



APPLICATIONS OF IONIZING RADIATION TO THE REMEDIATION OF MATERIALS CONTAMINATED WITH HEAVY METALS AND POLYCHLORINATED BIPHENYLS

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ABSTRACT

We have investigated the removal from water of heavy metals and chelated heavy metal compounds using electron beam and gamma radiation. Parameter analyses include the effect of dissolved oxygen and the influence of adding various buffers and radical scavengers. Complete removal (>99%) of mercury, lead and cadmium ions, both free and chelated within EDTA, was achieved using radiation doses ranging from 3-100 kGy. We have also studied the radiation induced degradation of polychlorinated biphenyls (PCBs) in aqueous-organic and aqueous micellar systems. Rates and extent of dechlorination have been quantified in different solution matrices; reaction by-products and intermediate species have been identified; and the influences of dissolved oxygen and pH have been evaluated. The presence of a carbonate buffer was observed to significantly enhance PCB dechlorination yields by reducing concentrations of H_3O^+ . Ionizing radiation was effective in degrading PCBs in micellar solutions but scavenging of e_{aq}^- by the surfactant lowered reaction efficiencies.

KEYWORDS

Ionizing radiation, gamma radiation, electron beam, lead, mercury, cadmium, polychlorinated biphenyls, surfactants

INTRODUCTION

We have recently investigated the treatment of industrial wastewater by ionizing radiation. This research has emphasized the role of the solvated electron in effecting desired transformations of noisome species, primarily polychlorinated biphenyls and heavy metals. These transformations occur principally through indirect effects of radiation in which interaction of ionizing radiation with a solvent creates a suite of radical species that subsequently react with a contaminant solute. The initial products formed in a solution upon absorption of ionizing radiation are dependent upon the solvent and solution conditions. For water irradiated by low mean linear energy transfer

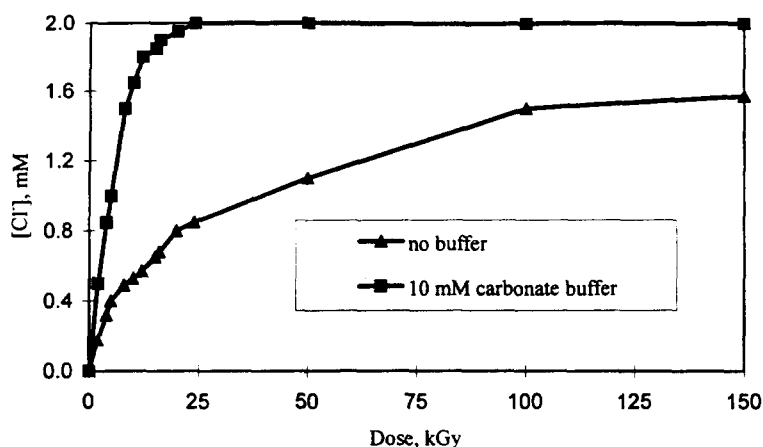


Figure 1. Comparison of chloride release during gamma irradiation of buffered and unbuffered solutions of 1 mM 2,6-dichlorobiphenyl. (Solution is nitrogen sparged water:methanol 1:1)

(LET) radiation, such as ^{60}Co γ -rays and fast electrons, the primary yields in the pH range 3 to 11 are the following: (Buxton, 1987)

$$G(e_{\text{aq}}^-) = G(\text{OH}) = G(\text{H}_3\text{O}^+) = 0.28; \quad G(\text{H}) = 0.062; \quad G(\text{H}_2) = 0.047; \quad G(\text{H}_2\text{O}_2) = 0.072 \quad (\mu\text{M/J})$$

Radical yields are greater in the presence of higher concentrations of electron or hydroxyl radical scavengers (Spinks and Woods, 1990). Solvated electrons are also formed in organic solvents. However, their yield decreases in nonpolar solvents due to higher rates of recombination with their geminate cations (Spinks and Woods, 1990).

RESULTS AND DISCUSSION

Aqueous-alcohol systems

During our initial work on radiolysis of PCBs, we examined the mechanisms of dechlorination of 2,6-dichlorobiphenyl (DCB). The reaction rate constant of e_{aq}^- with DCB was measured by pulse radiolysis and found to be $3.8 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$. The resultant monochlorobiphenyl radical, MCB^\bullet , reacts with oxygen to produce a peroxy radical whose spectrum was found to have a broad peak around 500 nm. The transformation of 1 mM DCB in aqueous methanol was achieved by irradiation with a dose of 30 kGy. However, much higher doses (600 kGy) were required to convert >99.5% of the initial organic chlorine to the chloride ion. The radiation yield for the first dechlorination step was $0.03 \mu\text{mol J}^{-1}$ and was observed to decrease by a factor of 20 for the second dechlorination step. These yields are considerably lower than the yield of e_{aq}^- and were due to the radiolytic formation of H_3O^+ which competes for e_{aq}^- . To prevent this competition, carbonate was added to the solution to keep the pH alkaline during the irradiation. This decreased the dose required for essentially complete dechlorination of DCB to 20 kGy, which corresponds to scavenging greater than 50% of e_{aq}^- by DCB and its first dechlorination product, MCB (see Figure 1).

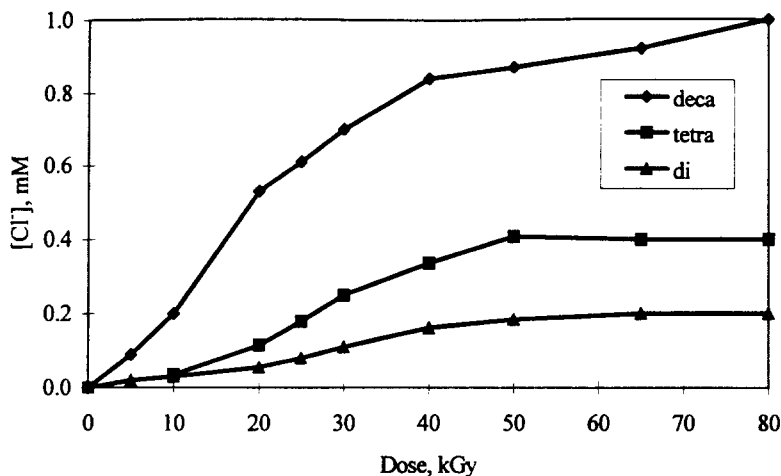


Figure 2. Formation of chloride ion during γ -radiolysis of 0.1 mM aqueous micellar solutions of 2,6-dichlorobiphenyl, 2,6,2',6'-tetrachlorobiphenyl and decachlorobiphenyl. Each solution contains 2% (v/v) Triton X-100 surfactant and 10 mM carbonate buffer.

Surfactant systems

Our more recent studies have been centered on the radiolytic dechlorination of PCBs in aqueous micellar systems. In general, highly chlorinated PCBs are only soluble in very nonpolar solvents. However, through the use of surfactants we have been able to study the radiolytic behavior of even the most chlorinated PCBs in aqueous solution. Aqueous surfactant solutions can be utilized to extract PCB contaminated oil from soil (Scholz and Milanowski, 1984; Nash and Traver, 1986; Abdul *et al.*, 1990 & 1992; Abdul and Gibson, 1991) and radiolysis may be effective in degrading the extracted PCBs in this matrix. In addition, the free electron yield in nonpolar solvents, such as mineral oil, is usually quite small in comparison to that measured in water (Arbon *et al.*, 1996). Therefore, our approach based on mixing water with the contaminated oil in an emulsion prior to radiolysis has the potential to substantially increase the PCB destruction efficiency by raising the overall yield of free electrons.

We have investigated the rate and extent of γ -radiolytic dechlorination of three PCB congeners, 2,6-dichlorobiphenyl (BZ# 10), 2,6,2',6'-tetrachlorobiphenyl (BZ# 54), and 2,3,4,5,6,2',3',4',5',6'-decachlorobiphenyl (BZ# 209), in aqueous micellar systems. Pulse radiolysis was used to quantify rate constants for the reaction between e_{aq}^- and a variety of surfactants and PCBs. Degradation pathways and specific transformation rates of intermediate species were determined using gas chromatography equipped with electron capture and mass selective detection (GC, ECD, and MSD respectively). The results obtained in micellar systems have been compared to those we observed in solvent systems, primarily methanol and isopropanol, to examine differences in reaction rates and pathways between the two types.

Figure 2 shows the formation of chloride anion during gamma radiolysis of the three PCB congeners, 2,6-dichloro-, 2,6,2',6'-tetrachloro-, and 2,3,4,5,6,2',3',4',5',6'-decachlorobiphenyl.

The PCBs were solubilized in an aqueous solution of 2% (v/v) Triton X-100; a nonionic ethoxylated alkylphenol surfactant. The initial concentration of the PCB in each experiment was 0.1 mM. For each congener, essentially all of the initial organic chlorine was converted to inorganic chloride ion. For example, 0.2 mM of chloride was generated from 0.1 mM of dichlorobiphenyl; 0.4 mM of chloride was produced by 0.1 mM of tetrachlorobiphenyl; and 1 mM of chloride was released from 0.1 mM of decachlorobiphenyl. This demonstrates that PCBs can be fully dechlorinated by gamma radiation in aqueous micellar systems. The initial yields of Cl^- were 0.004, 0.008, and 0.021 $\mu\text{mol J}^{-1}$ for dichloro-, tetrachloro-, and decachlorobiphenyl respectively. These yields are relatively low and reflect scavenging of the aqueous electron by the surfactant, Triton X-100. It is also interesting to note that the Cl^- yields are directly proportional to the initial carbon-chloride bond concentration.

The Triton X-100 was used at a 2% concentration (34 mM) because this was found to be the lowest level which solubilized 0.1 mM decachlorobiphenyl in a stable solution. A 2% surfactant concentration is also typical of what has been used in washing PCBs from contaminated soil (Nash and Traver, 1986; Abdul and Gibson, 1991). The critical micellar concentration for Triton X-100 is approximately 0.3 mM (Rosen, 1989) which is well below the 34 mM concentration which was used in these experiments. Considering this, as well as the very low solubility of PCBs in water, we conclude that essentially all of the PCBs were contained within micelles.

In general, rates of reaction between e_{aq}^- and solutes contained within nonionic micelles are reduced in comparison to homogeneous aqueous phase reactions (Wallace and Thomas, 1973; Thomas, 1977). This is due to lower rates of diffusion and to the higher chemical potential of an electron in the lipoidic interior of the micelle (Henglein and Grätzel, 1977). The rate constant for the reaction between e_{aq}^- and Triton X-100 was analyzed using pulse radiolysis and was determined to be $1.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$; a value slightly lower than that reported in earlier work (Thomas, 1977). For the reaction between decachlorobiphenyl and e_{aq}^- in the 2% Triton solution the rate constant was measured as $2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Rates of reaction with e_{aq}^- could not be quantified for either tetrachlorobiphenyl or dichlorobiphenyl because they were not sufficiently higher than the background scavenging of electrons by the Triton surfactant. Given the relative concentrations of the PCBs and the Triton, these rate data demonstrate that a greater fraction of solvated electrons in the degradation experiments reacted with the surfactant than with the PCBs. Triton X-100 was chosen for this initial work because it is an effective emulsifying agent and solubilizes hydrophobic organic compounds well. However, its pejorative influence on the overall radiolytic dechlorination rate of PCBs makes it a poor choice for use in this application and testing of different surfactants is currently underway in our laboratories.

The decay of the parent compound and the formation of lower chlorinated biphenyls during γ -radiolysis of 2,3,4,5,6,2',3',4',5',6'-decachlorobiphenyl in the Triton micellar system were analyzed by GC-MS and results are shown in Figure 3. Each line in Figure 3 is equal to the molar sum of all the quantified PCBs whose number of chlorine atoms corresponds to the prefix shown in the legend. The concentrations of deca-, nona-, octa- and heptachlorobiphenyls are plotted using the concentration scale on the left vertical axis while the concentrations of hexa-, penta-, tetra-, tri-, di- and monochlorobiphenyl as well as biphenyl are plotted using the concentration scale of the right vertical axis. Initially decachlorobiphenyl degraded predominantly through reductive dechlorination, forming less chlorinated PCBs as a result. At a dose of 5 kGy,

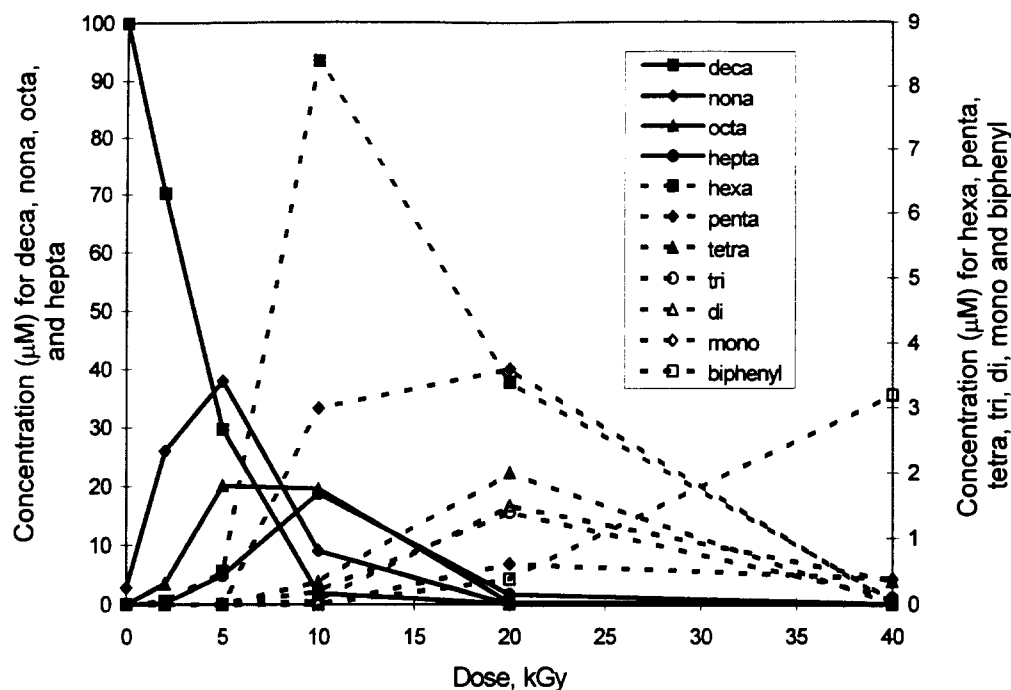


Figure 3. Decay of 0.1 mM decachlorobiphenyl and formation of intermediate PCBs in aqueous micellar solution by γ -radiolysis. Initial solution contained 2% (v/v) Triton X-100 surfactant + 10 mM carbonate buffer. See text for details.

approximately 70 μM of decachlorobiphenyl were transformed and 63 μM of lower chlorinated PCBs, primarily nona- and octa-, were produced. However, the observation that the total concentration of PCBs decreased at higher radiation doses, combined with the fact that only 3 μM of biphenyl were present at a dose of 40 kGy when almost no PCBs remained, suggest that transformation mechanisms other than reductive dechlorination were operative as well. These data also support the hypothesis that gamma radiation is effective in fully transforming PCBs in micellar solutions.

Heavy metals

Another aspect of our research on mechanisms of high energy electron treatment of industrial wastewater has been a study of the removal of heavy metals and chelated heavy metal compounds from water using electron beam and gamma radiation. In this process, radiolytically generated reducing radicals, such as e_{aq}^- and H , reduce metal cations to lower valence states where they precipitate and can be removed by filtration. Our work complements the results of previous studies (Stein *et al.*, 1952; Nazhat and Asmus, 1973; Barkatt and Rabani, 1975; Breitenkamp *et al.*, 1976; Henglein *et al.*, 1992). We have investigated the removal of lead, mercury and cadmium, both in solution and complexed within ethylenediaminetetraacetic acid (EDTA), as a function of dissolved oxygen concentration, pH, and the presence of a hydroxyl

radical scavenger. In this work, complete removal (>99.9%) of mercury from a 1 mM HgCl_2 solution was achieved by 3 kGy of γ -radiation. Irradiation of a 1 mM PbCl_2 solution by electron beam produced 96% removal of lead at a dose of 20 kGy. Metals were also effectively removed when they were complexed in EDTA. Gamma irradiation of a 1 mM solution of lead, fully complexed in EDTA, resulted in 99% removal of lead with 100 kGy of radiation. Removal of metals occurred more efficiently in deaerated (nitrogen sparged) solutions. Addition of carbonate increased the removal of chelated lead by approximately 25% through reducing the concentration of H_3O^+ . It was also necessary to add a hydroxyl radical scavenger (1% ethanol) as suggested by Nazhat and Asmus, 1973.

CONCLUSIONS

Ionizing radiation can produce full dechlorination of PCBs in both aqueous-alcohol and aqueous-surfactant matrices. PCB degradation rates are enhanced significantly by the addition of a carbonate buffer to raise the pH and, thereby, limit scavenging of solvated electrons by H_3O^+ . In the micellar solutions, the reaction rate between aqueous electrons and the surfactant was significant and this lowered the efficiency of PCB degradation. The initial yield of chloride ion during radiation induced degradation of PCBs was observed to be directly proportional to the concentration of carbon-chlorine bonds. Radiation induced precipitation of heavy metals was highly effective, even when the metal was chelated within EDTA. The efficiency of precipitation increased in deaerated solutions and was also improved by addition of a carbonate buffer.

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REFERENCES

- Abdul A. S., Gibson T. L. and Rai D. N. (1990) Selection of surfactants for the removal of petroleum products from shallow sandy aquifers, *Ground Water* **28**, 920-926.
- Abdul A. S. and Gibson T. L. (1991) Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyl from sandy material, *Environ. Sci. Technol.* **25**, 665-671.
- Abdul A. S., Gibson T. L., Ang C. C., Smith J. C. and Sobczynski R. E. (1992) In situ surfactant washing of polychlorinated biphenyls and oils from a contaminated site, *Ground Water* **30**, 219-231.
- Arbon R. E., Mincher B. J. and Knighton W. B. (1996) γ -Ray destruction of PCBs in isooctane and transformer oil, *Environ. Sci. Tech.* **30**, 1866-1871.
- Barkatt A. and Rabani J. (1975) Metal precipitation from pulse irradiated solutions of cadmium (II) and similar cations, *J. Phys. Chem.* **79**, 1359-1362.
- Breitenkamp M., Henglein A. and Lilie J. (1976) Mechanism of the reduction of lead ions in aqueous solution (a pulse radiolysis study), *Ber. Bunsenges. Phys. Chem.* **80**, 973-976.

- Buxton G. V. (1987) Radiation chemistry of the liquid state: (1) Water and homogeneous aqueous solutions, *Radiation Chemistry, Principles and Applications*, (Farataziz and M. Rodgers, Eds.) VCH Publishers Inc., New York, 321-376.
- Henglein A. and Gratzel M. (1977) Electron transfer in heterogeneous photochemical reactions, *Solar Power and Fuels*, (J. R. Bolton, Ed.) Academic Press, Inc., New York, 53-73.
- Henglein A., Janata E. and Fojtik A. (1992) Reduction of Pb^{2+} in aqueous solution: Early steps and colloid formation, and the atom to metal transition, *J. Phys. Chem.* **96**, 4734-4736.
- Nash J. and Traver R. P. (1986) Field evaluation of in situ washing of contaminated soils with water/surfactants, *Proceedings of the 12th annual research symposium*, EPA/600/9-86/022.
- Nazhat N. B. and Asmus K. -D. (1973) Reduction of mercuric chloride by hydrated electrons and reducing radicals in aqueous solutions. Formation and reactions of $HgCl$, *J. Phys. Chem.* **77**, 614-620.
- Rosen M. J. (1989) *Surfactants and Interfacial Phenomena*, 2nd ed., John Wiley & Sons, New York, 326-329.
- Scholz R. and Milanowski J. (1984) EPA project summary: Mobile system for extracting spilled hazardous materials from excavated soils, *J. Hazard. Mater.* **91**, 241-252.
- Spinks J. W. and Woods R. J. (1990) *An Introduction to Radiation Chemistry*, 3rd Ed., John Wiley and Sons, Inc., New York.
- Thomas J. K. (1977) Effect of structure and charge on radiation-induced reactions in micellar systems, *Accs. Chem. Res.* **10**, 133-138.
- Wallace S. C. and Thomas J. K. (1973) Reactions in micellar systems, *Radiat. Res.* **54**, 49-62.