Removal of Benzene and Selected Alkyl Substituted Benzenes from Aqueous Solution Utilizing Continuous High-Energy Electron Irradiation

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Abstract

Continuous high-energy electron irradiation was employed in the removal of mixtures of benzene, toluene, *m*-xylene, and *o*-xylene from potable water and secondary wastewater effluent in the presence of an extremely efficient radical scavenger (3.3 mM methanol). In the potable water, >99% removal of all aromatic solutes was achieved at 787 krad (7.87 kGy, $[OH\cdot] \approx 2.2 \times 10^{-3}$ M) with influent concentrations of each of the solutes approximately 1 μM, whereas in the secondary wastewater solute removal was 91 to 96% for similar initial concentrations. At an initial solute concentration of approximately 20 μM, for each of the four aromatic solutes, the removal increased in absolute concentration but the percent removal in both waters decreased. Reaction by-products identified were phenols and various carbonyl compounds. The carbonyl compounds include glyoxal and other as yet unidentified aldehydes. The product distribution is consistent with hydroxyl radical ($OH\cdot$) addition and continued oxidation of intermediate by-products.

Introduction

As a result of increased urbanization and industrialization, groundwaters have become contaminated with anthropogenic organic compounds. Many of these compounds persist for considerable periods in the subsurface environment. One such group of compounds which has attracted special interest, because of their occurrence in wastewater, groundwater and surface water, are the aromatic hydrocarbons; specifically benzene, toluene and the xylenes (BTXs) (*1*). The prevalence of these compounds in the environment is due to their high production and use worldwide (*2-4*). In particular, these compounds are important constituents of gasoline and other commercial fuels, having an aromatic content of up to 45% (*5*). Known mechanisms of transport to the environment include inadvertent dumping, leaking underground storage tanks, landfill leachate and re-entry into the hydrosphere in rain (*6*). As a result of their widespread occurrence, considerable research is being conducted on processes for removing these compounds from contaminated environments.

Several methods have been proposed and/or are currently used to remove hazardous chemicals from contaminated waters. For example carbon adsorption (*7-12*), oxidation using ozone (O_3) (*13,14*), and aeration stripping (*15-19*).

All of the above processes have been and are being used. However, considerable research is being conducted to optimize these processes, as well as explore new innovative treatments for the removal and destruction of solutes from contaminated environments. This paper describes one such innovative treatment process, currently being tested in Miami, Florida.

High-Energy Electron Irradiation

High-energy electron accelerators have been used for years in industry for the cross-linking of polyethylene, the polymerization of lubricants, and the vulcanization of rubber. The number of applications has grown to include treatment for food preservation, and the sterilization of medical instruments (*20*). One of the most promising uses for this evolving technology is for the treatment of hazardous wastes prior to discharge to the environment, or as a remediation technique for already contaminated waters.

Although early studies with high-energy electrons showed the process to be effective for the disinfection of wastewater sludges (*21-24*), only limited studies were conducted with respect to the removal of toxic organic chemicals from aqueous based systems (*25-31*). The conceptual basis for the use of high energy electrons for the treatment of toxic organic compounds was presented in 1975 (*32*) followed by a direct comparison to the ozone process (*33)*. However, the applications of these concepts, as it relates to high energy electron irradiation, has not been explored in any detail. More recently, the use of high-energy radiation for the treatment of wastewater has been reviewe attesting to the renewed interest in exploiting this technology for the treatment of industrial, municipal and agricultural wastewater.

This paper will present the results of a study initiated to define the removal of benzene, toluene, *m*-xylene, and *o*-xylene from waters of differing quality using high-energy electron radiation in a large scale continuous flow (454 L min^{-1}) process. The effect of irradiation of aqueous solutions of benzene (*35-42*), toluene, *m*-xylene and *o*-xylene (*43*) has been reported in studies conducted under highly controlled conditions. However, no studies have been conducted to examine the potential of using high-energy electrons for the removal (destruction) of these organic compounds in a continuous flow pilot scale process. The variables that have been examined are, absorbed radiation dose, water quality, and organic solute concentration. The effect of adding hydrogen peroxide was also studied as a possible process modification to enhance compound removal efficiency.

Experimental Section

Electron Beam Research Facility (EBRF). All experiments were conducted at the EBRF which is located at the Virginia Key Wastewater Treatment Plant in Miami. The EBRF houses a horizontal 1.5 MeV insulated-core transformer (ICT) electron accelerator, a water delivery system, and ancillary equipment. Aqueous streams of varying quality are presented to a scanned electron beam in a falling stream approximately 114 cm wide and 0.40 cm thick. The beam current is continuously variable from 0 to 50 mA, providing radiation doses of 0 to 800 krad (8 kGy) (1 rad is defined as the absorption of 100 erg per gram of material).

The influent streams connected to the facility are: digested sludge, potable water, and chlorinated secondary effluent. The facility is designed to treat aqueous streams of 454 L min^{-1} (120 gallons min^{-1}).

The electron beam system is instrumented with resistance temperature devices (RTDs) to obtain direct estimates of absorbed dose. Five RTDs are mounted in the influent (2 sensors), and effluent (3 sensors) stream immediately before and after irradiation. The RTDs are connected via an interface to a computer which continuously reads and records temperatures, allowing the absorbed dose to be estimated by converting the observed temperature differences to the equivalent energy transferred to the water. That is, 1000 krad (10 kGy) = 1.0×10^8 erg g^{-1} = 2.39 cal g^{-1}, which is equivalent to a temperature change of 2.39°C g^{-1} or 418 krad $°C^{-1}$ (*44*).

Sample Preparation. All organic compounds studied were reagent grade or better, and used without further purification. A concentrated stock solution of all four test compounds (benzene, toluene, *m*-xylene, and *o*-xylene), dissolved in methanol, was injected into the influent stream of the EBRF utilizing a diaphragm pulsed metering pump to give the desired concentration of each compound in each aqueous stream. The flowing stream was then irradiated at pre-determined beam currents, thereby, delivering different absorbed radiation doses.

Water quality and concentration combinations were selected and run in random order. Dose levels (beam current settings), within each combination, were also set in random order. In addition, each experiment was replicated to ensure the validity of the results over a range of plant operating conditions.

Studies were also conducted where H_2O_2 was added to the influent (50% w/w) to give a final concentration of 0.5 mM H_2O_2 prior to irradiation.

Sample Collection and Analysis. Influent and effluent samples were collected in 47 mL screw cap vials, and quenched with 30 mg sodium thiosulfate to remove any residual oxidant. The vials were completely filled, leaving no headspace, chilled on ice, and immediately returned to the lab for analysis.

Five milliliters (5.0 mL) of the sample was removed from the vial and 3.0 mL of hexane was immediately added and the vial resealed. The 2.0 mL headspace allows the solvent and sample to mix thoroughly, which is required for effective extraction. The samples were agitated at 300 rpm for 5 min, and the hexane layer was allowed to separate from the water (approximately 2 min), then transferred to 2.0 mL amber crimp top autosampler vials. One microliter (1.0 μL) of the extracted hexane mixture was then injected into a Hewlett-Packard Model 5890 gas chromatograph equipped with a 30 m x 0.539 mm DB-5 bonded phase Megabore™

column (*J&W Scientific*) and HNU Systems, Inc., Model PI-52-02A photoionization detector.

Concentrations of H_2O_2 were determined by colorimetric titration of influent and effluent samples with standardized sodium thiosulfate after addition of molybdate catalyst and potassium iodide (*45*).

Other general water characteristics that were measured included dissolved oxygen (YSI electrode), total alkalinity, pH, nitrate, and dissolved organic carbon (persulfate-ultraviolet oxidation to CO_2), using standard methods (*46*).

Irradiation Product Identification. Influent and effluent samples were also collected in 1 liter amber glass bottles preserved with excess ferrous ammonium sulfate, 1 g L^{-1} of copper sulfate, and acidified ($pH<4$) with sulfuric acid. Total phenols were analyzed spectrophotometrically at 490 and 520 nm after distillation and derivatization with 3-methyl-2-benzothiazolinone (*47*).

Various aldehydes were analyzed by high performance liquid chromatography after pre-column derivatization with 2,4-dinitrophenylhydrazine. The resulting hydrazones were analyzed spectrophotometrically at 370 nm. The analytical instrumentation, as well as the methodology used, have been described elsewhere (*48*).

Water Quality. Two waters were used for the study, potable water and secondary wastewater effluent. The potable water is softened groundwater with chloramination. The secondary wastewater is chlorinated, and is the effluent of a pure oxygen extended aeration biological treatment system. The water quality characteristics of the two waters are shown in Table I.

Statistical Analysis. Parameter estimates for Equation [6] were obtained using a General Linear Models procedure of the Statistical Analysis System (SAS) package (*49*).

Results and Discussion

Aqueous Chemistry of High-Energy Electrons. High-energy electron irradiation of pure water results in the formation (10^{-16} - 10^{-12} sec) of electronically excited states, including ions, and/or free radicals along the path of the electron. The initial radiolysis products are formed in isolated volume elements called "spurs". As the spurs expand through diffusion, a fraction of the species recombine while the remainder escape into the bulk solution where they are free to interact and transfer their energy (*i.e., 50*). The reaction products formed after approximately 10^{-7} sec are shown in Equation [1]:

$$
\begin{aligned}
H_2O \rightsquigarrow \quad & [2.7]\ OH\cdot + [2.6]\ e^-_{(aq)} + [0.6]\ H\cdot \\
& + [0.7]\ H_2O_2 + [2.6]\ H_3O^+ + [0.45]\ H_2 .
\end{aligned}
\qquad [1]
$$

Since the energy required to produce chemical change is only a few electron volts (eV) per molecule, a high-energy electron is capable of initiating several thousand reactions.

The degree to which ionizing radiation initiates chemical reactions is measured by G values (shown in brackets in Equation [1]). G is defined as the number of radicals, excited states or other products, formed or lost in a system absorbing 100 eV of energy. Of the products formed in Equation [1], the most reactive are the oxidizing, hydroxyl radical (OH·), the reducing, aqueous electron ($e^-_{(aq)}$) and the hydrogen radical (H·). Thus, the chemistry of primary interest in this study is that of these three species. The presence of both $e^-_{(aq)}$ and OH· in aqueous solution, at similar steady state concentrations, is unique to this process and distinguishes it from other advanced oxidation processes (*50*). Table II summarizes the second order reaction rate constants of these three reactive species with the four solutes of interest in this study.

Solute Removal. Figures 1(a)-1(d) show the effective removal of benzene, toluene, *m*-xylene and *o*-xylene from potable water. Table III summarizes the percent removals of the four solutes at various absorbed doses in both potable water and secondary wastewater.

Three experimental factors affected removal efficiency: water quality, solute concentration, and dose. All four compounds were removed to below detection limits in potable water when added at the lower initial concentration. However, in the secondary wastewater, at the lower solute concentration, 90 - 96% removal was observed for all four solutes at 787 krad (7.87 kGy).

Concentration effects were also examined by irradiating mixtures with solute concentrations approximately 20 times higher in concentration (Table III). For example at 0.96 μM (75 μg L^{-1}) removal of benzene to below detection limits (0.01 μg L^{-1}) was observed in potable water while at 17.5 μM (1370 μg L^{-1}) the benzene was reduced by 93%, at an absorbed dose of 787 krad (7.87 kGy). Similar results were observed for all other compounds studied in both potable water and secondary wastewater.

Another way to describe solute removal is through G values which are commonly used in the radiation chemistry literature. The G value for solute R removal at a given dose, G_D, is defined by the disappearance of the solute in aqueous solution, and is determined experimentally using the following equation:

$$G_D = \frac{(\Delta R_D)(N_A)}{(D)(6.24 \times 10^{17})} \qquad [2]$$

where, ΔR_D is the change in organic solute concentration in mol L^{-1} at a given dose, D is the dose in krad, 6.24×10^{17} is the constant to convert krad to 100 eV L^{-1}, and N_A is Avogadro's number (see Equation [8]).

The G_D values at all doses for potable water were very similar to those observed in the secondary wastewater at the low solute concentration (Table IV). At the high solute concentration, the G_D values in potable water were higher when compared to secondary wastewater, only at the lowest dose. At the two higher doses the G_D values were very similar in both waters, with the exception of benzene where the G_D value appeared to be higher in potable water. At the higher solute concentrations the observed G_D values were an order of magnitude higher than those observed for low solute concentrations. This observation is consistent with removal being first order in solute concentration (see below).

Destruction Models. Figures 2(a)-2(d) show the results of ln[R] against dose for all compounds studied in both potable water and secondary wastewater. These plots are essentially straight lines, thus, the loss of the solutes is first-order, with respect to absorbed dose (D), and can be described by the following:

$$-\frac{d[R]}{dD} = k[R] \qquad [3]$$

or equivalently

$$R_D = R_o e^{-kD} \qquad [4]$$

Where R_D is the theoretical solute concentration at any dose D and R_o is the theoretical initial solute concentration, in moles L^{-1}.

Dose constants (k) were calculated for each compound by fitting the following regression equation to the concentration/dose data obtained under each of the four experimental conditions (2 concentrations x 2 water qualities):

$$-\ln \frac{R_{effl}}{R_{infl}} = k_o + kD \qquad [5]$$

Where R_{effl} is the measured solute concentration at any dose D and R_{infl} is the measured initial solute concentration, in moles L^{-1}.

One full replication of the experiment plus a partial replication, using only secondary wastewater, yielded six dose constants for each compound. The average dose constants, under each experimental condition are presented in Table IV.

Also, shown in Table V are the doses required for 90% destruction of the initial solute concentration. These values were obtained solving Equation [5] for $D_{0.90}$ assuming $R_{effl} = (1-0.10)R_{infl}$, $k_o = 0$, and k equal to the corresponding average dose constant.

The dose ($D_{0.90}$) required to remove 90% of the initial toluene and *o*- and *m*-xylene concentration in potable water was approximately 1.5-fold lower than the dose required to remove a similar concentration in secondary wastewater. At high concentration the required doses were similar for both water qualities. The dose required for benzene in secondary wastewater was higher when compared to potable water at both low and high concentrations. Similar observations apply to the dose constants which vary inversely with $D_{0.90}$.

A two factor (concentration and water quality) analysis of variance was performed for each compound using the dose constants as dependent variables. No replicate differences were found, but concentration, water quality, and concentration x water quality interaction effects were all highly significant at the $\alpha = 0.001$ (the probability of rejecting the null hypothesis of no effect, when indeed there is no effect) level for benzene, toluene, and *o*-xylene, and at $\alpha = 0.01$ for *m*-xylene.

The above results clearly indicate that water quality and initial concentration determine the dose constant (k) appropriate for use in the destruction model given by Equation [4]. In order to quantify the concentration and water quality effects, the following model was fit to the 24 individual data points (2 concentrations x 2 water qualities x 4 dose settings) available for each compound.

$$-\ln \frac{R_{effl}}{R_{infl}} = k_o + (k_1 + k_2 R_{infl} + k_3 I_{WQ} + k_4 R_{infl} I_{WQ}) D \qquad [6]$$

where $I_{WQ} = 0$ for secondary wastewater and 1 for potable water.

The terms involving k_1 through k_4 represent a model for k in Equation [4] that reflect the effects of initial concentration and water quality. The k_o term is included to allow for the possibility of unequal influent and effluent concentrations at the zero dose level. This can occur because of compound volatilization as the waste stream flows over the weir delivery system or simply from experimental error.

The results of solving equation [6] using the General Linear Model procedure from SAS are summarized in Table VI. All parameter estimates were highly significant. The resulting destruction model is thus of the form:

$$R_{effl}=R_{infl}e^{k_o+k_1'D+k_2'R_{infl}D} \qquad [7]$$

where the values of the parameters are given in Table VII. This model can be used to provide initial estimates of the destruction of BTX over the concentration range of 1.0 μM to 20 μM, in both potable water and chlorinated secondary wastewater.

Influence of Reactive Species. The concentration of the reactive radicals formed in the irradiated solutions can be determined using the following *(32, 52)*:

For a solute with G=1, where G is molecules $(100\ \text{eV})^{-1}$,

$$1\ \text{krad} = 1.04\ \mu\text{M of reactive species formed} \qquad [8]$$

Thus, for a G of 2.7, the concentration of OH· from Equation [1], is 0.28 mM at an absorbed dose of 100 krad (1 kGy). Based on these calculations, the total reactive radical species concentration formed in all experiments ranged from 0.40 - 2.23 mM for OH·.

In an attempt to explore the influence of the individual reactive species and the possible influence of radical scavengers on the removal of each solute studied, pseudo-first order rate constants were determined (*32*). The overall removal of each solute can be described by the following kinetic expression:

$$-\frac{d[R]_t}{dt} = k_5[R][OH\cdot] + k_6[R][e^-_{(aq)}] + k_7[R][H\cdot] \qquad [9]$$

where, k_5, k_6, k_7, are the respective second order rate constants (Table II). To estimate the relative concentration of the three reactive species the G values of equation 1 were used. The absolute concentration of these species, in irradiated natural waters, is determined by numerous reactions with the chemical constituents in solution and may not follow directly from the G values. However, to a first approximation, at any dose the product of the second order rate constant of a given solute and the G value (Equation [1]) of the respective reactive species is a pseudo-first order rate constant, k_5', k_6', k_7'. Summing these pseudo-first order rate constants provides an indication of the net removal rate of each solute (Equations [10] and [11]).

$$\text{Removal Rate}_{[R]} = (k_5' + k_6' + k_7')[R] \qquad [10]$$

$$= k_T'[R] \qquad [11]$$

The relative contribution of each reactive species, for solute removal, can be determined as (k_i'/k_T') x 100%, Table VIII.

From Table VIII it appears that benzene, *m*- and *o*-xylene should be removed with approximately the same efficiency, while toluene would be removed least efficiently. This assumption would hold true if water quality does not effect the distribution of the reactive species. Thus, in distilled water the OH· would be the radical most responsible for the removal of the individual solutes for all of the four compounds studied. However, in the case of toluene the H· could account for up to 16% of the removal. This may be significant in explaining the increased removal of toluene relative to the other solutes. In a natural water the observed removal efficiencies will vary because of the presence of natural radical scavengers and it is therefore difficult to predict *a priori* the removal efficiency of the various organic solutes, due to irradiation.

Radical Scavenger Effects

Oxygen. The average dissolved oxygen concentration was very similar in both waters tested, that is, of 3.7 mg L^{-1} (0.12 mM). Both $e^-_{(aq)}$ and H· rapidly reduce O_2 to form O_2^- ($pK_a = 4.8$) with second order rate constants of 1.9×10^{10} and 2.1×10^{10} M^{-1} s^{-1}, respectively (*i.e., 50*). Therefore, at 100 krad (1 kGy) the reaction of O_2 would remove approximately 35% of the two reactive species, while at 800 krad (8 kGy) only 5% would be removed. Because of the small contribution of e^-_{aq} to the removal of the solutes, this would presumably not effect the removal efficiency. For toluene, where up to 16% removal may be accounted for by reaction with the H· radical, the efficiency of removal would increase with increasing dose, i.e. less scavenging of the H· by O_2. To the best of our knowledge no reports have appeared that discuss the direct reaction of O_2^- with the solutes of interest in this study, and it is very likely that no direct reaction takes place.

Bicarbonate/Carbonate Ion. A common OH· scavenger in natural waters is alkalinity. It has been reported that the presence of CO_3^{2-} has inhibited the reduction of total organic carbon concentration in irradiated aqueous solutions of humic substances (*53*). The relative effects of these ions on radical scavenging can be predicted as:

$$OH\cdot + HCO_3^{1-} \longrightarrow H_2O + CO_3^{1-}\cdot \qquad [12]$$

$$OH\cdot + CO_3^{2-} \longrightarrow OH^- + CO_3^{1-}\cdot \qquad [13]$$

The second order rate constants are 8.5×10^6 $M^{-1}s^{-1}$ and 3.9×10^8 $M^{-1}s^{-1}$, respectively (*i.e., 50*).

Although the alkalinity of the secondary wastewater in our tests was 5-fold higher than the potable water, the OH· scavenging is approximately 2.5 times higher in the potable water based on bicarbonate/carbonate equilibria. This relationship was determined by summing the product of the concentration of the carbonate and bicarbonate ions with OH· reaction rate constants in each water.

The reaction of the carbonate radical ion, $CO_3^{1-}\cdot$, with benzene and toluene has been studied with rate constants of 3 x

10^3 $M^{-1}s^{-1}$ and 4.3 x 10^4 $M^{-1}s^{-1}$, respectively (*54*). It is unlikely that the removal efficiency of benzene or toluene was affected by the presence of this radical.

It was shown above that toluene destruction may be effected by H·. And, indeed the removal efficiency of toluene observed, in both the potable water and secondary wastewater, was higher than predicted, in comparison to the other solutes, for pure solutions.

The reaction of H· with HCO_3^{1-} has been studied and the second order rate constant reported, 4.4 x 10^4 $M^{-1}s^{-1}$ (*i.e., 50*). Therefore, it can be concluded that HCO_3^{1-} dose not scavenge the H· efficiently in this system, and may account for the increased G_D (toluene) and dose constants, than would be predicted from relative removal efficiency calculations for OH·.

Nitrate Ion. The presence of high concentrations of nitrate ion (NO_3^{1-}) in the secondary wastewater tested (Table I) may have also affected solute removal efficiency by acting as an $e^-_{(aq)}$ scavenger (k = 9.7 x 10^9 M^{-1} s^{-1}). Aqueous electron initially reacts with NO_3^- to form $NO_3^{2-}\cdot$, which reacts further with water to form $NO_2\cdot$ (*55*). By scavenging $e^-_{(aq)}$ the effective concentration of the OH· would be increased (minimizing recombination of the $e^-_{(aq)}$ and OH·), and reactions involving OH· enhanced. No information is available on the reactions of these nitrogen oxide radicals with the solutes in this study.

Dissolved Organic Carbon. The difference in dissolved organic carbon concentration in secondary wastewater (6-fold higher than the potable water) (Table I) may have also reduced removal efficiency by acting as an OH· radical scavenger. At this time it appears that the DOC may account for decreased removal of solutes observed in secondary wastewater when compared to potable water.

Methanol. As noted earlier, the solutes were injected into both the potable water and secondary wastewater influent stream as a concentrated methanolic stock solution. Methanol not only acted as a co-solvent for the solutes of interest, but also acted as the primary scavenger of OH·. The resulting concentration of methanol for all experiments was approximately 3.3 mM. Methanol reacts with OH·, and to a lesser extent with H· and e^-_{aq}, in aqueous solution with second order reaction rate constants of 9.7×10^8 , $2.6 \times 10^6\ M^{-1}s^{-1}$ and $1.0 \times 10^4\ M^{-1}s^{-1}$, respectively (*i.e.*, *50*). Therefore, under the experimental conditions employed, the destruction of the solutes by OH· is grossly underestimated, relative to aqueous solution of the solutes in the absence of methanol, due to radical scavenging. The effect of removal efficiency of the aromatic solutes by the radical by-products of methanol ($\cdot CH_2OH$ and $CH_3O\cdot$) was not determined.

Reaction By-Products

Several reaction by-products have been identified in irradiated solutions of the solutes studies. Our results are consistent with reported findings showing that phenols are an initial product in the decomposition of the compounds studied

(*35-43,56-62*). Figure 3(a) shows the results of total phenol analysis, for the irradiation of an aqueous mixture of all compounds, at various doses in secondary wastewater. These results support the reported studies in that at low doses the effluent phenol concentration increases and then falls below the influent (or background) concentration at high doses.

The mechanism, for phenol formation upon irradiation of aqueous solutions of solutes, involves reaction of the compounds with OH· forming hydroxycyclohexadienyl radicals **(I)**. Hydroxycyclohexadienyl radicals generate phenol **(II)** either by the disproportionation reaction (Scheme I) (*35*)

Scheme I

or by the mechanism proposed by Mantaka, et al. (Scheme II) (*61*)

Scheme II

Alkyl substituted phenols would be expected for OH· reaction with toluene, *m*-xylene and *o*-xylene by similar mechanisms.

In addition to phenol **(II)**, more highly oxidized species have also been observed. Glyoxal **(VI)**, at sub-μM concentrations, was identified qualitatively in this study. The mechanism for the formation of glyoxal involves the irradiation of an aqueous solution of benzene, resulting in the initial formation of the hydroxycyclohexadienyl radical **(I)**, which forms phenol **(II)** or quickly combines with dissolved oxygen resulting in an unstable hydroxy-hydroperoxide **(III)**. Subsequent water elimination and ring opening leads to the formation of mucondialdehyde **(IV)** (*57,58*). Mucondialdehyde is further oxidized to muconic acid **(V)** (*62*). Continued oxidative processes ultimately result in the formation of glyoxal **(VI)** (see Scheme III). A control experiment in which only secondary wastewater (no added organic solutes) was irradiated showed no formation of glyoxal. Several other aldehydes were observed but the structures of these compounds have not yet been determined.

Radical Enhancer Effects - Hydrogen Peroxide

It appears as though hydroxyl radical is primarily responsible for the removal of the aromatic compounds studied. Therefore, if the OH· concentration could be increased then it would enhance the removal efficiency. The following reactions (Equations [14] and [15]) have been described, with second order rate constants of 9×10^{7} M^{-1} s^{-1} and 1.1×10^{10} M^{-1} s^{-1} (*63*), respectively, and should result in an increase in OH· if H_2O_2 is added prior to irradiation of the aqueous stream.

$$H\cdot + H_2O_2 \longrightarrow OH\cdot + H_2O \qquad [14]$$

$$e^-_{(aq)} + H_2O_2 \longrightarrow OH\cdot + OH^- \qquad [15]$$

A comparison between the removal of the organic solutes in secondary wastewater with and without the addition of H_2O_2 (0.5 mM) showed increased removal for all compounds at low irradiation doses (40 - 150 krad). Figure 3(b) shows that the addition of H_2O_2 to the influent resulted in the formation of fewer phenols (i.e. more effective destruction) at low doses and substantially reduced the phenolic content of the effluent at high doses.

Summary and Conclusions

In the absence of radical scavengers (e.g., methanol) the principle reactive species responsible for removal of the solutes studied is $OH\cdot$, that is, approximately 93-97% of the loss of benzene, *m*- and *o*-xylene can be attributed to reaction with $OH\cdot$ (Table VIII). $OH\cdot$ accounted for only 83.5% removal of toluene. This indicates that the $H\cdot$ (16.1% removal) may also play an important role in the removal of toluene from aqueous matrices. For all compounds studied $e^-_{(aq)}$ was found to contribute less than 0.5% in solute removal. Thus the data for the removal of benzene, toluene, *m*-xylene, and *o*-xylene, and subsequent formation of phenols, in addition to the results obtained after addition of H_2O_2, are consistent with the hypothesis that $OH\cdot$ is primarily responsible for their disappearance.

In the presence of 3.3 mM methanol, where 95 - 99% of the $OH\cdot$ were scavenged (comparing methanol to benzene at the high and low solute concentration, respectively), water quality was shown to affect removal of the aromatic solutes. After considering the various radical scavengers (O_2, HCO_3^{1-}/CO_3^{2-}, NO_3^{1-}, DOC), it appears at this time as though DOC may be responsible for the different removal efficiencies observed in the two waters. Presumably this results from increased radical scavenging by the higher concentration of DOC in the secondary wastewater.

In addition, as the concentration of the organic solute was increased, the G_D value and dose required to remove 90% ($D_{0.90}$) of the initial solute concentration, increased for all compounds studied. Therefore, increased radiation doses are required as the concentration of the target chemicals increases.

In summary, it has been demonstrated that high-energy electron irradiation is effective for the destruction of selected BTXs in aqueous streams of varying quality in a continuous flow process even in the presence of high concentrations of radical scavengers, methanol. For applications of this process in groundwater remediation, the removal of the BTXs was probably underestimated by up to 2 orders of magnitude because of the presence of the methanol. Additional studies are necessary to irradiate aqueous solutions of the solutes, in similar matrices, in the absence of methanol and presence of known concentrations of radical scavengers (i.e., O_2, HCO_3^{1-}/CO_3^{2-}, NO_3^{1-}, and DOC). These results will provide better estimates of the removal efficiencies likely to be encountered in contaminated groundwaters, and it will enable a better characterization of reaction by-products.

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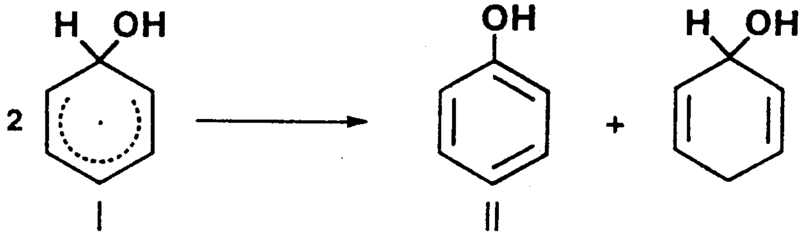
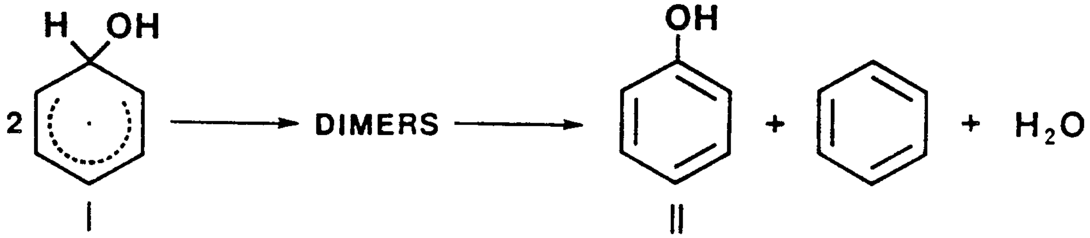
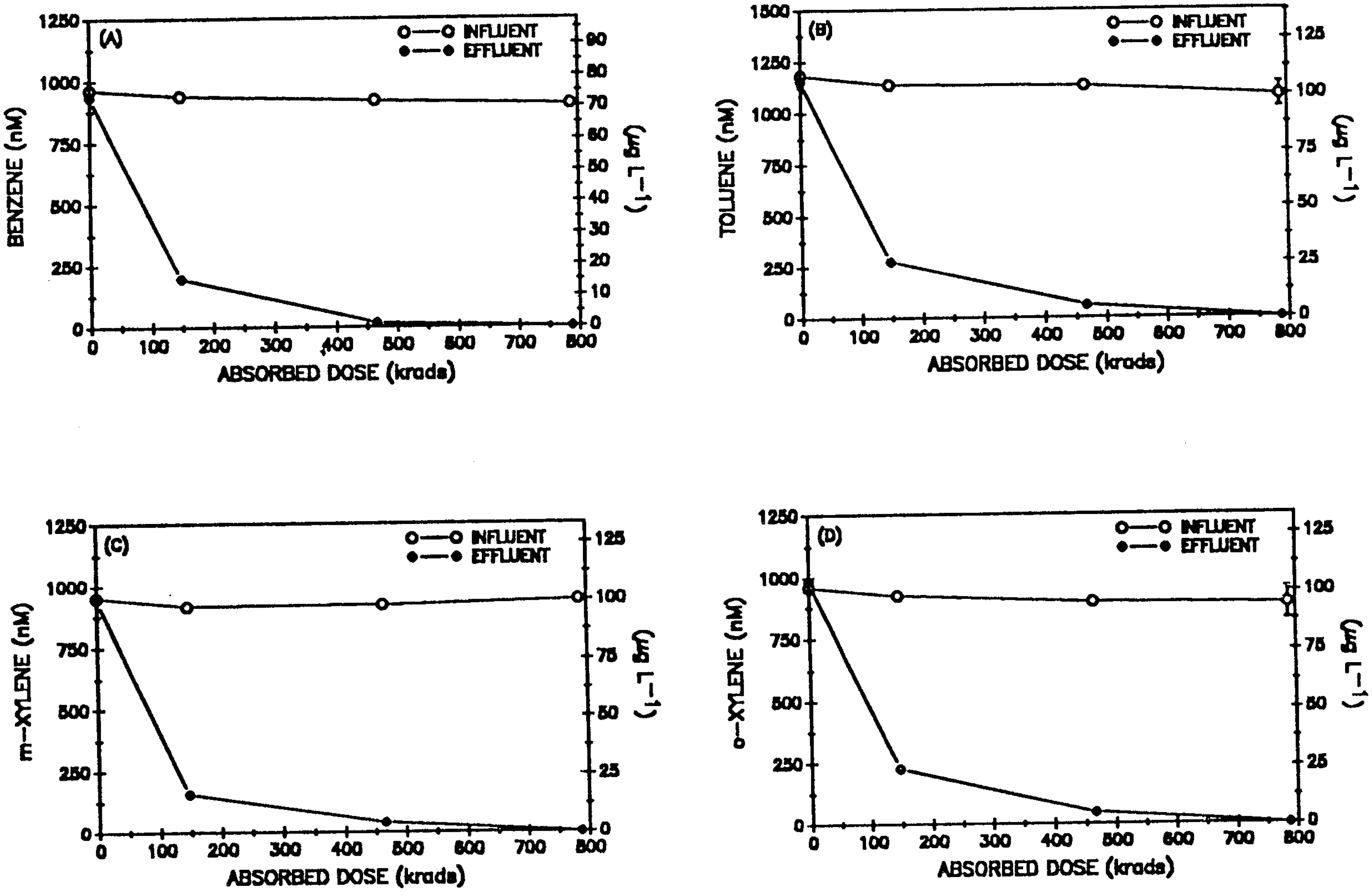
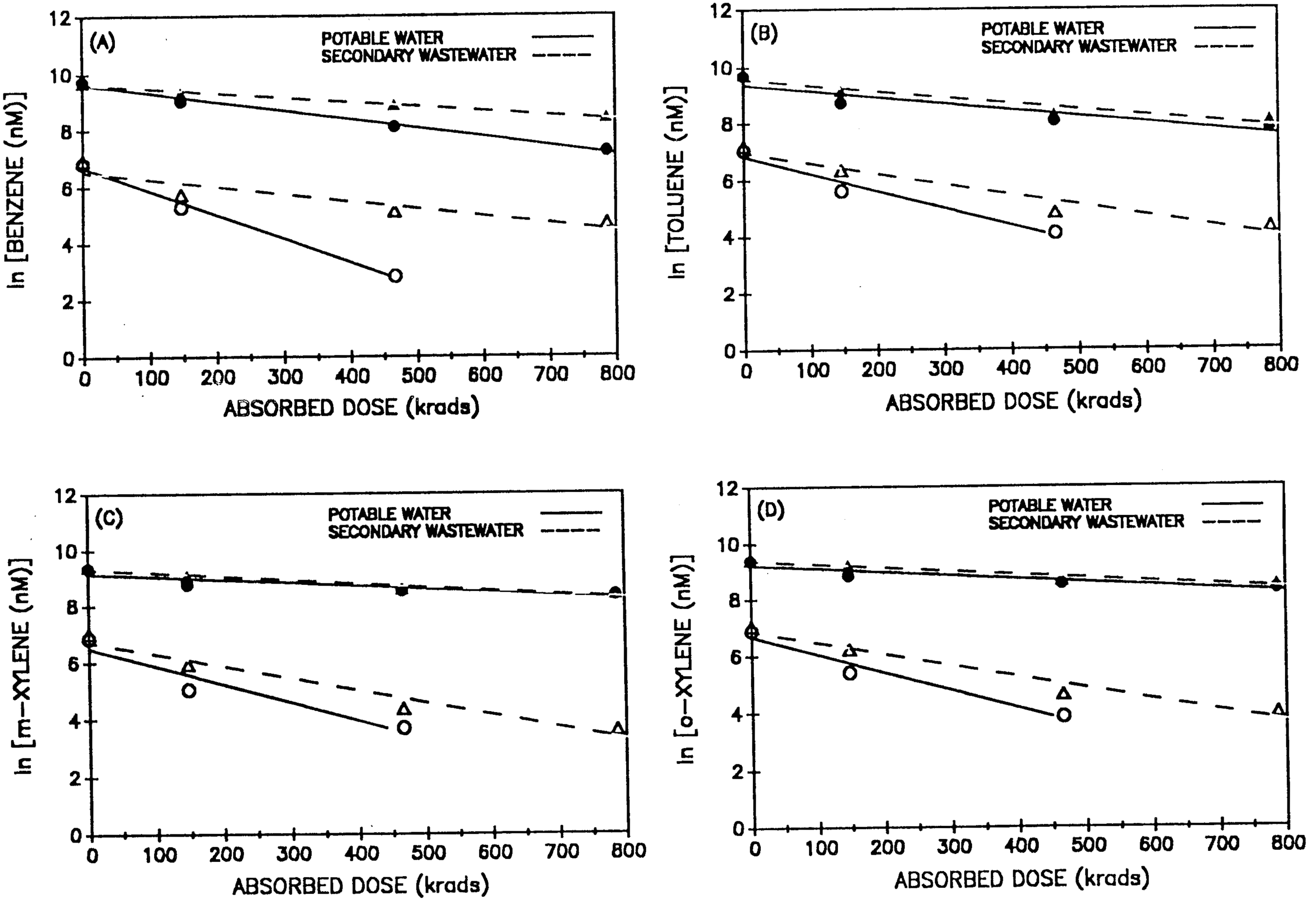
Scheme I

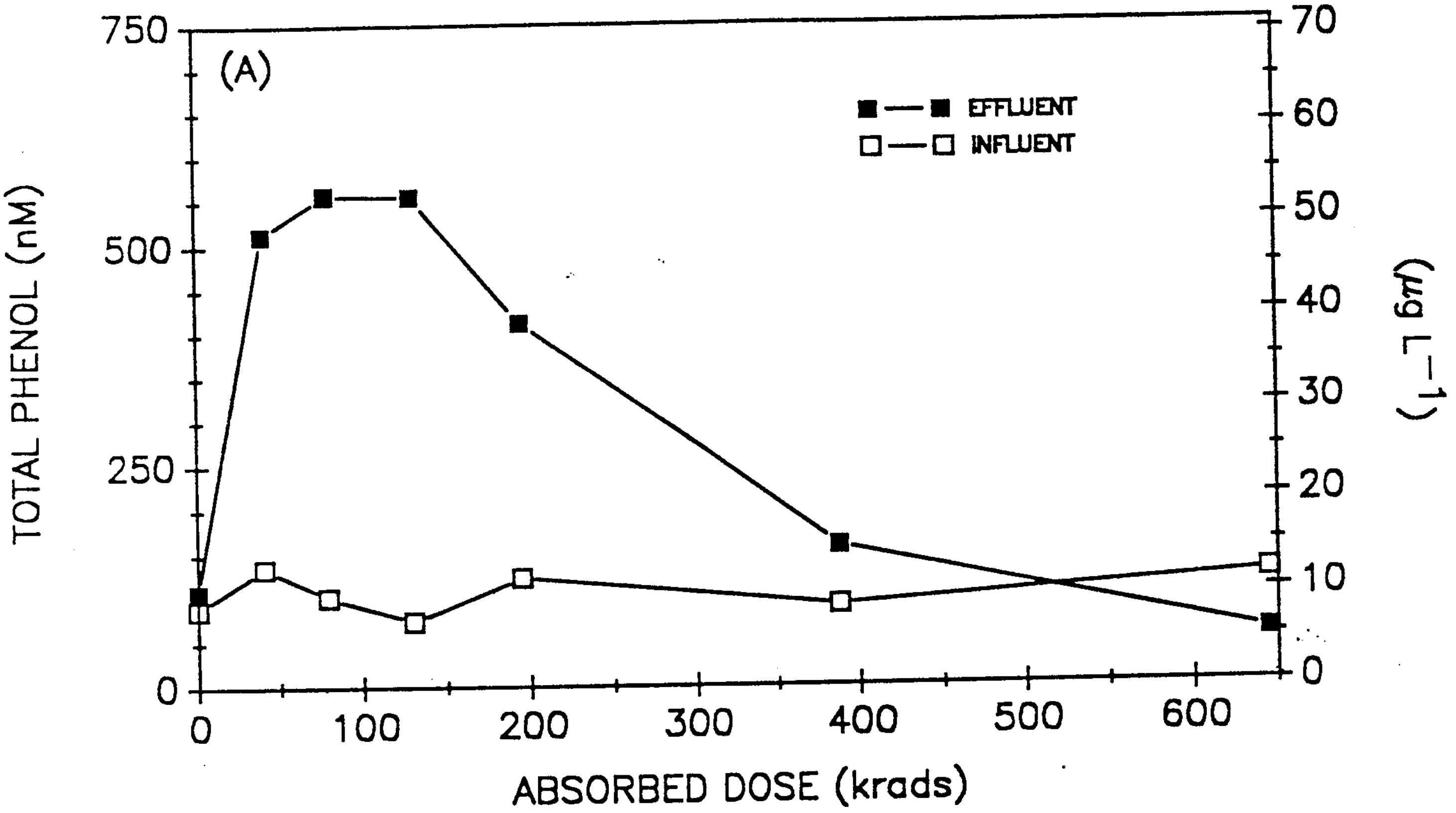


Scheme II




(A)
INFLUENT
EFFLUENT
BENZENE (nM)
(μg L⁻¹)
ABSORBED DOSE (krads)
0
250
500
750
1000
1250
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
(B)
TOLUENE (nM)
1500
25
75
125
(C)
m-XYLENE (nM)
(D)
o-XYLENE (nM)


(A)
POTABLE WATER
SECONDARY WASTEWATER
ln [BENZENE (nM)]
ABSORBED DOSE (krads)
(B)
POTABLE WATER
SECONDARY WASTEWATER
ln [TOLUENE (nM)]
ABSORBED DOSE (krads)
(C)
POTABLE WATER
SECONDARY WASTEWATER
ln [m–XYLENE (nM)]
ABSORBED DOSE (krads)
(D)
POTABLE WATER
SECONDARY WASTEWATER
ln [o–XYLENE (nM)]
ABSORBED DOSE (krads)
0
2
4
6
8
10
12
0
100
200
300
400
500
600
700
800



ADDITION OF 0.5 mM H_2O_2

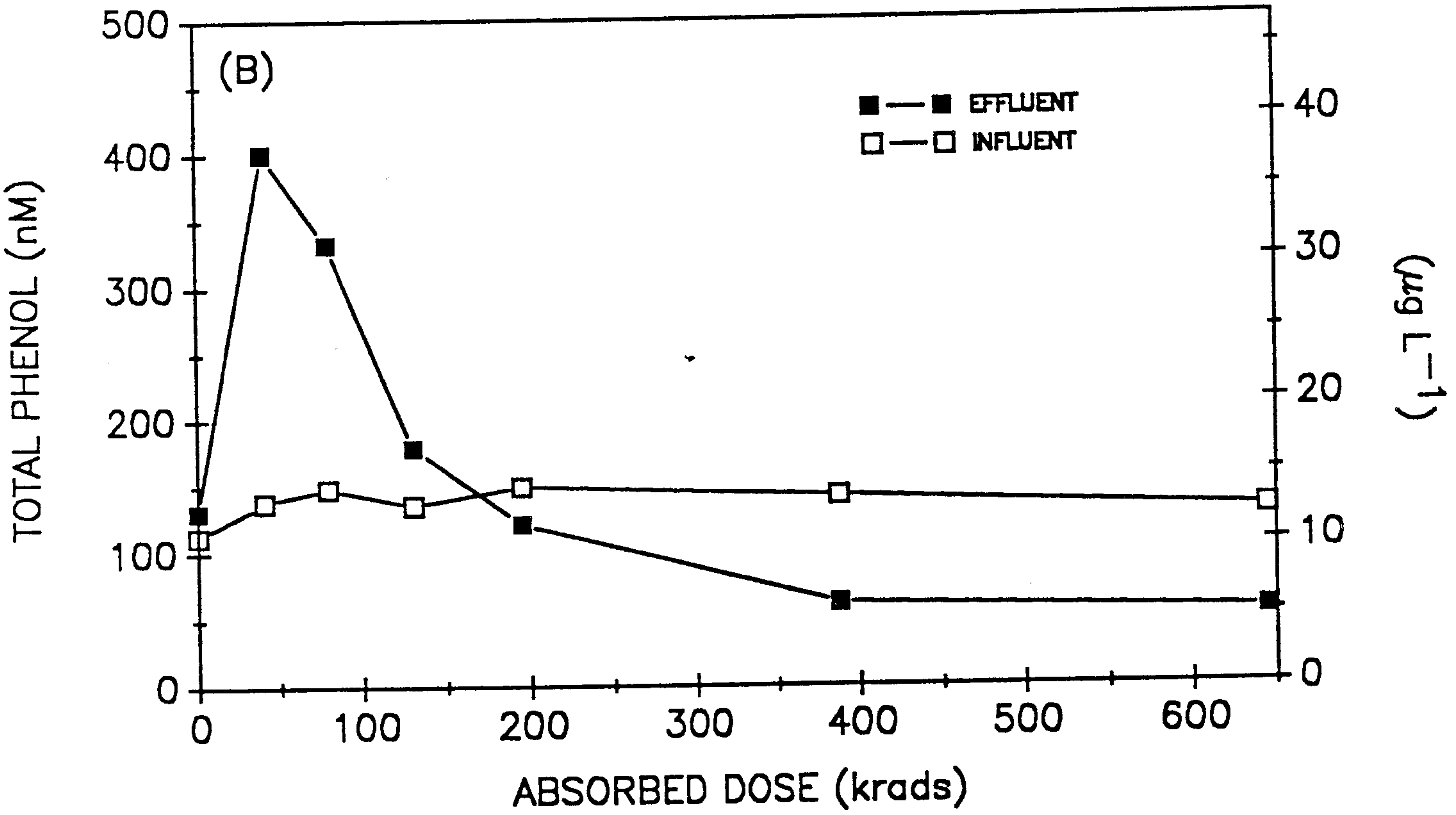


Table I. General Water Characteristics for Potable Water and Secondary Wastewater.

Parameter	Potable Water	Secondary Wastewater
pH	8.64	6.78
DO, mg L^{-1} O_2, (μM)	3.6 (113)	3.8 (119)
DOC, mg L^{-1} C, (μM)	10.2 (849)	62.7 (5220)
$CaCO_3$, mg L^{-1}, (μM)	36.0 (360)	190.2 (1900)
HCO_3^{1-} [a], mg L^{-1}, (μM)	21.4 (350)	85.4 (1400)
CO_3^{2-} [a], mg L^{-1}, (μM)	0.51 (8.50)	0.03 (0.46)
NO_3^{1-}-N, mg L^{-1}, (μM)	0.13 (2.14)	0.35 (5.71)

[a] calculated from equilibria.

Table II. Second Order Rate Constants ($M^{-1}s^{-1}$) of Aromatic Organic Compounds with Reactive Species Formed in Aqueous Solution During Irradiation (*i.e., 50*).

Compound	$e^-_{(aq)}$	**H·**	**OH·**
Benzene	9.0×10^6	9.1×10^8	7.8×10^9
Toluene	1.4×10^7	2.6×10^9	3.0×10^9
m-Xylene	NR	2.6×10^9	7.5×10^9
o-Xylene	NR	2.0×10^9	6.7×10^9

NR = not reported in the literature.

Table III. Summary of Percent Removal of Benzene, Toluene, *m*-Xylene and *o*-Xylene in Potable Water and Secondary Wastewater.

Compound	Initial Conc. (μM)	Detection Limit (nM)	Absorbed Dose (krad) 0	147	466	787
	Potable Water			**% Removed**		
Benzene	0.934	0.102	2.9	79.1	98.1	>99.9
Toluene	1.15	0.087	2.5	75.7	94.7	>99.9
m-Xylene	0.942	0.075	0.9	83.0	95.6	>99.9
o-Xylene	0.982	0.075	0.5	75.4	94.7	>99.9
	Secondary Wastewater			**% Removed**		
Benzene	1.04	0.102	7.7	72.8	82.7	90.6
Toluene	1.35	0.087	13.9	64.3	89.5	95.4
m-Xylene	1.11	0.075	9.9	70.2	91.5	94.5
o-Xylene	1.15	0.075	9.3	60.8	89.1	95.9

Compound	Initial Conc. (μM)	Detection Limit (nM)	Absorbed Dose (krad) 0	147	466	787
	Potable Water			**% Removed**		
Benzene	17.0	0.102	2.6	50.2	80.3	92.1
Toluene	16.4	0.087	4.9	62.6	81.4	85.4
m-Xylene	11.4	0.075	6.9	52.8	56.3	63.1
o-Xylene	11.8	0.075	3.7	42.5	57.2	61.9
	Secondary Wastewater			**% Removed**		
Benzene	16.2	0.102	7.9	32.7	57.4	73.4
Toluene	17.1	0.087	4.7	47.9	78.1	82.1
m-Xylene	12.0	0.075	6.6	29.6	58.0	65.4
o-Xylene	12.1	0.075	6.3	20.2	54.1	60.7

Table IV. Summary of Solute Removed and G_D for Potable Water and Secondary Wastewater at Two Solute Concentrations.

Potable Water	Low Solute Concentration			High Solute Concentration		
	Dose[a]	$[\Delta R]_D$[b]	G_D	Dose[a]	$[\Delta R]_D$[b]	G_D
		(μM)	(10^{-3})		(μM)	(10^{-3})
Benzene	155	0.74	4.6	144	8.6	57.8
	469	0.92	1.9	469	14	28.1
	797	>0.9	-	794	16	19.0
Toluene	155	0.88	5.5	144	10	68.0
	469	1.1	2.3	469	13	27.1
	797	>1.2	-	794	14	17.0
m-Xylene	155	0.79	4.9	144	6.0	33.7
	469	0.90	1.9	469	6.4	13.1
	797	>0.9	-	794	7.1	8.6
o-Xylene	155	0.75	4.7	144	4.8	32.1
	469	0.93	1.9	469	6.6	13.6
	797	>0.9	-	794	7.6	9.2

Secondary Wastewater	Low Solute Concentration			High Solute Concentration		
	Dose	$[\Delta R]_D$	G_D	Dose	$[\Delta R]_D$	G_D
		(μM)	(10^{-3})		(μM)	(10^{-3})
Benzene	144	0.73	4.9	144	5.1	33.9
	465	0.88	1.8	469	9.0	18.7
	779	0.94	1.2	794	12	14.7
Toluene	144	0.78	5.2	144	7.8	51.8
	465	1.2	2.5	469	13	27.3
	779	1.3	1.6	794	14	17.5
m-Xylene	144	0.73	4.9	144	3.3	21.7
	465	1.03	2.1	469	6.7	13.9
	779	1.07	1.3	794	7.7	9.6
o-Xylene	144	0.65	4.4	144	2.0	13.2
	465	1.05	2.2	469	6.4	13.2
	779	1.10	1.4	794	7.3	9.0

[a] Units = krad.
[b] $[\Delta R]_D$ = organic solute concentration removed at an absorbed dose d.

Table V. Summary of Observed First-Order High-Energy Electron Irradiation Dose Constants.

Potable Water	Initial Concentration (μM)	Observed k (krad^{-1})	$D_{0.90}$ (krad)	r^2
Benzene	0.934	8.40×10^{-3}	274	0.99
	17.0	3.05×10^{-3}	755	0.99
Toluene	1.15	6.09×10^{-3}	378	0.99
	16.4	2.22×10^{-3}	1040	0.86
m-Xylene	0.942	6.35×10^{-3}	363	0.99
	11.4	1.06×10^{-3}	2170	0.79
o-Xylene	0.982	6.24×10^{-3}	369	0.99
	11.8	1.17×10^{-3}	1970	0.87
Secondary Wastewater				
Benzene	1.04	2.63×10^{-3}	876	0.86
	16.2	1.60×10^{-3}	1440	0.99
Toluene	1.35	3.75×10^{-3}	614	0.95
	17.1	2.18×10^{-3}	1060	0.92
m-Xylene	1.11	4.32×10^{-3}	533	0.96
	12.0	1.30×10^{-3}	1170	0.95
o-Xylene	1.15	3.99×10^{-3}	577	0.96
	12.1	1.24×10^{-3}	1860	0.95

Table VI. Concentration and Water Quality Model Parameter Estimates for Equation [8].

	Parameter Estimate	t Value[a]	STD Error of Estimate
Benzene:			
k_0	-2.46×10^{-1}	-3.10	7.92×10^{-2}
k_1	-3.06×10^{-3}	-12.65	2.42×10^{-4}
k_2	1.03×10^{-7}	5.95	2.00×10^{-8}
k_3	-5.32×10^{-3}	-9.11	5.84×10^{-4}
k_4	2.09×10^{-3}	5.33	4.00×10^{-8}
Toluene:			
k_0	-3.07×10^{-1}	-3.88	7.90×10^{-2}
k_1	-3.88×10^{-3}	-15.78	2.46×10^{-4}
k_2	1.05×10^{-7}	6.30	2.00×10^{-8}
k_3	-2.15×10^{-3}	-3.63	5.93×10^{-4}
k_4	1.14×10^{-3}	2.79	4.00×10^{-8}
***m*-Xylene:**			
k_0	-2.68×10^{-1}	-3.61	7.42×10^{-2}
k_1	-4.73×10^{-3}	-20.29	2.33×10^{-4}
k_2	2.90×10^{-7}	13.09	2.00×10^{-8}
k_3	-2.24×10^{-3}	-3.98	5.63×10^{-4}
k_4	2.11×10^{-3}	3.84	5.00×10^{-8}
***o*-Xylene:**			
k_0	-1.98×10^{-1}	-3.41	5.80×10^{-2}
k_1	-4.30×10^{-3}	-23.53	1.83×10^{-4}
k_2	2.66×10^{-7}	15.02	2.00×10^{-8}
k_3	-2.13×10^{-3}	-4.84	4.40×10^{-4}
k_4	2.00×10^{-3}	4.50	4.00×10^{-8}

Units for Estimate and STD Error of Estimate: k_0 = unitless; k_1, k_3 = krad^{-1}; k_2, k_4 = $\text{nmol}^{-1}\text{krad}^{-1}$.

[a] Observed student's t value for the null hypothesis with parameter = 0.

Table VII. Destruction Model Parameter Estimates for Equation [9].

		Secondary Wastewater[a]		Potable Water[b]	
Compound	k_o	$k_1' \times 10^{-3}$	$k_2' \times 10^{-6}$	$k_1' \times 10^{-3}$	$k_2' \times 10^{-6}$
Benzene	-0.2456	-3.064	-0.1026	-8.383	-0.3121
Toluene	-0.3068	-3.877	-0.1052	-6.031	-0.2193
m-Xylene	-0.2681	-4.728	-0.2897	-7.127	-0.5007
o-Xylene	-0.1977	-4.302	-0.2663	-6.431	-0.4663

Units: k_o = unitless; k_1' = krad^{-1}; k_2' = nmol^{-1}krad^{-1}.

[a] $I_{WQ} = 0$.

[b] $I_{WQ} = 1$.

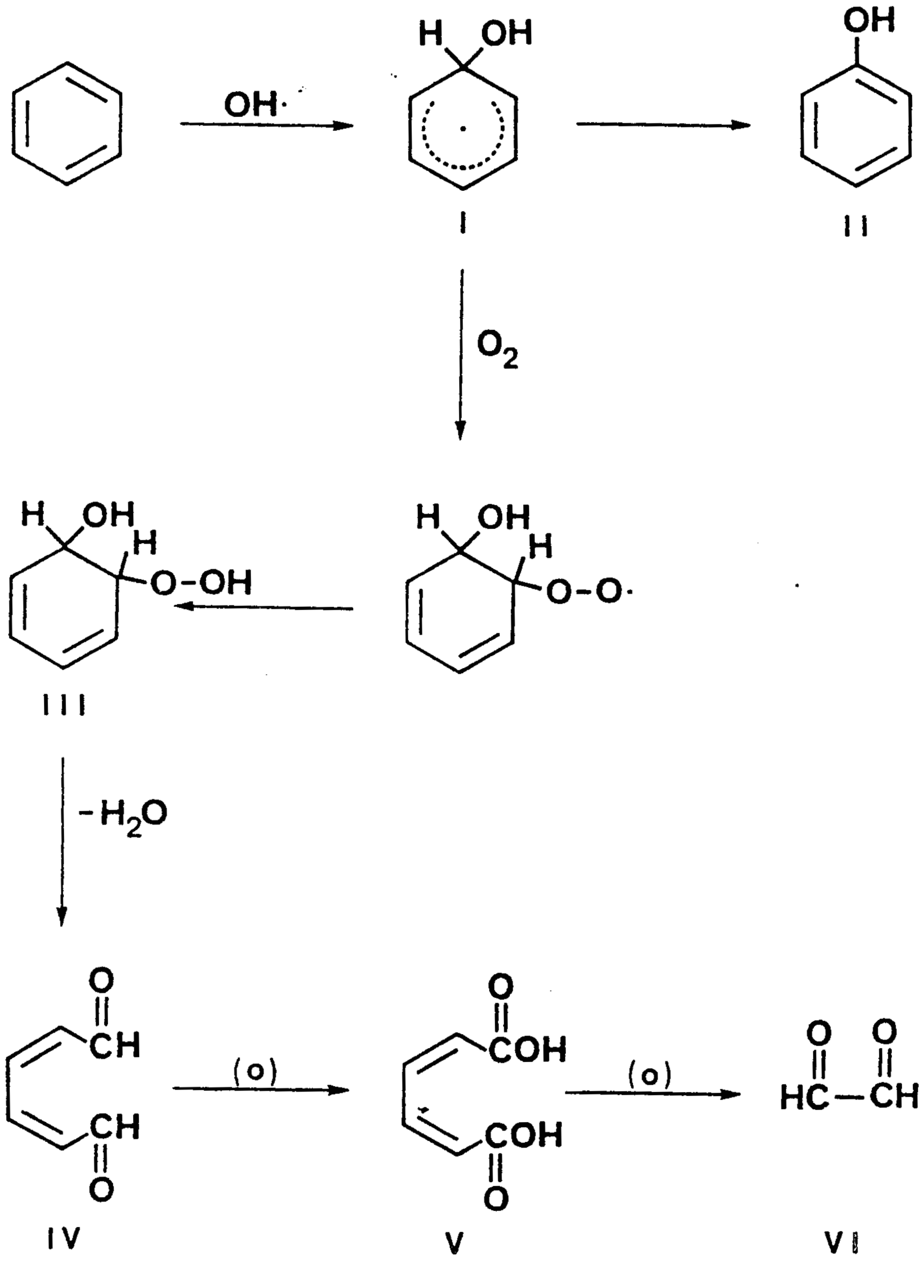
Table VIII. Summary of Pseudo-First Order Rate Constants of Solutes with Reactive Species Formed During Irradiation.

	OH·		$e^-_{(aq)}$		H·		
	k_5' ($\times 10^9$)	%[a]	k_6' ($\times 10^9$)	%[a]	k_7' ($\times 10^9$)	%[a]	k_T' ($\times 10^9$)
Benzene	21.1	97.5	0.02	0.1	0.55	2.4	21.7
Toluene	8.10	83.5	0.04	0.4	1.56	16.1	9.70
m-Xylene	20.3	92.9	0.03[b]	0.1	1.56	7.0	21.9
o-Xylene	18.1	93.7	0.03[b]	0.1	1.20	6.2	19.3

[a] Percent that each reactive specie is responsible for solute removal, $(k_i'/k_T') \times 100\%$.

[b] Assuming a second order rate constant of $1.0 \times 10^7\ M^{-1}s^{-1}$.

Scheme III



List of Figures:

Figure 1. Removal of benzene (a), toluene (b), *m*-xylene (c), and *o*-xylene (d), at various absorbed radiation doses, from potable water.

Figure 2. Plot of ln [BTX] *vs* dose for benzene (a), toluene (b), *m*-xylene (c), and *o*-xylene (d), at various absorbed radiation doses, in both potable water and secondary wastewater.

Figure 3. Formation of phenols in secondary wastewater, at various absorbed irradiation doses, before (a) and after (b) addition of 0.5 mM H_2O_2 to the influent waste stream.

FULL SCALE TREATABILITY STUDY

Electron Beam Research Facility

Full scale treatability studies can be undertaken at the Electron Beam Research Facility (EBRF) located in Miami, Florida (see attached description). The sample size should be at least 7,600 liters (2000 gallons), but the experimental design can accommodate other sizes. The sample will be transported to the Facility and returned to the client for disposal. Transportation to and from the Miami facility will be at the clients expense. Safety/liability considerations require that a full description of the composition of the sample be provided and the compound(s) of primary interest be identified.

1. The study will be conducted at a flow of 460 liters per minute (120 gallons per minute.
2. An experimental design will be developed based on volume and target parameters.
3. The water sample will be irradiated at doses between 0 and 800 krads. Experiments can be conducted either on a once through or recycle basis.
4. Samples will be collected as per the agreed upon test plan. Samples will be preserved in accordance with approved US Environmental Protection Agency protocol for the parameters of interest.
5. Certified copies of test results obtained by and for the client will be provided to the Electron Beam Research Facility. Any use of said data by the EBRF will <u>not</u> identify the source of the sample provided by the client.

   Engineering costs - **$7,300.00**
   Analytical costs - will be determined at the time of the study.

OPTIONAL

The Environmental Engineering laboratory at the University of Miami and the Drinking Water Research Center at Florida International University have complete facilities for analyzing water and wastewater. The Drinking Water Research Center is a Certified Laboratory in the State of Florida. If desired, the Universities can provide analytical support for sample analysis. The cost of specific analyses will be furnished upon request.

For further information please contact:

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