

RADIATION OXIDATION OF PHENOL IN THE PRESENCE OF PETROCHEMICAL WASTEWATER COMPONENTS

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Radiolytical decomposition of phenol was investigated at ^{60}Co gamma irradiation ($1\text{--}2\text{ Gy} \cdot \text{s}^{-1}$, $\leq 10\text{ kGy}$) of pre- and continuously aerated aqueous solutions at concentrations of phenol $1\text{--}100\text{ mg} \cdot \text{dm}^{-3}$ and in the presence of sodium hydroxide, sulphuric acid, sodium and ferrous sulphate, formaldehyde, 2-propanol, *n*-hexane, xylene, benzene, and commercial gasoline. From the decomposition rate at doses $50\text{--}400\text{ Gy}$, a phenomenological model of linear relation between the dose acquired for 37% decomposition (D_{37}), initial concentration ($\text{g} \cdot \text{m}^{-3}$) of phenol (p_0) and of an admixture (s_0) was confirmed in the form $D_{37} = 52f_{\text{tr}}(p_0 + f_{\text{eq}}s_0)$, where f 's are constants which can be attributed to the relative transformation resistance of phenol towards the OH radicals in given matrix (f_{tr} for pure water $f_{\text{tr}} = 1$) and relative acceptor capacity of competing substrate (f_{eq}). In real wastewaters, the efficient decrease of phenols content may be substantially lower than that in model solutions, obviously due to radiation oxidation of aromates, as proved by irradiation of aqueous solutions of benzene. Technical and economical feasibility of the process is discussed.

Since in 1969 TOUHILL, et al., had proposed waste water irradiation facility for destruction of noxious chemicals (cyanides, phenols, and petroleum-related wastes),¹ gamma- and electron irradiation was considered as a potential wide-spectral degradation technique in various steps of flow-sheets of chemical and biological treatment of aqueous effluents. Reviews of the processes can be found e.g. in WASHINO,² PETRYAEV et al.³ and SWINWOOD et al.⁴

According to BRUSENTSEVA et al.^{5,6} the irradiation decomposition of phenol in air saturated aqueous solutions proceeds with a radiation chemical yield up to $G(-\text{PhOH}) \cong 250 \pm 60$ molecules/100 eV in more concentrated solutions ($10^{-2}\text{ mol} \cdot \text{dm}^{-3}$) and results mainly in formation of much less toxic hydroquinone, and also pyrocatechol and resorcinol. In 1975–1985, numerous investigations in Russia, USA, Japan, Slovakia and Austria were performed to establish the feasibility of the process for large-scale applications.^{6–17} In spite of the problems of irradiation costs in case of industrial gamma sources vs. the environmental profit,¹² many

solution components strongly influence the yield of radiation oxidation: inorganic compounds terminate the radical oxidation chain⁸ and real waste behavior gave much lower yields than those reported for ideal conditions of pure water solutions, even in the presence of peroxide as oxidizing agent.^{9,10} Doses up to 1 MGy are necessary for efficient precipitation removal of phenols in presence of formaldehyde addition (1 : 1), with other impurities of industrial wastewaters.^{14,15}

The aim of present work was to obtain a phenomenological model of radiation decomposition of phenol in the presence of typical macroimpurities of raw and treated petrochemical wastewaters. The composition of solutions and radiation doses applied to get experimental substantiation of a model issued both from the facts, that the economical feasibility of the radiation treatment comes into consideration at the doses below 1 kGy,¹⁸ and at higher concentrations and doses the exhaustion of oxygen from pre-aerated samples takes place.

Experimental

Solutions: Phenol solutions were prepared by dissolving 1.00 g phenol (DAB-6) in 1 dm³ of freshly reboiled (30 min) distilled water. Water used for solution preparation was saturated after cooling by air scrubbed with basic and acidic 6% solutions of permanganate. All other solutions were prepared immediately before experiments to avoid spontaneous oxidation of phenol: in more diluted solutions (1–10 ppm) phenol in absence of the stabilizers used in analytical chemistry is oxidized to a considerable extent even after several hours.¹³ The solutions above were stable at least for 24 hours, but their irradiation was performed not later than 12 hours after preparation. The solutions of other components were prepared in aerated water prepared by the same procedure.

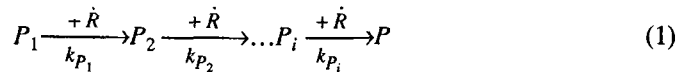
Analysis: Concentration of phenol in the samples was determined spectrophotometrically with 4-aminoantipyrin (AAP).¹⁹ Phenol was separated from 25 ml samples by distillation after addition of 25 ml of 8.5% phosphoric acid. After condensation of 20 ml of water, 5 ml of distilled water was added to the distillation residue and distillation was finished (40 min total time) to volume of 25 ml of distillate. To 5–20 ml of the distillate, 0.5 ml of ammonium buffer (12.5 g NH₄Cl in 100 ml conc. ammonium hydroxide), 0.5 ml of 2% AAP and 0.5 ml of 8% K₃Fe(CN)₆ were added and the volume was adjusted to 25 ml by distilled water. After 15 minutes, the absorbancy of the samples at 510 nm in 1 or 5 cm cuvette was measured by a spectrophotometer Specord UV-VIS (Zeiss, Germany). According to the calibration curve, the amount m (mg) of phenol in the sample was calculated from the absorbancy A_{510} measured in a cuvette of thickness d (cm) as $m = 170 A_{510} / vd$.

Irradiation: In batch mode preaerated solutions of the samples were irradiated by gamma doses 50, 100, 200 and 400 Gy in closed 25 ml analytical bottles in a γ -irradiation cell at dose rates of 1.1–2.1 Gy · s⁻¹ (W · kg⁻¹). In continuous aeration regime, about 1 dm³ of solution saturated by air at a rate of about 0.2 dm³ · min⁻¹ was irradiated in a bottle with a pneumatic sampling device.

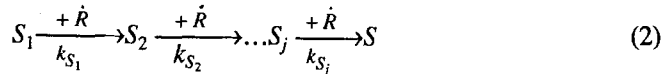
Mathematical modeling was performed on a PC by a scientific graph system SigmaPlot™, version 5.01 (Jandel Scientific).

Phenomenological model of radiation oxidation

Let us consider the radiation degradation of phenol or other principal solute (P_1) proceeds with radicals \dot{R} generated from water in a chain of i reactions yielded in a final, relatively “inert” at the given doses, product P (e.g., CO₂ or carboxylic acids):



Competing reaction with other components can be summarized through a chain of j reactions with a concrete or virtual admixture S_1 :



The rate of the principal reaction of P_1 decomposition is

$$-d[P_1] = k_{P_1}[P_1][\dot{R}] dt \quad (3)$$

In a steady state, the concentration of radicals $[\dot{R}]_{st}$ can be considered to be constant ($d[\dot{R}]/dt = 0$) and can be found from the algebraic equations^{20,21}

$$fdG_R\dot{D} - \sum_{i=1} k_{P_i}[P_i][\dot{R}] - \sum_{j=1} k_{S_j}[S_j][\dot{R}] = 0 \quad (4)$$

where G_R is radiation yield of radicals \dot{R} (molecules per 100 eV), \dot{D} is dose rate (Gy · s⁻¹ = W · kg⁻¹), d is density of solution (kg · dm⁻³) and f is the proportionality factor 1.04 · 10⁻⁷ mol · eV · J⁻¹. Product balances are

$$[P_1] + \sum_{i=2} [P_i] = [P_1]_0 \equiv p_0 \quad (5)$$

$$\sum_{j=1} [S_j] = [S_j]_0 \equiv s_0 \quad (6)$$

and because in steady state there is no delay between decomposition of substrate (P_1, S_1) and accumulation of products ($P_2 \dots P, S_2 \dots S$), the concentrations of the intermediates can be obtained from linear proportionality between the products (their mutual influence should be negligible) at any degree x ($0 \leq x \leq 1$) of P_1 decomposition,

$$[P_1] = (1-x)p_0 \quad (7)$$

$$k_{P_i}[P_i] = k_{P_1}xp_0 \quad (8)$$

$$k_{S_{i-1}}[A_{i-1}] = k_{S_1}[A_i] \quad (9)$$

Solution of Eq. (3) can be obtained upon replacement of $[\dot{R}]$ from the Eq. (4), integrated within intervals of doses 0 to D and decomposition 0 to x , in the form of a simple pseudo-monomolecular reaction:

$$[P_1] = p_0 \exp(-D/D_{37}) \quad (10)$$

where D is the radiation dose applied and D_{37} the dose necessary for 37% decomposition of substrate (phenol) P_1 , connected with radiation yield of decomposition, as follows from Eqs (3) and (4):

$$D_{37} = \frac{1}{fdG_R} [\langle k_P \rangle p_0 + \langle k_S \rangle s_0] \quad (11)$$

where the dimensionless $\langle k \rangle$'s are the effective, weighted rate constants for the radiolysis decomposition progressing within interval $x \in \langle 0, 0.37 \rangle$,

$$\langle k_P \rangle = 1 - x - \sum_{i=2} \frac{k_{P_i}}{k_{P_1}} \int_1^x p_i \, d \ln x \quad (12)$$

$$\langle k_S \rangle = - \sum_{j=1} \frac{k_{S_j}}{k_{S_1}} \int_1^x s_j \, d \ln x \quad (13)$$

and

$$p_i = [P_i]/p_0 \quad (14)$$

$$s_i = [S_i]/s_0 \quad (15)$$

are the concentrations normalized through the initial concentrations of phenol p_0 and other substrate s_0 respectively (integral from 0 to x was replaced by difference of integrals from 0 to 1, which equals p_0 , minus integral from 1 to x).

Obviously, the most attractive feature of this model is that D_{37} is connected with a pair of averaged kinetic parameters and concentrations of irradiated solution components and can be easily verified without a detailed knowledge of the reactivity of each particular species. Particularly, it would be convenient to characterize the radiolysis of phenol in the presence of a competing substrate by two parameters in the value D_{37} experimentally:

$$D_{37} = K f_{\text{tr}} (p_0 + f_{\text{eq}} s_0), \quad (16)$$

where f_{tr} is a dimensionless constant which can be attributed to relative resistance of phenol towards oxidative species in various matrices (e.g., aqueous solutions of various pH and salt concentrations), for pure water conventionally $f_{\text{tr}} = 1$, and $f_{\text{eq}} = \langle k_s \rangle / \langle k_p \rangle$ is relative acceptor reactivity of competing substrate and its radiolytical products. In case when the concentrations p_0 and s_0 are given in $\text{mol} \cdot \text{dm}^{-3}$ the coefficient K has dimension $\text{J} \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{kg}^{-1} (\text{Gy} \cdot \text{M}^{-1})$. For convenience of technical applications, the concentrations p_0 and s_0 can be given in $\text{mg} \cdot \text{dm}^{-3}$ (i.e., $\text{g} \cdot \text{m}^{-3}$ or ppm units alternatively) and then the value of a proportionality constant K is

$$K = \langle k_p \rangle / (10^3 f d G_R M) \cong 100 k_p / G_R \text{ J} \cdot \text{mg}^{-1}, \quad (17)$$

$M = 94.11 \text{ g} \cdot \text{mol}^{-1}$ being the mole weight of phenol, and $d \cong 1 \text{ kg} \cdot \text{dm}^{-3}$ for diluted aqueous solutions.

The D_{37} dose value can be easily transformed to the dose necessary for another yield of decomposition R (%) as

$$D_R = -2.3 \log (100 - R) D_{37}, \quad (18)$$

e.g. for $R = 99\%$, $D_{99} \cong 4.6 D_{37}$.

Results and discussion

Radiolysis of pre-aerated solutions of phenol at its concentrations $1.8\text{--}7.2 \text{ mg} \cdot \text{dm}^{-3}$ followed the model of consecutive scavenging of oxidizing radicals represented by Eqs (10) and (11), D_{37} value increasing with increasing initial concentration of phenol, p_0 (see Fig. 1).

As there was no statistically significant difference between the radiolysis of the solutions acidified by sulphuric acid ($4 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, pH 5.6–5.8) or doped with

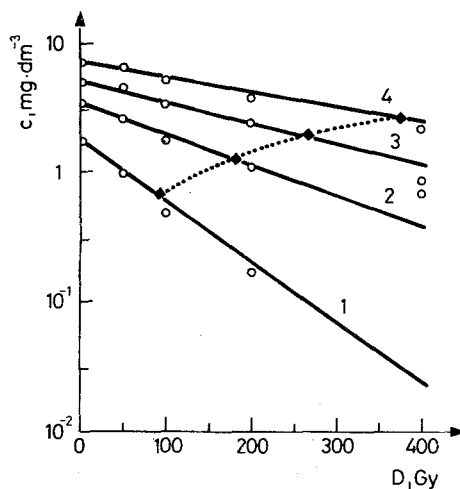


Fig. 1. Concentration of phenol c ($\text{mg} \cdot \text{dm}^{-3}$) in pre-aerated solutions as a function of radiation dose D (Gy) at various initial concentrations p_0 : $1.79 \text{ mg} \cdot \text{dm}^{-3}$ (curve 1), $3.49 \text{ mg} \cdot \text{dm}^{-3}$ (curve 2), $5.14 \text{ mg} \cdot \text{dm}^{-3}$ (curve 3) and $7.23 \text{ mg} \cdot \text{dm}^{-3}$ (curve 4). The dotted curve and full diamond symbols indicate D_{37} values

Table 1
Coefficients of D_{37} value [Eq. (11)]
 $p_0 = 1.8\text{--}7.2 \text{ mg} \cdot \text{dm}^{-3}$; $K = 52.2 \pm 1.1 \text{ J} \cdot \text{mg}^{-1}$

Competing solute or admixtures	s_0 , $\text{mg} \cdot \text{dm}^{-3}$	f_{tr}	f_{eq}
None	0	1	0
Isopropyl alcohol	2.55	1.00 ± 0.04	0
Formaldehyde	2.55	0.90 ± 0.11	0.73 ± 0.23
<i>n</i> -heptane	4.25	0.58 ± 0.09	0.55 ± 0.13
Gasoline	5.0	0.84 ± 0.17	0.53 ± 0.16
Benzene	4.65	1.26 ± 0.33	0.66 ± 0.23
Xylene	4.50	0.23 ± 0.25	4.4 ± 4.8
Mohr's salt,* $4.2 \cdot 10^{-5} \text{ M}$	0	0.42 ± 0.03	0

*Ferrous ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4$.

sodium sulphate of the same concentration, and the solutions alkalinized by sodium hydroxide ($4 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$), the set of 64 results of phenol decomposition by doses below 400 Gy was fitted simultaneously by generalized least-square method to obtain the parameters of Eqs (10) and (16) for $s_0 = 0$ and $f_{tr} \approx 1$. As a result, average absorbed radiation energy required for decomposition of 1 mg of phenol in the solutions was found to be $K = 52.2 \pm 1.1 \text{ J} \cdot \text{mg}^{-1}$, i.e., about 50 kJ per mole of phenol in its aqueous solution, with a very reasonable coefficient of variation less than 2%. The kinetic parameters from the results treated as above are summarized in Table 1.

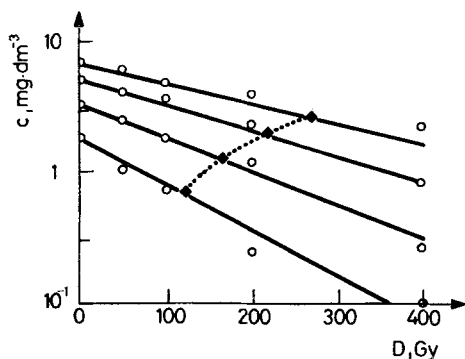


Fig. 2. Phenol decomposition in the presence of *n*-heptane ($s_0 = 4.25 \text{ mg} \cdot \text{dm}^{-3}$)

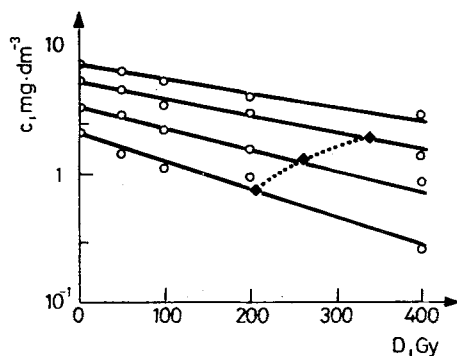


Fig. 3. Phenol decomposition in the presence of gasoline ($s_0 = 5.0 \text{ mg} \cdot \text{dm}^{-3}$)

The fitting of results of phenol decomposition in presence of isopropyl alcohol indicated a zero effect of presence of the latter on the f_{eq} value (0.00 ± 0.04) and for $f_{\text{eq}} \equiv 0$, f_{tr} was found identical with pure phenol solutions at uncertainty of 4%.

Formaldehyde, which can be added to promote the product precipitation,¹⁵ decreases both f_{tr} and f_{eq} values for only about 10–20%.

As expected, presence of alkanes (*n*-heptane, gasoline) and aromates (benzene, xylene) was clearly pronounced (Figs 2–5). A slow-down of the radiolysis is understandable especially in the case of aromates, because irradiation of aqueous solutions of benzene yields phenol as an intermediate of oxidation of the former (Fig. 6). However, the difference of f_{tr} from unity is difficult to explain, except the Mohr's salt solutions. The factors should be understand as an alternative for the better results fitting, and normally they will be hidden in value f_{tr} . In a mixture of n impurities of overall concentration s_0 and mole percentages w_n ($\sum w_n = 1$) of individual oxidizable

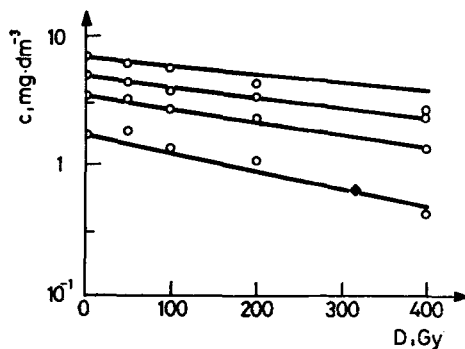


Fig. 4. Phenol decomposition in the presence of benzene ($s_0 = 4.65 \text{ mg} \cdot \text{dm}^{-3}$)

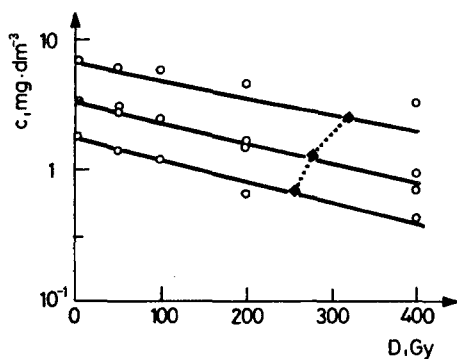


Fig. 5. Phenol decomposition in the presence of xylene ($s_0 = 4.50 \text{ mg} \cdot \text{dm}^{-3}$)

components, a formula using weighted parameters $(f_{tr})_n$ and $(f_{eq})_n$

$$D_{37} = K \sum_{n=1}^n (f_{tr})_n w_n \left(p_0 + s_0 \sum_{n=1}^n (f_{eq})_n w_n \right) \quad (19)$$

may serve as a reasonable approximation for D_{37} dose in more complex waste solutions.

Oxidation of phenol, studied in connection with oxidation of benzene^{22,23} proceeds due to reactions with molecular oxygen,



and



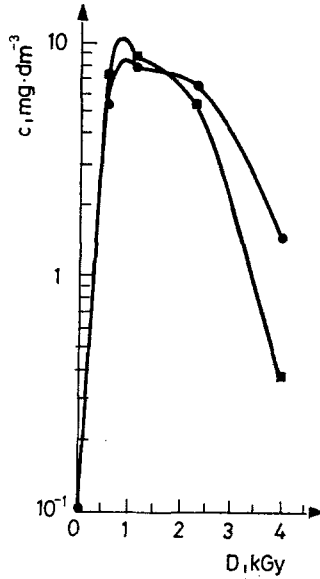
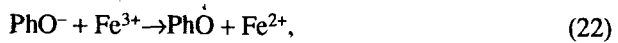
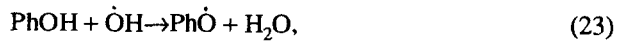


Fig. 6. Phenol production in aqueous benzene solutions ($200 \text{ mg} \cdot \text{dm}^{-3}$)

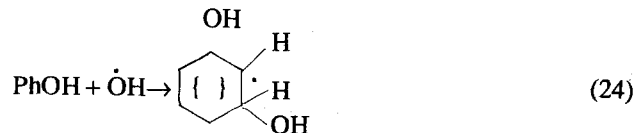
oxidation of phenol anion with Fe^{3+} ions



and oxidation with radicals $\dot{\text{O}}\text{H}$ or, at high pH, $\dot{\text{O}}^- (\equiv \dot{R})$, and in a much lower extent with HO_2 and $\text{H}_2\dot{\text{O}}_2$. The $\dot{\text{O}}\text{H}$ radicals are formed with radiation yield $G = 2.6$ molecules per 100 eV, i.e., at the dose rate used their production ($fdG_R\dot{D}$) was about $3\text{--}5 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$. Though the reaction with them could proceed according to the Gibbs energy criterion directly as



the results of pulse radiolysis^{8,24,25} indicate that phenol oxidation starts with the addition of OH radicals in *meta* position,



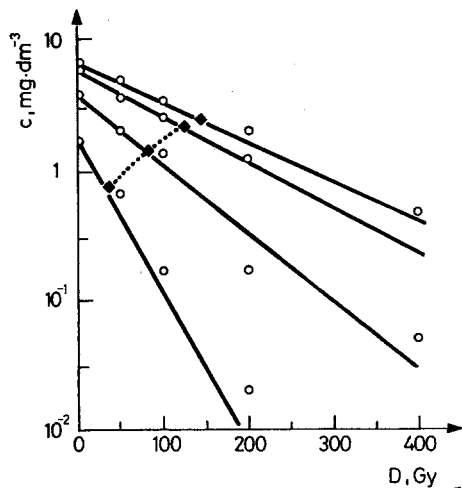


Fig. 7. Phenol decomposition in presence of Mohr's salt ($4.2 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$)

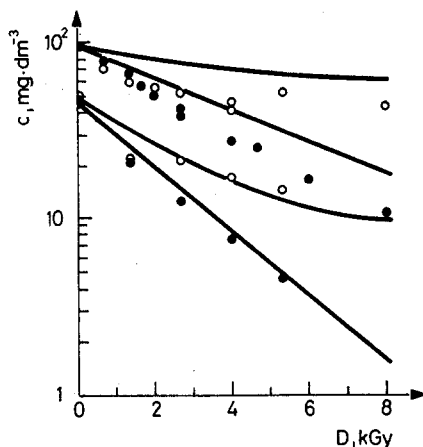
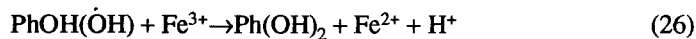


Fig. 8. Decomposition of phenol in aerated (full circles) and non-aerated (empty circles) solutions

($k_{p1} = 1.4 \cdot 10^{11} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$). Next the radicals adds oxygen ($k_{p2} = 1.5 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) and the adduct is decomposed



($k = 8 \cdot 10^3 \text{ s}^{-1}$). Fe^{3+} ions may take part in reactions with charge transfer



and also act as stabilizers of OH radicals (in form of ferril ion, $\text{Fe}\dot{\text{O}}^{2+}$) what can explain a considerable enhancement ($f_{\text{ir}} = 0.42 \pm 0.03$) of phenol oxidation in presence of Mohr's salt (Fig. 7).

At higher concentrations of phenol ($50\text{--}100 \text{ mg} \cdot \text{dm}^{-3}$, or $5 \cdot 10^{-4}\text{--}1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and doses above 2–3 kGy, a decrease of radiation oxidation occurs in non-aerated solutions (Fig. 8) what should be connected with exhaustion of the oxygen dissolved in water (about $1.3 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ at 25 °C). If K and f 's parameters were considered the same as in the experiments at low concentrations of phenol, the data were treated as there is only a certain maximal concentration of oxidizable phenol (p_{ox}), beside the non-oxidizable phenol (p_{nox}), which corresponds to the dissolved oxygen,

$$p_o = p_{\text{ox}} + p_{\text{nox}} \quad (27)$$

i.e., instead of Eq. (10) we have

$$[P_1] = p_o + p_{\text{ox}}[\exp(-D/D_{37}) - 1] \quad (28)$$

for the data given in Fig. 8 the oxidizable amount of phenol was found to be $p_{\text{ox}} = 40.5 \pm 2.3 \text{ mg} \cdot \text{dm}^{-3}$ (phenol concentration $4 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) what is in a good correspondence with the supposed oxygen content in preaerated solutions. Full curves were calculated using this value; it can be seen that the correspondence (overall variance coefficient 5.6%) is better for the solutions of lower concentrations of phenol. Higher rate of radiolysis at higher concentrations of phenol corresponds to the chain oxidation at these concentrations.^{5,6}

Feasibility of the radiation oxidation was considered for three types of irradiation reactors:¹⁸ (1) continuous stirred reactor, (2) continuous piston-flow reactor, and (3) batch reactor (Fig. 9).

Efficient dose rate for irradiation process, using radiation source with radiation power Z (W), irradiated volume V (m^3) and efficiency η (≤ 1) will be

$$\dot{D} = 10^3 \frac{Z\eta}{Vd} \quad (29)$$

At a flow rate v ($\text{m}^3 \cdot \text{s}^{-1}$) and input concentration of phenol p_0 and competing substrate s_0 , the dynamics of phenol concentration in the reactor, and also at its output (p), is given by a differential equation ($p \equiv [P_1]$):

$$\frac{dp}{dt} = -\frac{Z\eta}{Vd} \cdot \frac{p}{Kf_{\text{ir}}(p_0 + f_{\text{eq}}s_0)} + \frac{v}{V}(p_0 - p) \quad (30)$$

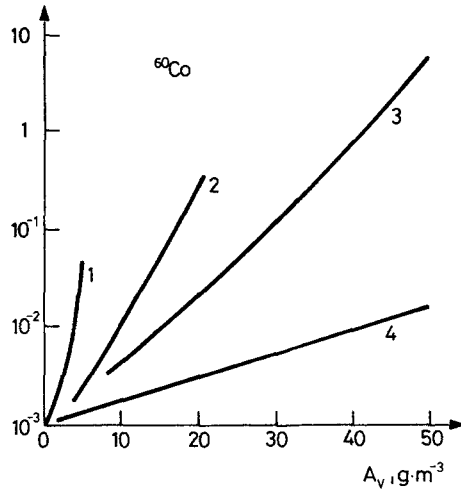


Fig. 9. Relative investment (curves 1–3) and operating (curve 4) costs for various types of irradiation facilities as a function of phenol concentration in waste: continuous stirred reactor (curve 1), piston-flow reactor (curve 2), batch reactor (curve 3)

At a steady state

$$p = \frac{p_0}{1 + \frac{Z\eta}{Vd} Kf_{tr}(p_0 + f_{eq}s_0)} \quad (31)$$

The stirred irradiation reactor can be controlled by a single parameter, the flow rate v and if the set point is a maximal concentration of phenol at output (p_{max}) the control equation becomes

$$v \leq \frac{Z\eta p_{max}}{Kf_{tr}(p_0 + f_{eq}s_0)(p_0 - p_{max})} \quad (32)$$

and can be constructed as a function of p_0 and p_{max} (e.g., for surface waters $p_{max} \equiv \equiv 0.2 \text{ mg} \cdot \text{dm}^{-3}$).

A piston-flow reactor can be constructed as a system of concentric tubes situated around a column (rod) radiation source. Then, average dose obtained in the reactor is

$$D = 10^3 \frac{Z\eta}{vd} \quad (33)$$

According to Eq. (10), control equation becomes

$$v \leq \frac{Z\eta}{Kf_{tr}(p_0 + f_{eq}s_0) \ln(p_0/p_{max})} \quad (34)$$

It can be shown that the piston-flow reactor is more effective at higher input concentrations of phenol, however, it may be more difficult to aerate the flow than in stirred reactor.

For a batch reactor of volume V the Eq. (32) is fully applicable when considering an efficient flow rate as

$$v = \frac{V}{t_0 + t_e} \quad (35)$$

where t_0 is necessary time for irradiation,

$$t_0 = \frac{VKf_{tr}(p_0 + f_{eq}s_0)}{Z\eta} \ln(p_0/p_{max}) \quad (36)$$

and t_e is time of emptying the reactor. For a centered point source the energetic efficiency of radiation with a linear coefficient of absorption $\gamma(m^{-1})$ and for matrix with linear coefficient of detenuation $\mu(m^{-1})$ can be calculated²⁵ as follows

$$\eta = 1 - [1 + (\mu - \gamma)r] \exp(-\mu r) \quad (37)$$

where r is efficient radius of irradiated volume. The time t_e can not be neglected because the batch reactors needs in efficient protecting from radiation source during the operation of emptying.

Operating costs (for pumping and monitoring) of the irradiations facility will be essentially small as compared with the investment costs at a large industrial radiation source.¹⁸ At the productivity of radiation facility $C(m^3 \cdot year^{-1})$ and dose necessary for purification D (Gy) the power of the source should be

$$Z = 3.16 \cdot 10^{-5} \frac{DC}{\eta} \quad (38)$$

and the efficiency η can include necessary periodic upgrading of the source, especially in case of ^{60}Co ($\eta = 91-76\%$, depending on the upgrading time-period 1-5 years, respectively).¹⁸ Contribution of investment expenditures to the unit price of sewage treatment ($\$/m^3$) by radiation dose D (Gy) can be well estimated as a fixed cost:

$$P_{inv} = 3.16 \cdot 10^{-5} \frac{R(1 + AT + U)}{\eta T} D \quad (39)$$

where R is unit price of radionuclide ($\$/W$), A is annuity at amortization time T (years) and U is ratio of building engineering to the radiation source price. In case of ^{60}Co , R

is of the order of $1\$/Ci = 68\$/W$, $A = 0.12-0.073$ at upgrading cycle 1–5 years,¹⁸ and $U \cong 2-6$ at pilot facilities.²⁷ Variable costs (pumping, supervision, monitoring) will be usually much lower than the fixed costs.

Technically, at the doses D under 5 kGy, a pilot plant with a source of about 13 PBq (0.35 MCi) can ensure the capacity about 100 m³ phenolic waste waters treatment per day ($3 \cdot 10^4$ m³/year). The economical feasibility, however, strongly depends on the permissible cost of final waste water treatment. Hence, the facilities larger for an order of magnitude, when the price of radiation source is a matter of more favorable contract, are more realistic to meet both ecological and economical demands.

References

1. CH. J. TOUHILL, E. C. MARTIN, M. P. FUJIHARA, D. E. OLLSEN, J. E. STEIN, G. MCDONELL, *J. Water Pollut. Contr. Fed.*, 41 (1969) R44.
2. M. WASHINO, *Radiat. Phys. Chem.*, 18 (1981) 383.
3. E. P. PETRYAEV, V. I. VLASOV, I. A. SAVUSHKIN, *Radiatsionnokhimicheskaya oshistka stochnykh vod i vybrosnykh gazov*, Izd. Universitetskore, Minsk, 1985.
4. J. F. SWINWOOD, T. D. WAITE, P. KRUGER, S. M. RAO, *JAEE Bulletin*, 36, (1994) No. 1, 11.
5. S. A. BRUSENTSEVA, P. I. DOLIN, V. N. SHUBIN, A. G. PRIBUSH, *Khim. Vys. Energ.*, 4 (1970) 88.
6. S. A. BRUSENTSEVA, A. G. PRIBUSH, V. N. SHUBIN, P. I. DOLIN, *Khim. Vys. Energ.*, 4 (1971) 83.
7. L. M. COFFMAN, D. D. WOODBRIDGE, *Bull. Environ. Contam. Toxicol.*, 11 (1974) 461.
8. O. I. MICIC, M. T. NENADOVIC, V. M. MARKOVIC, in: *Radiation for a Clean Environment*, Proc. Intern. Symp. 1975, IAEA Vienna, 1975, p. 233.
9. E. A. PODZOROVA, V. P. PLOTNIKOVA, N. V. BYCHKOV, A. I. KASPEROVICH, *Khim. Vys. Energ.*, 10 (1976) 423.
10. E. A. PODZOROVA, V. P. PLOTNIKOVA, N. V. BYCHKOV, A. I. KASPEROVICH, *Khim. Prom-st (Moscow)*, No. 1 (1979) 19.
11. K. TAKIMOTO, K. SATO, S. TSUDA, *Bunseki Kagaku*, 27 (1978) 514.
12. S. HASHIMOTO, T. MIYATA, M. WASHINO, W. KAWAKAMI, *Environ. Sci. Technol.*, 13 (1979) 71.
13. V. MIKULAJ, Z. KIRÁLYOVÁ, Ľ. MÁTEL, *Acta F.R.N. Univ. Comen. Form. Prot. Nat.*, No 5 (1979) 57.
14. L. V. NEMIROVSKAYA, N. A. VYSOTSKAYA, G. P. ALEEVA, L. G. SHEVCHUK, V. N. ALEKSANDROV, *Khim. Tekhnolog. (Kiev)*, No. 6 (1979) 50.
15. N. A. VYSOTSKAYA, L. G. SHEVCHUK, G. P. ALEEVA, *Khim. Tekhnol. (Kiev)*, No. 1 (1980) 53.
16. N. GETOFF, W. LUTZ, *Radiat. Phys. Chem.*, 25 (1985) 21.
17. N. GETOFF, *Appl. Radiation Isotopes*, 37 (1986) 1103.
18. F. MACÁŠEK, A. ŠVEC, *Acta F.R.N. Univ. Comen. Form. Prot. Nat.*, No. 5 (1979) 79.
19. L. A. KULSKII, I. T. GORONOVSKII, A. M. KOGANOVSKII, M. A. SHEVCHENKO, *Spravochnik po svoistvam, metodam analiza i oshistke vody*, Vol. 1, Naukova Dumka, Kiev, 1980, p. 464.
20. L. T. BUGAENKO, S. A. KABAKCHI, *Metod stacionarnykh kontsentratsii v radiatsionnoi khimii*, Moscow State University, Moscow, 1971.
21. O. NAVRÁTIL, J. HÁLA, R. KOPUNEC, F. MACÁŠEK, V. MIKULAJ, L. LEŠETICKÝ, *Nuclear Chemistry*, Ellis Horwood, Chichester, 1992, p. 154.
22. D. I. METELITSA, YE. T. DENISOV, *Neftekhimiya*, 7 (1967) 65.
23. D. I. METELITSA, YE. T. DENISOV, *Kinetika i Kataliz*, 9 (1968) 733.

24. E. J. LAND, M. EBERT, *Trans. Faraday Soc.*, 63 (1967) 1181.
25. E. J. FENDLER, J. H. FENDLER, *Prog. Phys. Org. Chem.*, 7 (1970) 229.
26. A. KH. BREGER, B. I. VAINSHTEIN, N. P. SYRKUS, V. A. GOLDIN, L. V. CHEPEL, *Osnovy radiatsionno-khimicheskogo apparato-stroeniya*, Atomizdat, Moscow, 1967.
27. J. LESSEL, H. MÁTSCH, E. HENNING, A. SUESS, A. ROSOPULO, G. SCHURMAN, in: *Radiation for a Clean Environment*, Proc. Int. Symp., STI/PUB/402, IAEA, Vienna, 1975, p. 447.