Degradation of benzene, toluene ethylbenzene and *p*-xylene (BTEX) in aqueous solutions using UV/H$_2$O$_2$ system

Abdel Hakim AM Daifullah[1]* and Mohamed Mokhtar Mohamed[2]

[1]*Hot Laboratories & Waste Management Centre, Atomic Energy Authority, PO 13759, Cairo, Egypt*

[2]*Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*

Abstract: The homogeneous degradation of benzene (B), toluene (T), ethylbenzene (E) and *p*-xylene (X) (BTEX) was studied in aqueous solutions, at pH 3.0, of hydrogen peroxide (5.8 mM) under UV irradiation in a photoreactor equipped with a 300 nm lamp of light intensity 3.5×10^{-5} Ein L^{-1} min^{-1}. BTEX was substantially degraded by the H$_2$O$_2$/UV system, with >90% disappearing in 10 min of irradiation. The decomposition of BTEX was studied either as single or as multi-component systems. The effects of irradiation time, amounts of H$_2$O$_2$ in molar ratios, rate of degradation and competition between components were thoroughly examined. It can be stated that the rate of BTEX degradation in mixture was higher than those for the individual components due to external effects of the absorption of UV light by the mixture, and their effects on enhancing the formation of OH$^\bullet$ radicals. The appropriate figure of merit, the electrical energy per mass (EE/M), was estimated at various molar ratios and it was confirmed that the best value was the one depicted for *p*-xylene (0.065 kWh kg^{-1}). A theoretical model for the degradation pathway was proposed.
© 2004 Society of Chemical Industry

Keywords: photo-oxidation; degradation rate; BTEX; UV/H$_2$O$_2$ system

1 INTRODUCTION

Liquid organic radioactive wastes typically include lubricating and hydraulic fluids from reactor operations, solvents and diluents from fuel reprocessing, seintillation fluids from analytical laboratories, dry-cleaning solvents and miscellaneous organic solvents from decontamination and decommissioning activities.[1] A specific source of contamination is encountered in nuclear hot laboratories where the burnt nuclear fuel is widely treated in solvent–solvent extraction processes involving many organic solvents. The most commonly used solvents belong to the benzene, toluene, ethylbenzene and xylene, BTEX, group of compounds, and kerosene. Both are extensively used as regular diluents in hot laboratory cells 'Purex Process'.[2,3] In addition, BTEX are among the organic compounds identified as hazardous air and industrial waste water pollutants.[4]

The pollution prompted the need for an intensive search for the best available technology (BAT) for the control and remediation of volatile organic compounds (VOCs) including BTEX. Application of the activated carbon adsorption systems has emerged and has been identified as one of the most effective technologies for the removal of VOCs[5–9] compared with impractical traditional methods (eg flocculation, sedimentation and filtration). It is, however, recognized that activated carbon is an expensive material for a large number of countries, particularly if they depend only on importation from the few leading producing countries. Thus, it becomes necessary to find alternative new technology for degrading BTEX either to less harmful intermediates or to complete mineralization.

Heterogeneous photocatalysis has emerged as an effective alternative method for purifying water and air.[10,11] The problems of fouling however and separation of catalysts especially in slurry-type photoreactors have proved to be cumbersome.[12,13] Other challenging problems facing the use of photocatalysts are concerned with their recovery (regeneration). Therefore, the uncatalysed photo-oxidative decomposition of some VOCs (BTEX) with H$_2$O$_2$ as oxidant has been stated in this work to observe the mechanism, rate constant, efficiency, and factors affecting these conversion reactions. The destruction of hazardous pollutants by the so-called Advanced Oxidation Processes (AOPs), where strong oxidizing agents (eg H$_2$O$_2$) are combined with the UV light (wavelength of light $\lambda \leq 300$ nm) to generate the

* Correspondence to: Abdel Hakim AM Daifullah, Hot Laboratories & Waste Management Centre, Atomic Energy Authority, PO 13759, Cairo, Egypt
E-mail: daifullah100@hotmail.com

highly reactive species, hydroxyl radicals (OH$^\bullet$), have been thoroughly studied.

2 EXPERIMENTAL

2.1 Materials and methods

Benzene, toluene, ethylbenzene and *p*-xylene were purchased from Aldrich (purity >98%) and used as received. These compounds were chosen as representing a range in solubilities, chemical structure, chemical configuration and importance as environmental pollutants.

Stock standard solutions of BTEX are made from pure analytes according to the procedure described elsewhere.[14] The pH values were kept constant at 3.0 with NaOH and HClO$_4$ solutions for optimizing the production of OH$^\bullet$ radicals. BTEX compounds were separated[15] by purge and trap (model: HP 7695) gas chromatography (model: HP- 6890) with a flame ionization detector (PT–GC–FID) according to US-EPA method 524.2 and according to the following conditions:

PT conditions: sample volume cm^3; purge cycle 11 min at 30 °C, desorb cycle 2 min at 220 °C, bake cycle 10 min at 220 °C, purge flow 40 cm^3 min^{-1}; trap: Tenax/silica-gel/charcoal; purge gas: N$_2$ 99.999% purity.

GC conditions: oven program 40 °C (12 min); 2 °C min^{-1} to 60 °C (8 min); carrier gas: N$_2$ 99.999% purity; column: HP-5 (30 m × 0.32 mm × 0.25 μm).

FID conditions: temperature 275 °C; H$_2$ flow 60 cm^3 min^{-1}; air flow 400 cm^3 min^{-1}; makeup gas: N$_2$; makeup flow 20 cm^3 min^{-1}.

At different time intervals, aliquots of the mixture were sampled and analysed by direct injection into the GC.

2.1.1 Purge efficiency tests

The purge efficiency (*P*) was determined by subsequently purging 1 cm^3 of the same sample several times and is expressed in percent by using the formula:[16,17]

$$P(\%) = A_1/A_i \times 100 \qquad (1)$$

where A_1 is the peak area of the compound in the first purge cycle and A_i is the peak area of the same compound in cycle *i*. Figure 1 shows the relationship between purge efficiency and the solubility of BTEX compounds. This inversely proportional relationship can be explained as solute solubility increases its releasing power from water by purge gas decreases. All BTEX compounds are observed to have purge efficiency greater than 90%, this means that the PT–GC method is suitable for quantitative determination of BTEX.

2.2 Reactor and light source

The UV irradiation of the magnetically stirred clear solutions containing the pollutants was carried out at 20 °C in a quartz cylindrical flask (12 cm^3). The
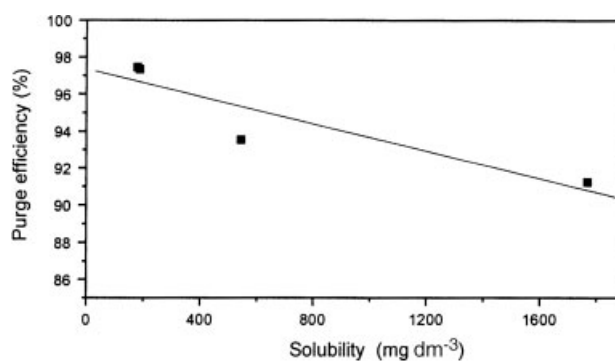

Figure 1. Purge efficiency of BTEX compounds.

output of the high pressure mercury lamp (Metrohm, 705 UV Digestor-500 W) was filtered by a circulating water cuvette (thickness 1.6 cm) to avoid the direct photolysis of BTEX. The UV lamp emits 300 nm light with an intensity of 3.5×10^{-5} Ein L^{-1} min^{-1}, as established by ferrioxalate actinometry.

2.3 Kinetic experiments of BTEX

Single bottle experiments were carried out by contacting 12 cm^3 of each solute (initial concentration 100 ppm) with H$_2$O$_2$ (initial concentration 100 ppm) in the following molar ratios: 1:0; 1:1; 1:2; and 1:4 in glass bottles. The bottles were then transferred to the UV-digester. The absorbance of each solute at the maximum wavelength was measured at different time intervals using a UV-spectrophotometer. The concentration of BTEX was determined using GC according to US-EPA method 524.2 as described above.

3 RESULTS AND DISCUSSION

The photo-oxidation kinetics of BTEX are presented in Figs 2–5 in the form of relative substrate concentrations (C/C_o) vs time (min). The rate of decomposition increased with time in a non-linear fashion especially for the BTEX : H$_2$O$_2$ molar ratios 1:0 and 1:1, whereas at molar ratios 1:2 and 1:4, a linear behaviour was observed with >95% of the BTEX disappearing in the first 10 min of photolysis. The observed decrease in the rate at lower H$_2$O$_2$ concentrations (1:1) is due to the smaller fraction of adsorbed incident light, leading to a decrease in the rate of formation of OH$^\bullet$ radicals. It is worth noting that:

(1) the relative concentration (C/C_0) vs time for *p*-xylene, as shown in Fig 5, is nearly constant at ratios 1:10 and 1:16 compared with the data at the ratio 1:4 after the exposure time of 1 h;

(2) a higher molar ratio of BTEX: H$_2$O$_2$ than 1:4 reduces to a large extent the volume of BTEX required to be treated;

(3) excess H$_2$O$_2$ causes self-scavenging of OH$^\bullet$, as presented below.[18]

$$\text{OH}^\bullet + \text{H}_2\text{O}_2 \longrightarrow \text{HO}_2{}^\bullet + \text{H}_2\text{O} \qquad (2)$$
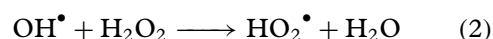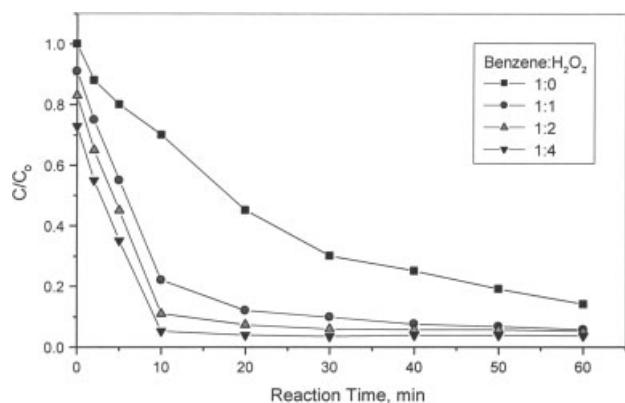
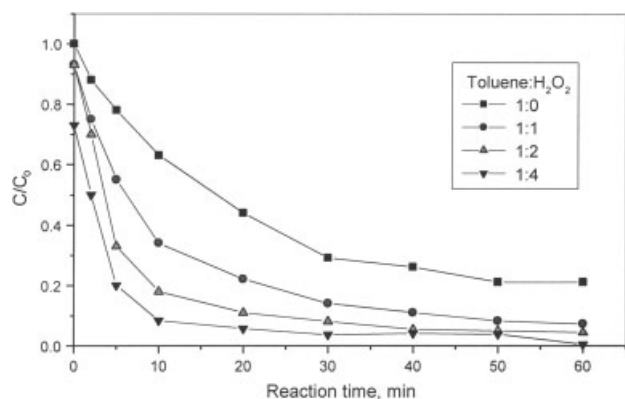**Figure 2.** Photo-oxidation kinetics of benzene.

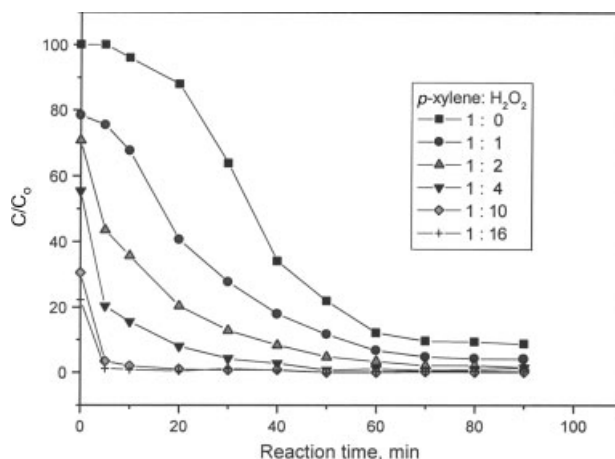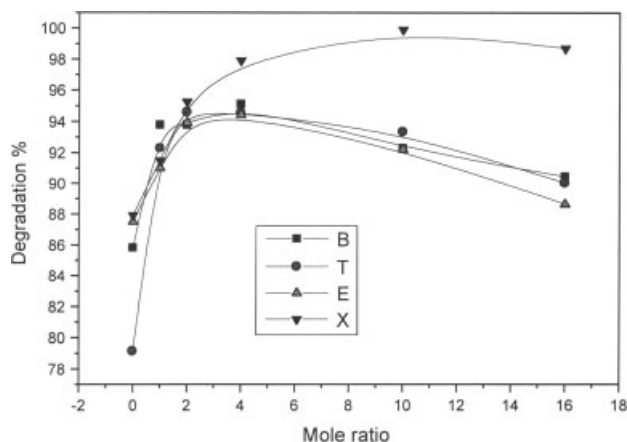**Figure 3.** Photo-oxidation kinetics of Toluene.
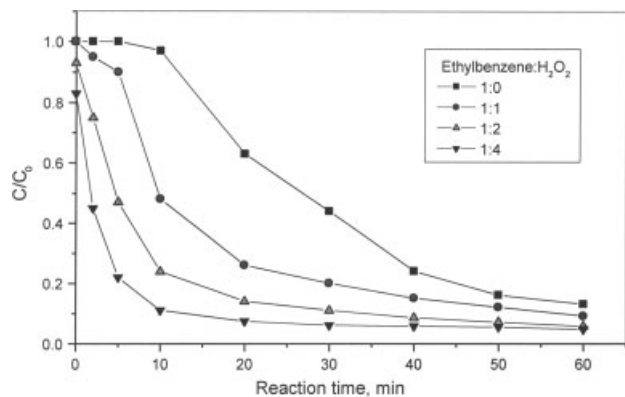
Figure 4. Photo-oxidation kinetics of ethylbenzene.

Figure 5. Photo-oxidation kinetics of *p*-xylene.

Figure 6. Effect of mole ratios (H_2O_2: BTEX) on BTEX removal.

Table 1. Rate constants ($K_p \times 10^5 \, s^{-1}$) and electrical energy per mass ($kWh \, kg^{-1}$) for BTEX at various molar ratios and at exposure time 1 hr

Mole ratio BTEX: oxidant	Benzene		Toluene		Ethylbenzene		*p*-xylene	
	K_p	EE/M	K_p	EE/M	K_p	EE/M	K_p	EE/M
1:0	5.4	0.515	4.60	0.475	5.2	0.525	4.5	0.528
1:1	7.7	0.256	6.30	0.257	5.94	0.273	5.5	0.215
1:2	8.3	0.156	6.96	0.176	6.16	0.175	7.1	0.135
1:4	8.6	0.083	7.04	0.083	6.40	0.095	7.5	0.065

(4) although the hydroperoxy radical ($HO_2^{\bullet}$) is formed, its reactivity with organic compounds is estimated to be low.[18]

The decrease in the rate of BTEX degradation with increasing H_2O_2 concentrations (at high molar ratios 1:10 and 1:16) after the rates go through a maximum at a specific value of mole ratio (as shown in Fig 6), clearly indicates that the Langmuir–Hinshelwood model is correctly followed.[19]

The reaction rate constants (k_p) of the BTEX as a function of substrate: oxidant mole ratio are presented in Table 1. The degradation data of BTEX were fitted to a pseudo first-order rate model. The dependence of rate constants for BTEX and their intermediates on H_2O_2 dosage were adequatedly regressed by a first-order equation:[20] $\ln C/C_o = -k_p t$ (where C_o and C are the molar concentrations of substrate (BTEX) at reaction times 0 and t, k_p is the pseudo first-order rate constant (in s^{-1}) and t is the photo-oxidation time), showing that the rate was in the order: B > X > T > E at molar ratios $R = 1/4$ and $1/2$ (where $R =$ moles of substrates [BTEX]/moles of H_2O_2). On the other hand, the above sequence was completely different when R was 1 or H_2O_2 was absent, being B > T > E > X and B > E > T = X, respectively. These results indicate the facile photo-degradation of benzene

by the electrophilic attack of OH$^\bullet$ radicals even at very low H_2O_2 dosage. Appreciable rates of benzene degradation were also obtained as remoted by the use of only photolysis, ie in the absence of H_2O_2.

The high dosage of H_2O_2 appears to favour *p*-xylene rather than toluene and ethylbenzene towards hydroxyl radicals in the sense of its strong absorbability of the UV light producing phenolic intermediates.[21] These intermediates are stronger absorbers for the UV light than their parent compounds, ie the more methyl groups the benzene contains, the quicker it will degrade. Changing the sequence at low H_2O_2 dosage ($R = 1$) and thus slowing the rate can be attributed to the limited amounts of OH$^\bullet$ radicals produced and to the expected competitiveness of BTEX with their intermediates for OH$^\bullet$ radicals. Thus, the substrate that has the probability of generating more intermediates will show a decrease in its degradation rate, only at low dosages of H_2O_2, due to scavenging the expected small amount of OH$^\bullet$ radicals. This can be confirmed from figs 4 and 5 at $R = 1$, these figures reflect the first-order kinetics, indicating the complexity of the media and intermediates at low H_2O_2 concentrations. This indeed brings about a decrease in rate constants as a result of competition between activated and non-activated substrates towards the small amounts of OH$^\bullet$ radicals. The dissociation constants of the different compounds,[22] for example when they form acid in intermediate degradation steps might be another plausible explanation of their varying degradation rates with varied H_2O_2 dosage. The presence of a side chain besides the acid group, expected to be formed, as in ethylene ($-CH_2CH_3$) or *p*-xylene ($-CH(CH_3)$ $(CH_3)CH-$) retarded the degradation pathways at low H_2O_2 concentration, due to the limited numbers of OH$^\bullet$ radicals. In other words, the presence of an aliphatic side chain delays the degradation processes as a result of decreasing the dissociation constants of the corresponding components. At higher OH$^\bullet$ concentration, the situation is different in the sense that increasing amounts of intermediates cause a remarkable increase in the competitive degradation due to an excess of OH$^\bullet$ radicals. This indicates that the relative increase in concentrations of intermediates and OH$^\bullet$ is necessary to avoid scavenging excess OH$^\bullet$ radicals.
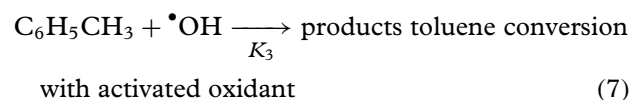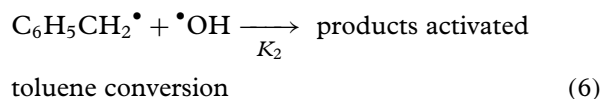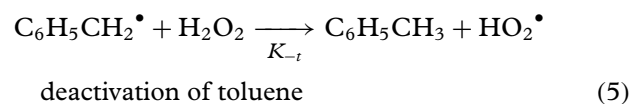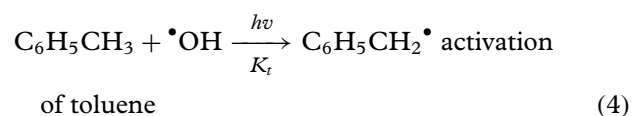
3.1 Kinetic analysis

A simplified kinetic approach was developed for toluene as a representative compound for BTEX. This was selected due to its intermediate affinity for degradation and to serve as a control for its behaviour when present in a mixture. This was on the basis of the previously confirmed pseudo first-order rate approximation verified for the degradation of BTEX, including toluene, especially at moderate concentrations of H_2O_2. The direct photolysis of

H_2O_2, requires $\lambda < 360\,nm$, to generate OH$^\bullet$ radicals according to:[19]

$$H_2O_2 \xrightarrow[K_1]{hv} 2\,OH^\bullet \qquad \text{activation of oxidant} \qquad (3)$$
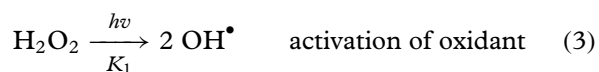
Although degradation products were not determined in this study, hydroxyl radicals are known to react with saturated organic chemicals by H-abstraction from the alkyl group (as in the present study)[23] or by an electron transfer process:

$$C_6H_5CH_3 + {}^\bullet OH \xrightarrow[K_t]{hv} C_6H_5CH_2^\bullet \text{ activation}$$

$$\text{of toluene} \qquad (4)$$

$$C_6H_5CH_2^\bullet + H_2O_2 \xrightarrow[K_{-t}]{} C_6H_5CH_3 + HO_2^\bullet$$

$$\text{deactivation of toluene} \qquad (5)$$

$$C_6H_5CH_2^\bullet + {}^\bullet OH \xrightarrow[K_2]{} \text{products activated}$$

$$\text{toluene conversion} \qquad (6)$$

$$C_6H_5CH_3 + {}^\bullet OH \xrightarrow[K_3]{} \text{products toluene conversion}$$

$$\text{with activated oxidant} \qquad (7)$$

In the above degradation pathway, all radicals that can be formed from H_2O_2 are considered to be OH$^\bullet$ radicals rather than the hydro-peroxy ones ($HO_2^\bullet$) due to its lower reactivity, as mentioned previously. In addition, the latter species tended to appear at increasing concentrations of H_2O_2, ie moderate concentrations only were used in this study in order to avoid the self-scavenging of OH radicals by excess H_2O_2.[24] It has been reported that benzaldehyde and benzoic acid are detected during toluene photo-oxidation[25] through the addition of OH to the aromatic ring of toluene and/or abstracting H atoms from the methyl group. The resulting intermediate radicals are subsequently oxidized by molecular oxygen. Finally, these intermediates are decomposed to CO_2 and CO via subsequent oxidation processes.[25] It may be plausible that the OH radicals attack the aromatic ring, forming dimerized species. On the other hand, all radicals that can be obtained from toluene, ie intermediates, are included in the term '[toluene*]', in the equations below. Thus the rate of toluene consumption can be expressed as:

$$\text{Rate} = -d[\text{toluene}]/dt \qquad (8)$$

$$= k_t[\text{toluene}] - k_{-t}[\text{toluene*}][H_2O_2]$$

$$+ k_3[\text{toluene}][HO^\bullet] \qquad (9)$$

By hypothesizing[20] pseudo-steady state:

$$d[{}^\bullet OH]/dt = d[\text{toluene*}]/dt = 0 \qquad (10)$$

$$d[{}^\bullet OH]/dt = k_1[H_2O_2] - (k_{-t}[\text{toluene}]$$

$$+ k_2[\text{toluene*}] + K_3[\text{toluene}][{}^\bullet OH] = 0 \qquad (11)$$

then : $^{\bullet}OH = K_1[H_2O_2]/Kt[\text{toluene}] + K_2[\text{toluene}^*]$

$\qquad + K_3[\text{toluene}] \qquad\qquad\qquad (12)$

$d[\text{toluene}^*]/dt = K_t[\text{toluene}][^{\bullet}OH] - (K_{-t})[H_2O_2]$

$\qquad + K_2[^{\bullet}OH])[\text{toluene}^*] = 0 \qquad (13)$

Then : $[\text{toluene}^*] = Kt[^{\bullet}OH][\text{toluene}]/K - t[H_2O_2]$

$\qquad + K_3[^{\bullet}OH] \qquad\qquad\qquad (14)$

and the rate equation may be simplified to:

$$\text{Rate} = [k_t[\text{toluene}] - ((k_{-t}k_t)/(k_{-t} + k_3))][\text{toluene}]$$

$$+ k_1[H_2O_2]/Kt[\text{toluene}] + K_2[\text{toluene}^*] (15)$$

Substituting k_1' for the coefficient of [toluene], we obtain:

$$\text{Rate} = k_1'[\text{toluene}] + k_1[H_2O_2]/Kt[\text{toluene}]$$

$$+ K_2[\text{toluene}^*] \qquad\qquad (16)$$

At the concentration of H_2O_2 used, the expected concentration of toluene and its activated form (toluene*) will be equal at steady state conditions, thus:

$$\text{Rate} = K_1'[\text{toluene}] + K_1[H_2O_2] \qquad (17)$$

At the relatively high proportions of the oxidant. The linearity of the $-d[\text{toluene}]/dt$ vs [toluene] plot is tested with the obtained data so as to confirm the above model of the degradation pathway. The conversion of BTEX in a comparatively shorter time was obtained, especially at relatively higher ratios of the oxidant to the substrate (4:1 ratio) as indicated by the calculated K_p values (Table 1).

3.2 Effect of the oxidant
The effect of H_2O_2 on the reaction was not linear (Fig 6) and degradation rates were retarded when peroxide was present in excess. The best molar ratio for BTEX: H_2O_2 is 1:4, and higher H_2O_2 concentrations will be: (i) economically undesirable;[26] and (ii) cause scavengers for hydroxyl radicals.[24] Also, the residual H_2O_2 in solution was observed at higher concentrations by a potassium iodide titration method[27] and it was obvious that the optimum dose of 5.88 mM H_2O_2 was sufficient for effective oxidative treatment.

3.3 Effect of UV-light intensity and dose
The UV dose (intensity × time) at BTEX: H_2O_2 molar ratio 1:4 is presented in Fig 7 and seems to have a significant effect especially in the case of *p*-xylene where the degradation reached 72% within 10 min of irradiation and increased to 97% after 1 h. For BTE however, the sensitivity towards the UV dose was comparatively lower. The degradation proceeds mainly through the reactivity of $OH^{\bullet}$ radicals rather than perhydroxyl and its conjugate base ($HO^{\bullet}_2/O_2^-$).
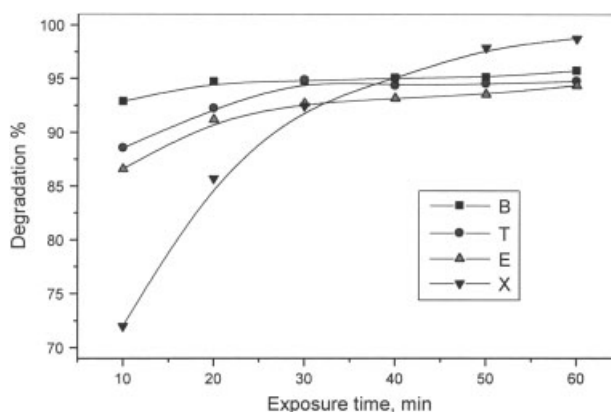

Figure 7. Effect of exposure time on BTEX removal.

Increasing the degradation rate for *p*-xylene and exceeding that of benzene may be due to the vulnerability of methyl groups in *para* positions to hydroxyl radical attack. Figure 7 also shows that at around 10 min exposure time, the degradation path of BTEX was similar to that at low dosage of H_2O_2 ($R = 1$; B > T > E > X), advocating that the attack of the benzene ring to be decomposed was easier, ie at low concentrations of $OH^{\bullet}$ radicals that monitored by UV light. Increasing the UV exposure time however, will help in releasing more $OH^{\bullet}$ radicals that favouring the attack on $-CH_3$ groups of *p*-xylene and, thus, the sequence in 60 min exposure time was X > B > T > E. It may also the seen that the longer the side chain in the benzene ring the lower will be the degradation either at low or high dosages of H_2O_2, as in ethylbenzene.

3.4 Effect of components
Results presented in Fig 8 show the degradation kinetics of toluene when it is solely degraded in comparison with its degradation within the multi-solute components (mixed system) at molar ratio of $R = 1$. The degradation rate of toluene is faster in the mixed system than in the single systems. This is expected for all the BTEX components due to the fact that the decomposition of H_2O_2 is enhanced by increasing the absorption of UV light by a BTEX
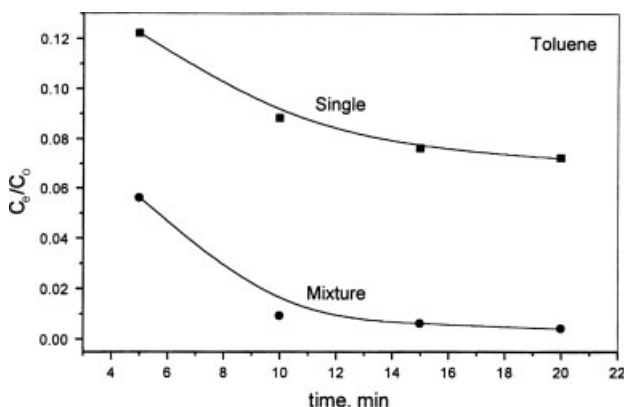

Figure 8. Photo-oxidation of toluene in single and multi-component systems.

mixture rather than the individual components.[28] This should have an influence on progressing the degradation process and thus increasing the intermediates to further speed up the treatment of BTEX. This could be accounted for by the influence of the different molecular structures of BTEX on their reactivities with OH$^\bullet$ radicals than with toluene only.

3.5 Calculation of figure of merit

The photodegradation of aqueous organic pollutants is an energy-intensive process. The appropriate figure of merit is the electrical energy per mass (EE/M) defined as the kilowatt hours of electrical energy required to remove 1 kg of the contaminant:[18]

$$EE/M = \frac{P \times t}{V \times (C_i - C_f)}$$

where P = power input of the UV lamp (kW); t = exposure time (h); V = volume of treated aqueous pollutant or waste water (m); and C_i and C_f = initial and final pollutant concentrations (kg m^{-3}), respectively. Calculation of the electrical energy requirements has proven to be very useful for AOPs employing artificial light sources (UV lamp), because the greater fraction of the operating costs of AOPs are the electrical energy costs.

The electrical energy per mass EE/M is listed in Table 1 for single-component systems at various molar ratios. As can be observed, the K_p values are inversely proportional to the EE/M ones, ie the degradation rates, K_p, increased as the molar ratios increased and thus the electrical efficiency increased too and thus the operating costs of the electrical energy are greatly reduced. The values of EE/M for toluene only in single and multi-component systems at constant molar ratio (toluene: H$_2$O$_2$, 1:1) are listed in Table 2 and it was clear that the EE/M in the multi-component system represents 70–93% compared with the single-component systems depending on the exposure time.

This proves that, for treatment purposes using a UV/H$_2$O$_2$ system, it is recommended to use sufficient amounts of the oxidant H$_2$O$_2$ at the appropriate exposure time as well as a multi-component system of pollutants to reduce the operating costs.

4 CONCLUSIONS

The UV/H$_2$O$_2$ oxidation of BTEX contaminants has advantages in that fast kinetics, no sludge production,

and a high degree of mineralization can be achieved. Besides, H$_2$O$_2$ is easy to handle and environmentally benign. The degradation rate of the multi-component system increases compared with that of the single component system. Therefore, the AOPs are useful and much better than adsorption by activated carbon and biodegradation systems, especially for small-scale treatment plans.

REFERENCES

1 International Atomic Energy Authority, *Technical Reports Series*, No 294, Vienna (1989).
2 Stoller SM and Richards RB, *Reactor Handbook*, Interscience Publishers, Inc NY (1961).
3 Skrabakova S, Matisova E, Benicka E, Novak I and Berek D, Use of a novel carbon sorbent for the adsorption of organic compounds from water. *J Chromatography A* **665**:27–32 (1994).
4 Chang SW, La HJ and Lee SJ, Microbial degradation of benzene, toluene, ethylbenzene and xylene isomers (BTEX) contaminated groundwater in Korea. *Wat Sci Technol* **44**(7):165–173 (2001).
5 Sorial GA, Papadimas SP and Suidan MT, Competitative adsorption of VOCs and BOM-oxic and anoxic environments. *Wat Res* **28**:1907–1919 (1994).
6 Yun JH, Hwang KY and Chio DK, Adsorption of benzene and toluene vapors on activated carbon fiber at 298, 323 and 348 K. *J Chem Eng Data* **43**:843–845 (1998).
7 Giffin SD and Davis AP, Prediction of carbon BTEX adsorption capacity using field monitoring data. *J Environ Eng* **10**:921–931 (1998).
8 Chenu M, Bouzaza A, Wolbert D and Laplanche A, Adsorption of VOC mixtures onto activated carbon: experimental study and simulation of multicomponent adsorption. *Environ Technol* **19**:1029–1038 (1998).
9 Kim JY, Park JK and Edil TB, Sorption of organic compounds in the aqueous phase onto tire rubber. *J Environmental Engineering* **Sep**:827–835 (1997).
10 Matthews RW, Solar–electric water purification using photocatalytic oxidation with TiO$_2$ as a stationary phase. *Solar Energy* **38**:405–413 (1987).
11 Ollis DF, Process economics for water purification: a comparative assessment in *Photocatalysis and Environment. Trends and Applications*, ed by Schiavello M. *NATO ASI Ser C: Math And Phys* Ser 237, Kluwer, London, pp 663–667 (1988).
12 Bielski BHJ and Cabelli DE, Highlights of current research involving superoxide and perhydroxyl radicals in aqueous solutions (Review). *Int J Radiat Biol*, **59**:291–319 (1991).
13 Glaze WH, Kang JW and Chapin DH, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation ozone. *Science and Engineering* **9**:335–352 (1987).
14 Kessels H, Hoogerwerf W and Lips J, The determination of VOCs from EPA method 524.2 using purge and trap capillary gas chromatography, ECD and FID. *J Chromatogr Sci* **30**:247–255 (1992).
15 *Hewlett Packard, 7695 Purge and Trap, Operating Manual*, USA (1995/1996).
16 Chatzopoulos D, Activated carbon adsorption and desorption of Toluene in the aqueous phase. *AIChE J* **39**:2027–2041 (1993).
17 Seidel A, Tzscheutsler E, Radeke K and Gelbin D, Adsorption equilibria of aqueous phenol and indol solution on activated carbon. *Chem Eng Sci* **40**:215–222 (1985).
18 Arslan I, Balcioglu IA, Tuula T and Detlef B, H$_2$O$_2$/UV-C and Fe^{2+}/H$_2$O$_2$/UV-C versus TiO$_2$/UV-A Treatment for reactive dye wastewater. *Environ Sci Technol* **October**:903–911 (2000).

Table 2. Rate constants ($K_p \times 10^5$ s^{-1}) and electrical energy per mass (kWh kg^{-1}) for toluene in single and multi-component systems at various exposure times and at mole ratio of toluene:oxidant, 1:1

Exposure time (min)	Rate, $K_p \times 10^5$ s^{-1}		EE/M		% EE
	Single	Mixed	Single	Mixed	M$_{mixture/single}$
5	0.122	0.056	0.788	0.732	92.80
10	0.088	0.006	1.526	1.400	91.70
15	0.076	0.004	2.255	2.090	92.68
20	0.072	0.004	2.963	2.090	70.50

19 Martin MH, *Photodegradation of Water Pollutants*. CRC Press, Boca Raton, Florida, p 68 (1996).

20 Resat A and Mehmet H, Photooxidation of some mono-, di-, and tri-chlorophenols in aqueous solution by hydrogen peroxide/UV combinations. *J Chem Technol Biotechnol* **67**:221–226 (1996).

21 Stephan R, Cater MI, Stefan J, Bolton R and Safarzadeh-Amiri A, UV/H_2O_2 treatment of methyl *tert*-butyl-ether in contaminated water. *Environ Sci Technol* **34**:659–662 (2000).

22 Di Paola A, Garcia-Lopez E, Ikeda S, Marci G, Ohtani B and Palmisano L, Photocatalytic degradation of organic compounds in aqueous systems by transition metal doped polycrystalline TiO_2. *Catal Today* **75**:87 (2002).

23 Willing CH, Fentons reagent revisited. *Acc Chem Res* **8**:125–131 (1975).

24 Stefan MI Hoy AR and Bolton LR, Kinetic and mechanism of the degradation and mineralization of acetone in dilute aqueous solutions sensitized by the photolysis of hydrogen peroxide. *Environ Sci Technol* **30**:2382–2390 (1996).

25 Hisahiro E, Shigeru F and Takashi I, Heterogenous photo-catalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition behaviour on photoirradiated TiO_2 catalyst. *Applied Catal B* **38**:215–223 (2002).

26 Jerome ON and Milagros SS, *Environmental Oxidants*. John Wiley & Sons, Inc, USA, p 534–541 (1994).

27 Snell FD and Ettre LS, *Encyclopedia of Industrial Chemical Analysis*, John Wiley & Sons, Inc, NY Vol 14 p 427 (1987).

28 Cater SR, Stefan MI, Bolton JR and Safarzdeh-Amiri A, UV/H_2O_2 Treatment of methyl *tert*-butyl ether in contaminated waters. *Environ Sci Technol* **34**:659 (2000).