H_2O_2), and titanium dioxide (TiO_2)-assisted photo-catalytic processes [Venkatadari et al, 1993; Rajeshwar et al, 1995].

The UV/ H_2O_2 oxidation system involves the single-step dissociation of H_2O_2 to form two (OH^o) radicals as shown in equation (1). Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals (R^o), which are highly reactive and can be further oxidized as shown in equation (2).

$$H_2O_2 \xrightarrow{UV} 2\ OH^o \qquad (1)$$

$$OH^o + RH \longrightarrow H_2O + R^o \qquad (2)$$

$$OH^o + H_2O_2 \longrightarrow HO_2^o + H_2O \qquad (3)$$

In addition, UV light alone can be utilized in the degradation of organic pollutants in a process called photolysis. Photolysis involves the interaction of light with molecules to initiate their dissociation into fragments [Ewa, 1992].

In general, little attention has been given to the treatment of phthalates by chemical methods and most research work was directed toward biological treatment [Jianlong et al, 1996]. However, these methods suffer from several drawbacks such as toxicity of phthalate to microorganisms [Madsen et al, 1999, O'Conner et al, 1989] and the long residence time needed to achieve appreciable removal. Extensive literature search showed that research in the area of degrading phthalate esters by photo-oxidation is lacking. The main objective of this study is to assess the efficiency of removing the DMP from contaminated water using direct photolysis and the UV/H_2O_2 methods.

2. MATERIALS & METHODS

The bench-scale photo-reactor consists of a 1.2-L cylindrical vessel made of Pyrex surrounded by an outer Plexiglas cylindrical vessel used for cooling purposes as shown in Figure (2). A low-pressure mercury UV lamp irradiating at a wavelength in the range of 240 to 260 nm with an output intensity of about 100 mWatt is used for illumination purpose. The reactor works in a batch mode. The residual DMP concentrations were measured at 0, 15, 30, 45 and 60 minutes.

Neat solution of DMP (99% purity), purchased from Chemical Service, England, was used to prepare stock standard dilutions. Aliquots of 20 ppm DMP were spiked in a de-ionized distilled water. Stock hydrogen peroxide (H_2O_2) of 35% purity was used to prepare about 6800 ppm of H_2O_2 stock solution [Bassett et al, 1978].

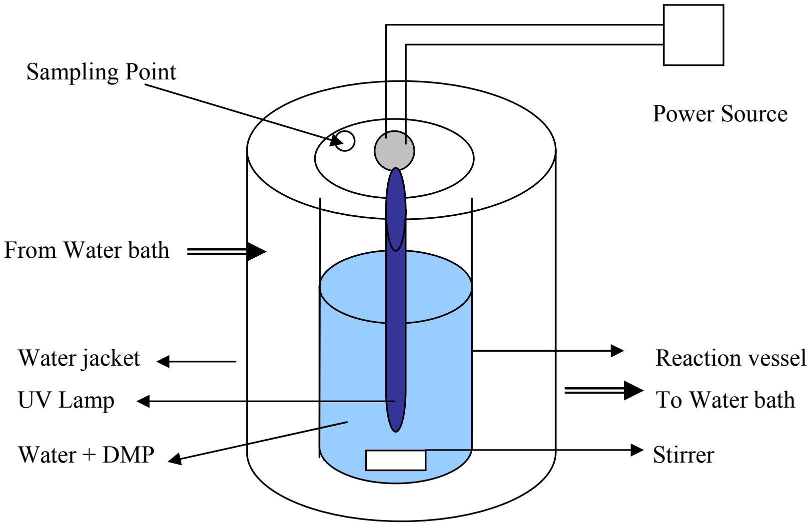

Figure 2: Bench-Scale Photo-Reactor

To measure the residual DMP concentrations after a certain reaction time, 20 mL water samples were extracted with 10 mL mixture of methylene chloride (MDC) and hexane (C_6) (v/v 1:3 MDC/C_6) by liquid-liquid extraction procedure. Gas Chromatograph (GC) equipped with a Photo-Ionization Detector (PID) was used for the analysis of DMP. A30 m long, 0.53 mm i.d. DB-5 fused silica capillary column, was used for the separation purpose. The oven temperature was programmed from 80 ^oC to 200 ^oC at a ramp rate of 20 ^oC. Both detector and injector temperatures were set at 280 ^oC. Helium gas was used as a carrier at a flow rate of 3 mL and a makeup of 27 mL. One (1) µL of the extract was injected was injected into the GC by splitless mode.

3. RESULTS AND DISCUSSION

3.1 Removal Of DMP By Direct Photolysis

To examine the extent of DMP removal by direct photolysis (i.e. UV only), an experiment was conducted in which a water sample spiked with 20 ppm of DMP was irradiated by UV light for 60 minutes. The results are shown in Figure 3. The results show that approximately 60% of DMP was removed after 60 minutes exposure to UV light. This means that DMP can be decomposed to a certain extent by direct photolysis action only. The DMP compound was found to absorb UV light fairly well in the range of 240 to 260 nm, which made it a good candidate for photodegradation.

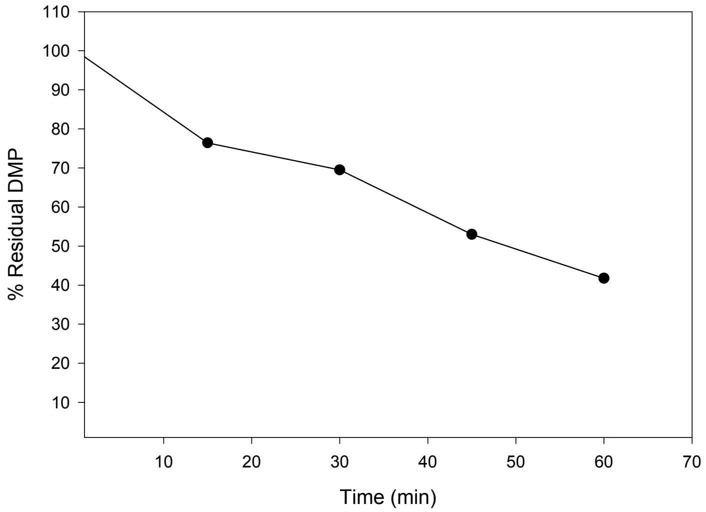

Figure 3: Removal of DMP by Direct Photolysis (DMP_i = 20 ppm, pH = 3, Temperature = 25^{o}C)

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3.2 Removal of DMP by UV/H_2O_2 process

3.2.1 Effect of H_2O_2 concentration

To study the effect of H_2O_2 concentration on the removal of DMP by UV/H_2O_2 process, experiments were conducted using initial concentrations of H_2O_2 of 34, 68 and 136 ppm. Temperature and pH levels were set at 25°C and 3, respectively. The results, shown in Figure 4, show that the addition of H_2O_2 improves the removal of DMP from water. More than 70% of DMP was removed after 60 minutes of reaction time when 34 ppm of H_2O_2 was added to the reactor, which contains water spiked with 20 ppm of DMP. Approximately 80% of DMP was removed at an initial H_2O_2 dose of 68 ppm, while the removal percentage increased to 98% when the initial dose was raised to 136 ppm of H_2O_2. It is clear that the combined action of H_2O_2 and UV light photooxidation has greatly improved the removal of DMP from water. Thus, in the UV/H_2O_2 system, as the concentration of H_2O_2 increases, the removal rate of DMP also increases. This is expected since according to the reaction shown in equation (1), more OH^o radicals will be formed when H_2O_2 concentration increases.

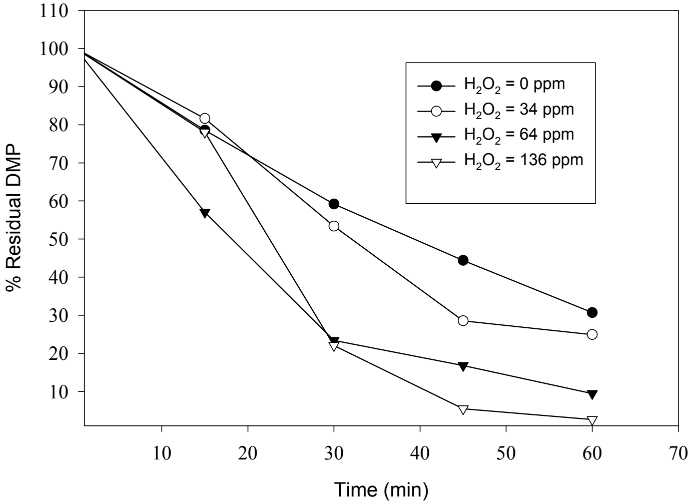

Figure 4: Removal of DMP by UV/H_2O_2 at Various H_2O_2 Concentrations (DMP$_i$ = 20 ppm, pH= 3, Temperature = 25°C)

From Figures 4, it can be noticed that the removal pattern of DMP by UV alone is different than the removal pattern by UV/H_2O_2 system. Figure 3 shows that DMP was removed in a fairly constant rate by UV alone; while the rate in the case of UV/H_2O_2 system was higher initially then it continued at a slower rate. This can be explained by the fact that the decomposition of DMP by UV alone may have occurred via photo-dissociation caused mainly by the intense energy of the UV light. However, in the UV/H_2O_2 system, additional factors such as oxidation by H_2O_2 and OH^o radicals was introduced which enhance the removal of DMP even further. Ultraviolet light in the UV/H_2O_2 system can also facilitate the reaction between DMP and OH^o radicals formed from the dissociation of H_2O_2 molecules by initiating a series of reactions that involve various organic radicals (R^o) as well as OH^o radicals. The intermediates formed due to the decomposition of DMP can also affect the extent and removal pattern of DMP since these intermediates may have different reaction rates with OH^o radicals. The overall conclusion is that the removal of DMP by UV/H_2O_2 system has been enhanced by the collective actions of UV light and OH^o radicals.

The removal rate of DMP in water by UV/H_2O_2 process for an initial H_2O_2 concentration of 136 ppm was determined assuming a pseudo first order reaction. A semi-log plot of the ratio of DMP at time (t) (i.e. DMP_t) to the initial DMP concentration (i.e. DMP_i) versus time is shown in Figure 5. The rate coefficient was calculated to be 0.0611/min according to the following equation of the best fitted formula:

$$\text{Ln}\ [DMP/DMP_i] = -\ 0.0611 * \text{tim} \qquad (4)$$

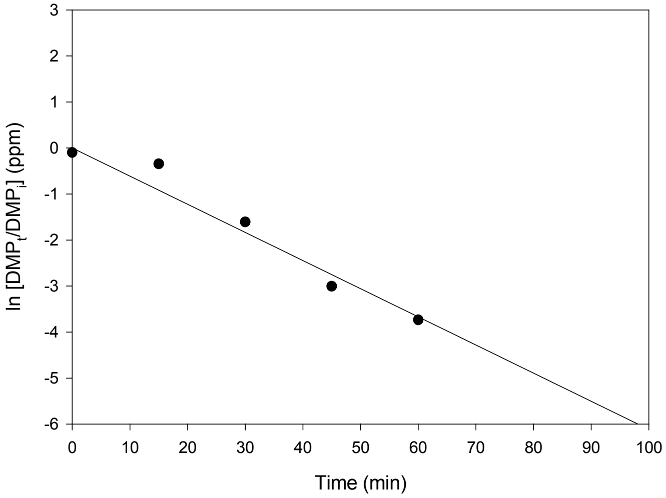

Figure 5: Plot of ln (DMP_t/DMP_i) versus time in the UV/H_2O_2 Process.
(DMP_i = 20 ppm, H_2O_2 = 136 ppm, pH = 3, Temperature = 25°C)

3.2.2 **Effect of UV dosage**

As indicated above, the UV light plays a significant role in the decomposition of DMP by UV/H_2O_2 process. In an attempt to study this effect closely, a set of three experiments was conducted by which three (3) different UV dosages were used. The UV dosage is determined by multiplying the lamp intensity (I) and the exposure time (t). However, since in this study, only one type of UV lamp of 100 mW intensity was used in all experiments, the dosage of UV light source was considered as a function of the exposure time only. For this reason the experiments were conducting by changing the exposure time of the UV lamp from 0 to 60 minutes. The three exposure times selected for this part of the study were: 0, 30 and 60 minutes. Other factors such as H_2O_2, pH and temperature were kept constant. The results of these experiments are shown in Figure 6.

The results show that UV radiation plays a significant role in the decomposition of DMP. It is clear that as the UV exposure time increases, and thus the UV dosage increases, removal efficiency of DMP by UV/H_2O_2 process also increases. It is also interesting to notice from Figure 6 that when the UV lamp was turned off at a certain time, no additional DMP removal was observed. By referring to the curve in Figure 6 when the UV exposure time of 30 minutes was used, removal of DMP remained at 80% even samples were taken 30 minutes after the UV light was cut off. This can be explained by the fact that when UV light is turned off, the reaction stops and no more production of OH^o radicals takes place as depicted in equation 1. The role of UV in this case is to produce OH^o radicals, which then attack the DMP molecules and degrade them. In addition, the photo-energy provided by the UV light as in the case of direct photolysis will not exist when the UV lamp is turned off.

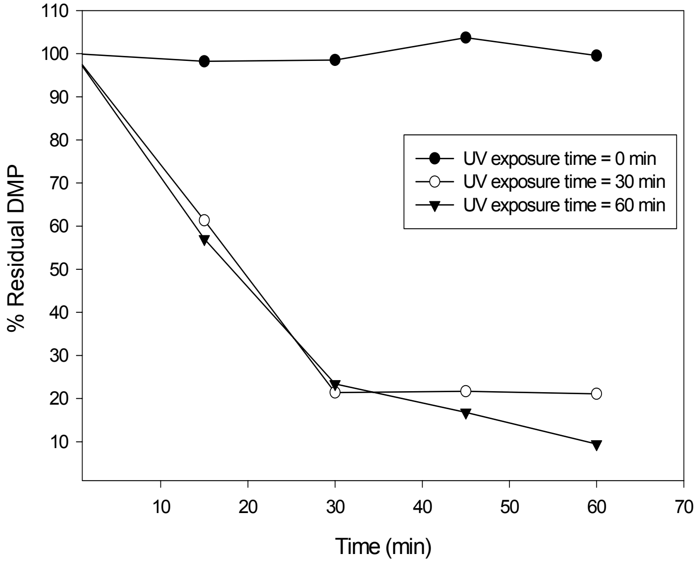

Figure 6: Removal of DMP by UV/H_2O_2 Process at Various UV Dosages
(DMP_i = 20 ppm, H_2O_2 = 136 ppm, pH = 6, Temperature = 25°C)

3.2.3 Effect of pH level

The effect of pH level on the removal efficiency of DMP by UV/H_2O_2 process was also studied. A set of experiments was conducted to observe the removal of DMP at various pH values. Initial concentration of H_2O_2 of 68 ppm and the temperature was set at 25°C for all experiments. The initial pH levels of the aqueous solution spiked with the DMP compound were set at several levels before the addition of the H_2O_2. The pH levels used were: 3, 6 and 9. The results are shown in Figure 7. The results clearly show that UV/H_2O_2 works better under acidic conditions in the range of pH = 3 to 6. On the other hand, when the pH was increased to 9, the removal efficiency of DMP dropped down. Even at a high pH of 9 for example, 50% of DMP was removed after 60 minutes of reaction time.

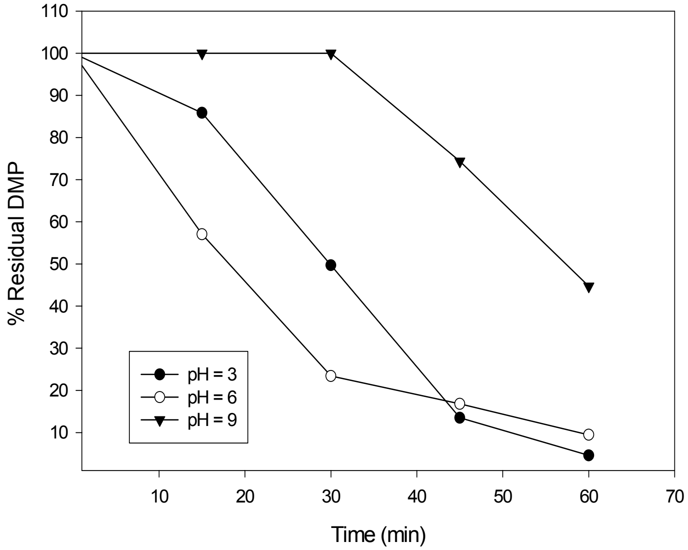

Figure 7: Removal of DMP by UV/H_2O_2 Process at Various pH values
(DMP_i = 20 ppm, H_2O_2 = 68 ppm, Temperature = 25°C)

3.4 Effect of Temperature

The effect of temperature on the removal efficiency of DMP by UV/H_2O_2 process was also investigated by carrying out several experiments in which the temperature of the water spiked with 20 ppm DMP was raised from 15°C to 35°C. Other parameters such as initial concentration of H_2O_2 and pH were kept constant at 68 ppm and 6, respectively. Samples were taken after 0, 15, 30, 45 and 60 minutes. The results of these tests are shown in Figure 8. The results clearly show that temperature plays a significant role in enhancing the reaction rate between OH^o radicals and DMP, consequently the removal rate of DMP increases.

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Complete removal of DMP was achieved in less than 30 minutes when the temperature of the solution was raised to 35°C. On the other hand, when the temperature was only 15°C, it took nearly 30 minutes for the DMP to start to be degraded. In fact, the usual practice when dealing with irradiation by UV lamp, a warming up period of few minutes is needed to obtain the desired radiation intensity. It seems that the temperature of the spiked water increases few degrees due to the heat coming from the UV lamp, even-though the water jacket was used. However, the water jacket would keep the temperature with a range of ± 3°C.

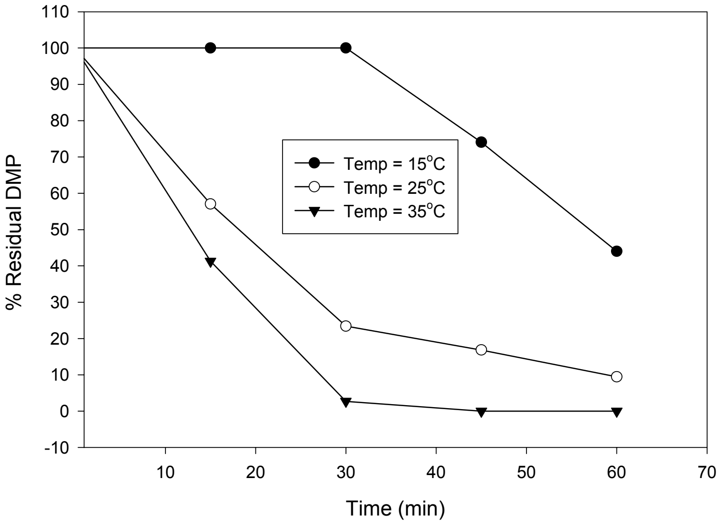

Figure 8: Removal of DMP by UV/H_2O_2 Process at Various Temperatures ($DMP_i = 20$ ppm, $H_2O_2 = 68$ ppm, pH= 6)

4. CONCLUSION

This study demonstrates the removal of dimethyl phthalates (DMP) from pure water using UV/hydrogen peroxide process. The results showed that up to 60% of the 20 ppm of DMP was removed by direct photolysis. However, the removal efficiency was greatly enhanced when hydrogen peroxide (H_2O_2) was utilized along with the UV irradiation. More than 90% of DMP was removed after 60 minutes of reaction time when 68 ppm of H_2O_2 was applied. The removal of DMP by UV/H_2O_2 process followed a pseudo-first order reaction. The results also showed that both pH level and the temperature play a role in enhancing the process in removing DMP. Higher temperature and neutral pH improves the performance of the UV/H_2O_2 process.

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