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# RADIATION CROSS-LINKING OF MOLECULES OF ORGANIC IMPURITIES OF RESERVOIRS ON THE SURFACE OF SMALL-CAT WOODEN CHIPS, THE PREVENTION OF EVAPORATION OF THE SPILLED OIL

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***Abstract:*** At irradiation of the contaminated water reservoir with observed relatively high values of the weight of removed petroleum products, which indicates the presence of chemical sorption in addition to the physical adsorption on the surface of wood chips. This important effect will be take into account at radiation purification of water contaminated with various organic compounds, crude oil and phenol. Addition of small amount of water solution of the salts of potassium, sodium oxides or quaternary ammonium organic alkali associated with the acid group of silicic acid for a short period of time practically completely (96-100%) coagulates the organic colloidal system, spilled petroleum products and modifies the components of the oil product, reducing their fluidity and evaporation. The spilled oil products localized in the form of huge viscous, amorphous bunches and frozen spots laying the surface of the land plot with relatively small dimensions and settle on the bottom of the reservoirs.

***Key words:*** impurities, irradiation of wooden chips, evaporation, spilled oils, coagulation

There are numerous oil production facilities, oil refineries, huge oil reservoirs and vessels for storing oil products with unique medical properties on the territory of Azerbaijan. These territories characterized by high seismic activity. It is possible the spillage of oil, pollution of huge areas of the earth, water reservoirs and atmospheric air at the natural disasters cases.

Initiation of the process of decomposition of organic contaminants occurs in the entire volume of contaminated water because of the high penetrating possibility property of the ionizing rays of $^{60}Co$.

The processes of spilled petroleum products "modification" by exposure of small quantities of chemical reagents - bulk powders of metal oxides, activated carbon, aqueous solutions of alkalis studied in order to reduce of their fluidity and evaporation.

High fluidity and the ability to evaporate (high saturated vapor pressure) of petroleum products contribute to the spread of spilled oil products to huge areas, pollution of nearby water reservoirs and the surrounding air basin [1, 2].

## Methodical part

Decomposition of organic contaminants can also take place in the mass of cut wooden chips added to contaminated water. Hence, the process of radiation treatment of water contaminated with organic contaminants or petroleum products will be more efficient. In order to do more understandable represent main directions of the process, it is necessary to compare the rates of elementary reactions from the scheme for the radiation conversion of organic contaminants in oxygen-containing waters, given in Table 1 [3-8]. The value of the absorbed dose rate of ionizing radiation in the case of our installation with a $^{60}Co$ isotope is 0.33Gy/s or $2.06 \cdot 10^{15}$ eV/g·s.

Determination of components in solutions and the fractional composition of petroleum products carried out by physicochemical methods (liquid chromatography LC-10AVP, gas chromatography GC-2100, mass-spectroscopy GCMS-QP 2010). Analysis provided also by traditional methods of analytical chemistry such as qualitative reactions analysis of components of inorganic compounds, vacuum pumping, measurement of saturated vapor pressure of liquids with oil and mercury manometers, viscosity measurement, centrifugation, separation of fractions by distillation at fixed temperatures.

## The discussion of the results

Taking into account concentrations of organic pollutants (10-1000 μg/kg) of wastewater of the country's manufacturing plants the conversion rate of these pollutants according to reaction (1) is $3\cdot(10^{-13}-10^{-15})$ M/s. For comparison the rate of reaction (3) is equal to $5\cdot(10^{-6}-10^{-7})$ M/s. The ratio of the rates of each elementary reaction to the rate of reaction 3 ($W_n/W_3$) are estimated taking into account the rate constants, the values of the primary concentrations of the initial and intermediate products. Reactions (1) and (2) are reaction initiation reactions, reactions (4), (5), (8), (9), (11), (12), (17), (22), (23), (24), (28), (29), (33), (34) are the chain termination reactions.

As can be seen from Table 1, the elementary reactions (7), (8), (9), (11), (17), (20, 21, 22, 23, 24) are reactions, which is necessary for the formation of new products of the process. The ratio of the rates of these elementary reactions to the rate of elementary reaction (3) for irradiation of contaminated with organic compounds water shows that the rates of reactions (11) and (24) forming new organic compounds have comparable values and these values far exceed the rates of other product-forming reaction. Consequently, the main channels for the radiation conversion of organic compounds in water are the formation of hydroxyl-substituted derivatives, organic peroxides and the products of their mutual recombination, mainly connected by an oxygen bridge.

As can be seen from Table 1, the macromolecules of the organic matrix of the wood chips are actively involved in the reaction process by means of the reactions (10), (11) and (14). They are characterized by high velocities ($W_{10}$ / $W_3$ = 100, $W_{11}$ / $W_3$ = $10^{-4}$-$10^{-5}$ and $W_{14}$ / $W_3$ = $10^{-5}$-$10^{-6}$) and ultimately hydroxyl-substituted and peroxide radicals of organic compounds (petroleum products) are joined in the presence of wood chips not only to other hydroxyl-substituted radicals but also to macro radicals of the organic matrix of wood chips.

This fact confirmed by higher values of the weight of organic compounds (petroleum products) detected on the surface of wood chips when they removed from irradiated water. These values at an absorbed dose of 10kGy are 1.5-2.2 times higher than the weight of organic compounds (petroleum products) adsorbed on the surface of wood chips in non-irradiated water, held under identical conditions.

When the airflow injected into the experimental tank containing 10 $m^3$ of contaminated water, wooden chips, with a total weight of 10 kg, float around the entire volume of the reservoir, which favors the adsorption of oil products from their entire volume of water.

Relatively high values of the weight of removed petroleum products during irradiation of the reservoir indicate in addition to the chemical adsorption on the surface of wood chips in addition to the physical adsorption. This important effect will be take into account in radiation purification of water contaminated with various organic compounds, crude oil and phenol.

A sample of crude oil and samples of oil products, accumulated at the treatment plants, the remains of production processes for processing and transporting crude oil used as a model system. The heavier the oil, the higher its viscosity and more heavy hydrocarbon fractions it contains. Nitrogen-containing gases increase the viscosity of oil. Fluidity is inversely proportional to the dynamic viscosity. The viscosity of a liquid and oil is their most important physical characteristic, since it directly affects their fluidity [1, 2]. The dynamic viscosity of water at 20 ° C is 1 m Pa· s, for the oil under study at standard conditions (20°C and 1 atm.) is 20 m Pa· s. The dynamic viscosity of the "liquid glass" increases from 1000 Pa· s to 100,000 Pa· s at decrease the water content in the silicate solution from 58% to 52% at 20°C [9-12].

**Table 1.**

*Comparison of the rates of elementary reactions for radiolysis of contaminated with organic substances, oil products (RH, ROH) oxygen-containing waters, in the volume of which was added the mass of cut wood chips.*

| n | Reactions | $W_n/W_3$ |
|---|---|---|
| (1)<br>(2) | $RH \rightsquigarrow H^{\cdot} + R^{\cdot}$ ($ROH \rightsquigarrow H^{\cdot} + RO^{\cdot}$)<br>$H_2O \rightsquigarrow H$, $^{\cdot}OH$, $e^-_{aq}$, $H^+_{aq}$, $H^-_{aq}$ | $10^{-8}$<br>0,03-0,3 |
| (3) | $H^{\cdot} + RH \leftrightarrow R^{\cdot} + H_2$ | 1 |
| (4) | $H^{\cdot} + R^{\cdot} \rightarrow RH$ | $10^{-5}$- $10^{-6}$ |
| (5) | $H^{\cdot} + H^{\cdot} \rightarrow H_2$ | 1 - 10 |
| (6) | $H^{\cdot} + H_2O \rightarrow {}^{\cdot}OH + H_2$ | 2 - 20 |
| (7) | $R^{\cdot} + RH \rightarrow$ products | $10^{-8}$- $10^{-11}$ |
| (8) | $R^{\cdot} + H^{\cdot}$ RH $\rightarrow$ products | $10^{-18}$-$10^{-20}$ |
| (9) | $R^{\cdot} + R^{\cdot} \rightarrow$ products | $10^{-14}$-$10^{-17}$ |
| (10) | ${}^{\cdot}OH + RH \rightarrow R^{\cdot} + H_2O$ | 100 |
| (11) | ${}^{\cdot}OH+R^{\cdot}$ **(*RH*)**$\rightarrow$HORH (*R*$^{\cdot}$**)** | $10^{-4}$-$10^{-5}$ |
| (12) | $H^{\cdot} + OH^{\cdot} \rightarrow H_2O$ | 10 - 100 |
| (13) | $H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$ | $10^5$- $10^8$ |
| (14) | $RH + HO_2^{\cdot} \rightarrow R^{\cdot} + H_2O_2$ | $10^{-5}$- $10^{-6}$ |
| (15) | $2HO_2^{\cdot} \rightarrow 2{}^{\cdot}OH+O_2$ ($H_2O_2 + O_2$) | $10^{-3}$- $10^{-4}$ |
| (16) | $H_2O_2 \rightsquigarrow 2{}^{\cdot}OH$ | $10^{-9}$- $10^{-10}$ |
| (17) | $R^{\cdot} + HO_2^{\cdot} \rightarrow HOOR$ ($O_2 + RH$) | $10^{-7}$ |
| (18) | $H_2O_2+RH\rightarrow{}^{\cdot}OH+R^{\cdot}+H_2O$ | $10^{-8}$ |
| (19) | $RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}$ | $10^{-13}$- $10^{-15}$ |
| (20)<br>(21)<br>(22)<br>(23)<br>(24) | $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$<br>$RH + RO_2^{\cdot} \rightarrow R^{\cdot} + ROOH$<br>$R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR$<br>$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow$ products<br>$RO_2^{\cdot} + HO_2^{\cdot} \rightarrow ROOH + O_2$ | $10^4$- $10^6$<br>$10^{-7}$- $10^{-8}$<br>$10^{-8}$-$10^{-10}$<br>$10^{-9}$-$10^{-12}$<br>$10^{-4}$- $10^{-6}$ |
| (25) | $H_2O_2 + R^{\cdot} \rightarrow RH + HO_2^{\cdot}$ | $10^{-9}$- $10^{-10}$ |
| (26) | $H^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2$ ($2{}^{\cdot}OH$) | 1-10 |
| (27) | $H^{\cdot} + H_2O_2 \rightarrow {}^{\cdot}OH + H_2O$ | 0,1- 0,01 |
| (28) | ${}^{\cdot}OH + HO_2^{\cdot} \rightarrow H_2O + O_2$ | 1-10 |
| (29) | ${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ | 10-100 |
| (30) | ${}^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$ | 0,1-0,01 |
| (31) | $e^-_{aq} + RH \rightarrow$ products | $10^{-1}$- $10^2$ |
| (32) | $e^-_{aq} + H_2O \rightarrow$ products | $10^1$- $10^2$ |
| (33) | $e^-_{aq} + H^+_{aq} \rightarrow H^{\cdot} + H_2O$ | $10^2$- $10^3$ |
| (34) | $OH^-_{aq} + H^+_{aq} \rightarrow H_2O$ | $10^2$- $10^3$ |
| (35) | $e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-_{aq}$ | $10^2$- $10^3$ |

| | | |
|---|---|---|
| (36) | $e^-_{aq} + {}^{\cdot}OH \rightarrow OH^-_{aq} + H_2O$ | $10^2$- $10^3$ |
| (37) | $e^-_{aq} + {}^{\cdot}H \rightarrow H_2 + OH^-_{aq}$ | $10^1$- $10^2$ |
| (38) | ${}^{\cdot}OH + OH^-_{aq} \rightarrow O^- + H_2O$ | $10^1$- $10^2$ |
| (39) | $O^- + RH \rightarrow R^{\cdot} + OH^-_{aq}$ | $10^{-2}$- 1 |
| (40) | $H^+_{aq} + RH \rightarrow$ products | $10^2$- $10^3$ |
| (41) | $OH^-_{aq} + RH \rightarrow$ products | 1- 100 |
| (42) | $H_2O^+ + H_2O \rightarrow H_3O^+ (H^+_{aq}) + {}^{\cdot}OH$ | 1-10 |
| $W_3 = 5 \cdot (10^{-6}$-$10^{-7})$M/s, $W_1 = 3 \cdot (10^{-13}$-$10^{-15})$ M/s [3-8] | | |

The most significant effects of viscosity increasing and fluidity decreasing observed (50-100 times) at using aqueous solutions of "liquid glass". The composition of the "liquid glass" includes oxides of potassium or sodium associated with the anions of silicic acid ($Na_2O(SiO_2)_n$, $K_2O(SiO_2)_n$) with impurities of aluminum's, iron's, calcium's and magnesium's oxides.

The results of the observed change in the physical properties of the spilled crude oil, depending on the amount of the 10% aqueous solution of "liquid glass", which is poured into the spreading stream of spilled oil given in Table 2.

**Table 2.**

*Change in the physical properties of spilled crude oil at watering with an aqueous solution of "liquid glass."*

| Physical properties of oil | Quantity of 10% aqueous solution of "liquid glass" (% of total weight of oil product) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 |
| The ratio of the viscosity of the spilled oil, after watering with a 10% solution of "liquid glass" to the viscosity of oil, not watered 10% solution ($\eta_{watered}/\eta_{original}$). | 1 | 38-42 | 64-66 | 82-84 | 98-102 | 118-120 |
| The ratio of the fluidity of the spilled oil, after watering with a 10% solution of "liquid glass" to the fluidity of oil, not watered 10% solution ($F_{watered} / F_{original}$) | 1 | 0,025 | 0,016 | 0,012 | 0,010 | 0,008 |
| Saturated vapor's pressure of spilled oil after watering with a 10% solution of "liquid glass", mm. Hg column | 500 | 330 | 200 | 100 | 40 | 18-20 |
| The amount of distilled (without water) to 200°C fraction of spilled oil after watering with a 10% solution of "liquid glass", % vol. | 29-31 | 16-18 | 10-12 | 8-10 | 5-6 | 4-5 |

Note: $\eta_{watered}/\eta_{original}$ ($F_{watered} / F_{original}$) - the ratio of oil's viscosity (fluidity) watered with the solution of "liquid glass" to the similar indicators for untreated crude oil.

Adding a small amount (1-5% of the weight of oil) 10% of the aqueous solution of potassium or sodium "liquid glass" coagulates for a short time (less than 10 seconds) almost completely (96-100%) the spilled oil and modifies it. This process accompanied by partial evaporation and oxidation of some components. There is a significant (more than 100 times) increase in viscosity and decrease in fluidity along with the process of modification of spilled oil.

The sample of spilled crude oil watered with an aqueous solution of "liquid glass" coagulates and is localized in the form of huge viscous, amorphous bunches and frozen spots covering the surface of a piece of land with relatively small dimensions, and settle in the reservoir to the bottom. The area covered with a sample of spilled oil (not watered with a solution of "liquid glass") is many times larger.

It is desirable to use helicopters, aircraft and cars that create large flows and jets of water or water solutions, as well as special cars that drive powerful steam-air streams from aqueous solutions in the arsenal of the fire service to increase the efficiency and stop the process of spreading huge amounts of spilled oil.

The developed method for reducing the spread of spilled oil products allows to reduce the contaminated soil area, reduce the intensive evaporation of light hydrocarbons (saturated vapor pressure), hence the degree of danger of fires and prevent the spread of oil throughout the reservoir.

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## SU HÖVZƏLƏRİNİ ÇİRKLƏNDİRƏN ÜZVİ MADDƏLƏRİN MOLEKULLARININ TAXTA YONQARLARIN SƏTHİNƏ RADİOLİTİK FİKSASİYASI, DAĞILMIŞ NEFTİN BUXARLANMASININ DAYANDIRILMASI

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***Xülasə:*** Neft məhsulları ilə çirklənmiş su hövzələrinin ionlaşdırıcı radiasiya ilə şüalandırılması zamanı sudakı taxta yonqarların səthinə hopmuş (yapışmış) neft qalıqlarının miqdarının artması, onların sətində fiziki sorbsiya ilə yanaşı kimyəvi sorbsiyanın da baş verdiyini göstərir. Bu mühüm effect müxtəlif üzvi birləşmələrlə, xam neft və fenolla çirklənmiş suların radiolitik təmizlənməsi proseslərində nəzərə alına bilər. Az miqdarlarda kalium duzlarının, natrium oksidinin, silikat turşusu qrupu ilə birləşmiş ammonyakın sulu məhlullarının dağılmış üzvi birləşmələrin, neft məhsullarının səthlərinə səpilməsi onları /üzvi kolloid sistemlər/ qısa müddətdə praktiki olaraq tam (96-100%) koaqulyasiya edir /amorflaşdırır/. Dağılmış neftin tərkibi dəyişir, onun axımlılığı və buxarlanması azalır, özlü və amorf kütlələr şəklində nisbətən kiçik ölçülü torpaq sahələri səthlərində lokallaşır, suya dağılmış neft məhsulları qatılaşmış dib çöküntülərinə çevrilir.

***Açar sözlər:*** çirkləndiricilər, ağac yonqarlarının şüalandırılması, buxarlanma, dağılmış neft, koaqulyasiya.

## РАДИАЦИОННОЕ СШИВАНИЕ МОЛЕКУЛ ОРГАНИЧЕСКИХ ПРИМЕСЕЙ В ВОДОЕМАХ НА ПОВЕРХНОСТЬ ДРЕВЕСНЫХ СТРУЖЕК, ПРЕДОТВРАЩЕНИЕ ИСПАРЕНИЯ ПРОЛИТОЙ НЕФТИ

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***Резюме:*** Наблюдаемые высокие значения массы нефтепродуктов прилипшие к поверхности добавленных в водоем деревянных стружек при облучении загрязненного нефтепродуктами водоема указывают на протекание помимо физической сорбции и химической сорбции на поверхности стружек. Этот важный эффект может быть учтен при радиационной очистке воды, загрязненной различными органическими соединениями, сырой нефтью и фенолом. Добавление небольшого количества водного раствора солей калия, оксидов натрия или органической щелочи четвертичного аммония, связанных с кислотной группой кремниевой кислоты в течение короткого периода времени, практически полностью (96-100%) коагулирует органическую коллоидную систему, пролитую нефть и модифицирует компоненты нефти, уменьшая ее текучесть и испарение. Пролитые нефтепродукты, локализуются как вязкие и аморфные сгустки, покрывают поверхность земельного участка с относительно небольшими размерами или оседают на дно водоемов.

***Ключевые слова:*** примеси, облучение древесной стружки, испарение, разлитые нефтепродукты, коагуляция.