Effects of Gamma Radiation on Aqueous Solutions of Phenol

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Increasing activity in the petrochemical industry, refineries, coke ovens, and steel mills has created a demand for advanced and efficient methods of waste treatment. In highly urbanized and industrialized areas, the expected volume of complex wastewater requires development of new approaches to supplement the present capabilities of biological treatment methods.

The beneficial use of radiation has been investigated for many applications. Radiation research and development applied to wastewater treatment has been limited. However, sufficient research has been done to indicate that the use of radiation may be beneficial in the treatment of urban and industrial wastewater (BALLANTINE et al.1969;WOODBRIDGE et al.1970; WOODBRIDGE et al.1972a;WOODBRIDGE et al.1972b).

Radiation as a wastewater treatment technique is effective because:
(a) it has the capability of altering the structure of organic and inorganic molecules,
(b) it initiates oxidation of organic and inorganic molecules,
(c) it can cause agglomeration of colloidal compounds.
Therefore, the possibility exists that radiation may alter phenols to a form which is more readily biodegradable.

The aromatic hydrocarbons comprise one of the most important classes of materials which finds its way into the wastewater streams (ALBERT and FRAZIER 1967). This large group contains many of the basic cyclic compounds such as phenol, resorcinol, pyrogallol, cresol, naphthol, hydroquinone, and many of the phenol derivatives such as those containing chlorine, sulfur, nitrogen, and others. These chemicals are finding increased use in large quantities both in pure chemical form and in combination with many other materials. Some of the most common uses are coating, stripping and cleaning agents, materials for surface treatment of metals, paint for vehicles, plastics, solvents, fertilizers, rubber substitutes, explosives, wood preservatives, textiles, medicines, perfumes, and pharmaceuticals. Many of the phenolic compounds have been used in the processing of leather, soap, paper, petroleum, dyes, and in the agricultural industries.

Bulletin of Environmental Contamination & Toxicology,
Vol. 11, No. 5 © 1974 by Springer-Verlag New York Inc.

The effectiveness of phenols and their derivatives as germicidal agents is well known. The phenol index has been used for a long time by pharmacists as a means of comparison of germicidal quality. These chemicals and their derivatives prohibit the growth and development of many common organisms which normally ferment or degrade organic materials which may be present in wastewater (BURROWS 1965). This sterilizing action results in delayed breakdown or complete inhibition of organic degradation. Nonetheless, there are certain microscopic plants and animals which are able to survive in environments containing relatively high concentrations of phenolics.

Effective treatment of industrial and municipal wastes containing phenols has been a very serious problem confronting industry and governmental agencies the world over. For more than half a century, workers have been engaged in serious attempts to find techniques for the treatment of phenols which would be truly effective and economical (ALBERT and FRAZIER 1967;LEWIS 1968).

IRRADIATION PROCESS

Destructive oxidation of organics with the aid of radiation may take place by direct energy absorption which ruptures the bonds in the organic molecules followed by oxygen combining with the free groups. Most of the oxidation is generally considered to occur because of an indirect attack by the hydroxyl radical resulting from radiolysis of water. The oxidation process in some instances may involve chain reactions and, in principle, can go to completion with the formation of CO_2 and water.

Simplification of this process is as follows:

$$\mathrm{HOH} \rightarrow \mathrm{H.} + \mathrm{.OH}$$

Production of Initiators

$$\mathrm{RH} + \mathrm{.OH} \rightarrow \mathrm{R.} + \mathrm{H_2O}$$

Chain Initiation

$$\mathrm{R.} + \mathrm{O_2} \rightarrow \mathrm{RO_2.}$$

$$\mathrm{RO_2.} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R.}$$

Chain Propagation

and in the presence of proper ionic species:

$$\mathrm{ROOH} + \mathrm{M^{+2}} \rightarrow \mathrm{RO.} + \mathrm{OH^-} + \mathrm{M^{+3}}$$

$$\mathrm{ROOH} + \mathrm{M^{+3}} \rightarrow \mathrm{ROO.} + \mathrm{H^+} + \mathrm{M^{+2}}$$

Chain Acceleration

There are many empiric values which can be used to assess the efficiency of a radiation initiated reaction. One of these is called the G value and another is the absorbed radiation dose which is usually expressed in rads or megarads required to achieve the destruction of a specific compound or combination of organic chemicals.

The G value can be defined as the number of molecules of chemical compounds which are formed, changed, or disappear; or the number of oxidation reactions which occur as a result of the absorption of 100 electron volts of energy. For most reactions, a number of different values for G can be measured. Therefore, an understanding of the specific G values being considered is necessary. For example, if methanol is irradiated, formaldehyde, hydrogen, methane, ethylene, glycol, ethane, and other products appear in the reaction by-products. Thus, a G value for the destruction of methanol requires that a series of G values for each of the above products must be determined. The G values, which are useful in evaluating efficiency, can be from one to twenty for nonchain reactions and may go as high as 10^6 for the more efficient chain reactions.

One of the very important discoveries relative to irradiation chemistry has been the establishment of the hydrated electron (KEENE,1960;MATHESON,1962;HART,1962). The hydrated electron is a highly reactive negative ion that appears to be a more powerful reducing agent than the hydrogen atom. This particle has been considered to be the dominant species in irradiated water and can be utilized to explain many of the radiolytic processes (HART,1967). Many of the detailed natures of the hydrated electron are still unsettled, but a great deal is known about the chemical reaction of e^-_{aq} towards a wide range of substances (STEIN,1952). Reducing effects of the hydrated electron on ions and molecules, organic and inorganic, have been widely studied (STEIN,1952). The hydrated electron can be created from various hydrated substances in aqueous solutions. Examples of these can be :

$$I^-_{aq} + h\nu \rightarrow I_{aq} + e^-_{aq}$$

$$Fe^{2+}{}_{aq} + h\nu \rightarrow Fe^{3+}{}_{aq} + e^-_{aq}$$

$$C_6H_5NH_2 + h\nu \rightarrow C_6H_5NH_2^+ + e^-_{aq}$$

The nature of the reaction of the hydrated electron is given by:

$$e^-_{aq} + X \rightarrow Y^-$$

However, it is still generally concluded that our knowledge of the reaction of e^-_{aq} is far from complete even though it is well known that these reactions do occur. Thus, results of irradiation of aqueous solutions that are not completely theoretically explainable must be considered in terms of this reactive particle.

EXPERIMENTAL PROCEDURES

Various synthetic concentrations of phenols were made from Phenol with a boiling point of 185 C. These samples were irradiated in the Cobalt-60 irradiation facility of the University Center for Pollution Research of Florida Institute of Technology. The gamma-ray sources are located in a 4½ foot diameter, 3/16 inch thick, stainless-steel water tank located in a concrete-enclosed hole 24 feet deep. Irradiation sources in the pool are normally stored at a depth of 22 feet from the surface of the water which provides more than the necessary amount of shielding.

Calibration of the radiation sources is performed on a monthly basis by a standardized solar cell. During the period of time for which the experimental tests were performed, the dose rate at the center of the ring of eight B.N.L. strips of Cobalt-60, (strips designed by Brookhaven National Laboratory) was approximately 1.00 megarads per hour.

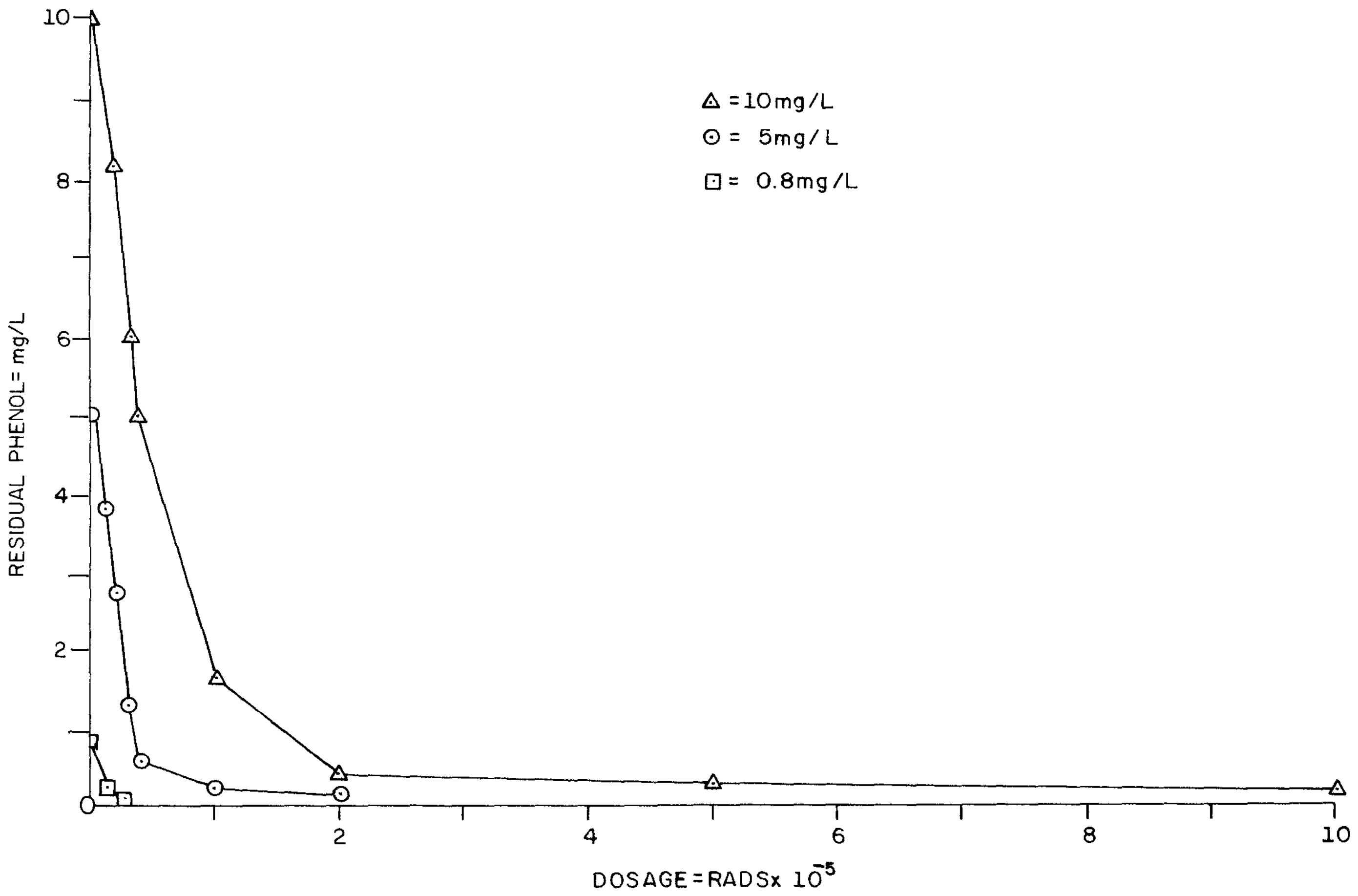
Aqueous solutions containing concentrations of phenol ranging from 0.1 mg/l to 10.0 mg/l were irradiated. Solutions were placed in 125 ml bottles and tightly capped. They were then lowered into the center of the ring of Cobalt-60 at the bottom of the University Center for Pollution Research's irradiation facility. Each concentration was irradiated for a sufficient length of time so that it absorbed various energy doses ranging from ten thousand rads to one million rads. For each concentration and each radiation dose, three independent samples were irradiated. A total of 665 independently irradiated samples were tested to determine the effects of the gamma irradiation on the aqueous solutions of the phenols.

All methods of analysis were performed according to the 13th edition of Standard Methods for the Examination of Water and Wastewater. A Bausch and Lomb Spectronic-20 was used for all of the analyses.

RESULTS

Irradiation of the aqueous solutions of phenols showed that the phenol structure could be destroyed by gamma radiation. At phenol concentrations of 10 mg/l, almost complete destruction occurred at a dose rate of one million rads. Figure 1 shows the effect of the gamma radiation for concentrations of 0.8 mg/l, 5.0 mg/l, and 10.0 mg/l.

The shape of the concentration curve as a function of the radiation dosage is of particular interest. For concentrations of less than 5.0 mg/l a dose of 10,000 rads reduces the phenol concentration to less than 0.6 mg/l which is an 88 per cent reduction.



PHENOL REDUCTION BY IRRADIATION

FIG. 1

Results of this work indicate that the destruction of phenols by gamma radiation from Cobalt-60 is feasible. Combining other effects of gamma radiation on wastewater (WOODBRIDGE, D. ,et al. 1972c) with the reduction inphenols makes this process of treating wastewater worthy of serious consideration for industrial application.

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