

New radiation-chemical method for the removal of petroleum products from water

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The possibility of water purification with the removal of petroleum products present in the dissolved state, as an oil-in-water emulsion and as a film at the water surface by radiation-chemical treatment has been shown.

The radiation-chemical methods of water and wastewater treatment for removing various pollutants were described.¹⁻⁴ Taking into account that water pollution by petroleum products is a high environmental hazard, and these products are difficult to remove by ordinary methods, we have examined the application of radiation treatment to solve the problem.

A cobalt-60 γ -ray facility was used as a source of ionising radiation. Dosimetry was conducted by the ferrosulfate method.⁵ The dose rates were 0.1–2 Gy s⁻¹.

A mixture of three kinds of petroleum products (diesel fuel, motor oil and residual fuel oil) was investigated. Two systems (aqueous solutions of the petroleum products in equal amounts and heterogeneous water-petroleum product systems in which the products were present in the dissolved state, as oil-in-water emulsions and as films at the water surface) were studied. Because petroleum products are poorly soluble in water, and they form films at the water surface and on the walls of vessels, in the majority of experiments, the products were initially dissolved in CCl₄ and a portion of the prepared solution was inserted into water. This procedure was performed to simplify the experiments and to exclude large errors in quantitative analysis. Therefore, these aqueous solutions were saturated with CCl₄ (the concentration is 5×10^{-3} mol dm⁻³ at room temperature⁶). The total amounts of petroleum products in aqueous solutions and heterogeneous systems were 10 and 150 mg dm⁻³, respectively, and the amounts of the individual products in both systems were equal to each other.

The systems saturated with air were subjected to radiation treatment. The irradiation was conducted in ampoules with ground-glass stoppers. Gravimetric⁷ and spectrophotometric analysis was used for the determination of petroleum products in the initial and irradiated systems. In the case of aqueous solutions, petroleum products were also determined from the absorbance in the UV and IR regions using 'Specord M-40' and 'Perkin-Elmer 1720' spectrophotometers, respectively. For the analysis of the products in the heterogeneous system, IR absorbance was utilised in addition to gravimetry. For the IR-spectrometric determination, petroleum products contained in both of the systems were extracted by CCl₄, the extracts

were evaporated on a KRS-5 window of the spectrophotometer or placed in cells, and then spectra were recorded.

The values of chemical oxygen demand (COD) were also measured according to a published procedure.⁸

We found that irradiation of both of the systems leads to a decrease in the concentrations of petroleum products. In the case of aqueous solutions, this is evident from Figure 1 which shows the dose dependence of the UV absorbance for solutions containing CCl₄ and from Table 1 which summarises concentrations of the products as a function of absorbed dose. The addition of hydrogen peroxide to solutions in the absence or the presence of CCl₄ gives rise to an increase in the efficiency of the removal of petroleum products (Table 1). The COD values determined at different doses for solutions containing CCl₄ in the absence and the presence of H₂O₂ are plotted in Figure 2. It is seen that the values initially increase with increasing dose, reaching maxima at 32 and 25 kGy in the absence and the presence of H₂O₂, respectively, and then decrease. In solutions containing no CCl₄, the maxima are shifted to higher doses in both the absence and the presence of H₂O₂.

A precipitate was formed upon irradiation of the heterogeneous system. The precipitate is easy to filter off and insoluble in CCl₄. This fact allowed us to extract petroleum products from the systems by CCl₄ (after separation of the precipitate from the irradiated heterogeneous system by centrifugation). The weight of the precipitate increased with increasing absorbed dose, and gravimetric analysis demonstrated that 96% of petroleum products were precipitated at a dose of 25 kGy. Similar results were obtained by IR spectrophotometry. The COD values for the initial and irradiated heterogeneous systems are shown in Figure 2. The COD values (unlike aqueous solutions) decrease with increasing dose. As it follows from Figure 2, the addition of a flocculant (aqueous 25 mg dm⁻³ polyacrylamide solution) leads to somewhat lower COD values (at the same doses) in comparison with the systems containing no flocculant.

The composition of the petroleum products is complicated.⁹ Therefore, it is very difficult to present the detailed mechanism of radiolytic conversions in the studied systems. Thus, we can

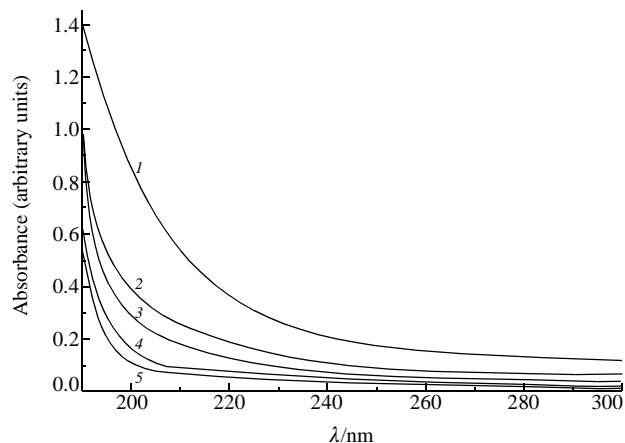


Figure 1 Optical absorption spectra of aqueous solutions of petroleum products (10 mg dm⁻³), containing 5×10^{-3} mol dm⁻³ CCl₄ (1) before irradiation and after irradiation to doses (kGy): (2) 5, (3) 15, (4) 25 and (5) 40.

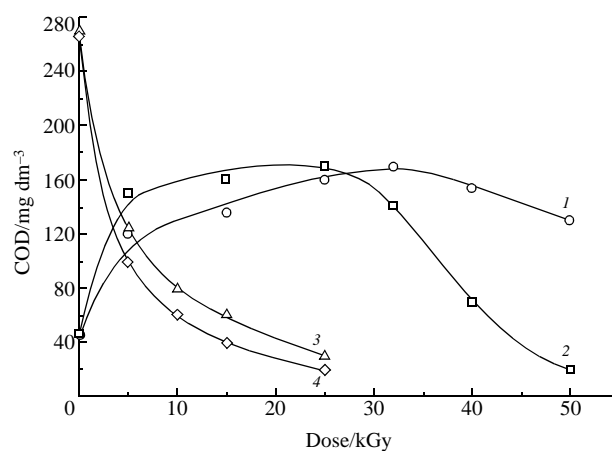


Figure 2 Dose dependences of the COD values for (1) an aqueous solution of petroleum products (10 mg dm⁻³) containing 5×10^{-3} mol dm⁻³ CCl₄, (2) for the same solution additionally containing 5×10^{-3} mol dm⁻³ H₂O₂, (3) for a heterogeneous system and (4) for the same system containing 25 mg dm⁻³ polyacrylamide.

Table 1 Dose dependence of the concentration of petroleum products in aqueous solution.^{a,b}

Dose/kGy	Concentration/mg dm ⁻³				
	No additives (gravimetry)	In the presence of CCl ₄		In the presence of H ₂ O ₂ (gravimetry)	In the presence of CCl ₄ and H ₂ O ₂ (gravimetry)
		UV spectrophotometry	gravimetry		
0	10.0	10.0	10.0	10.0	10.0
5	8.0	4.5	4.2	5.0	3.0
15	4.5	2.0	1.5	3.0	1.1
25	2.8	1.5	0.8	1.5	0.4
32	1.5	—	0.4	0.8	0.2
40	—	0.8	0.2	—	—

^aConcentrations of CCl₄ or H₂O₂ were 5×10⁻³ mol dm⁻³. ^bThe UV-spectrophotometric data at high doses are somewhat overestimated because of significant absorbance of the products of fragmentation.

give only the main features of these conversions in aqueous solutions.

Hydrocarbons, which are the main components of petroleum products, have various reactivities towards the products of water radiolysis. Hydrocarbons exhibit a low reactivity towards hydrated electron (e_{aq}⁻) and a high reactivity towards ·OH radicals.¹⁰ Hence, the removal of dissolved petroleum products from water is initiated by the reactions with ·OH radicals. This is confirmed, in particular, by an increase in purification efficiency in the presence of hydrogen peroxide and CCl₄. These compounds, reacting with e_{aq}⁻, convert this species into ·OH and ·CCl₃ radicals, respectively:



The ·CCl₃ formed is also an oxidising agent, and it can react with hydrocarbons. Since the addition of H₂O₂ to a solution containing CCl₄ leads to an increase in the purification efficiency, we can conclude that the reactivity of the ·CCl₃ radical is lower than that of the ·OH radical. Apparently, the increase in the COD values at the initial stage of irradiation is caused by the radiation-induced fragmentation of hydrocarbon molecules.

In the heterogeneous system at high doses used in this study, oxygen of the dissolved air is consumed, and dimerization and polymerization are the most important radiolytic processes under these conditions (see, e.g., refs. 11 and 12). These processes lead to the appearance of insoluble high-molecular-weight compounds which form a precipitate. Upon the formation and separation of the precipitate, it can capture considerable amounts of pollutants resulting in additional purification of the system. The purifying effect of the precipitate formation can be enhanced by a radiation-induced change in the state of the double electric layer at the surface of disperse particles formed. The influence of a flocculant can be explained by the appearance of coarser and, as a consequence, easier-to-filter-off particles.

The difference between the dose dependences of the COD values for solutions of petroleum products and the heterogeneous system can be caused by the fragmentation of hydrocarbon molecules in the solutions (unlike the heterogeneous system). This can be due to much lower pollutant concentrations in the solutions in comparison with the heterogeneous system. This circumstance can lead to a longer life-time of colloid particles formed in the solution upon irradiation (higher stability of colloid solutions at low concentrations was observed,

for example, by Schiller and Ebert¹³ in a study on the radiation-induced precipitation of AgCl from Ag⁺ solutions) and, as a result, to the subsequent reactions with products of water radiolysis, which can lead to fragmentation. These reactions do not occur in the heterogeneous system owing to much lower stability of the colloid solution formed (because of a considerably higher concentration).

Thus, radiation treatment can be applied to remove petroleum products from water.

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