

## Radiation-Assisted Waste Water Treatment Using Nanocatalyst and Fenton's Reagent

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Received October 15, 2019

**Abstract** – The effect of nanocatalyst and Fenton's reagent on the efficiency of wastewater treatment under the influence of  $\gamma$ -radiation was studied. Model samples of aqueous solutions of phenol were used for examining radiolytic decomposition patterns under the influence of  $\gamma$ -radiation (at doses in the range of 1.4–18 kGy) in the presence or absence of nano- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst accompanied by *in situ* Fenton's reagent formation. It was established that the addition of the nanocatalyst to the system resulted in an increase in the rate of phenol decomposition and an increase in the radiation-chemical yields of the radiolytic transformation. Industrial and municipal wastewater samples were applied for studying possibility of their biochemical treatment under the influence of  $\gamma$ -radiation in the presence of the nanocatalyst and a component of Fenton's reagent system. Irradiation of wastewater samples taken from an oil refining enterprise led to an enhancement of water quality and a substantial improvement in bacteriological parameters (indicators of *E. coli* and total microbial count).

**Keywords:** radiation water treatment, gamma radiation, nanocatalyst, phenol, radiolytic degradation, Fenton's reagent.

## Радиационная очистка сточных вод в присутствии нанокатализатора и реактива Фентона

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Поступила в редакцию 15.10.2019 г.

**Аннотация** – Изучено влияние нанокатализатора и реактива Фентона на эффективность очистки сточных вод под действием гамма-излучения. На модельных образцах водных растворов фенола установлены закономерности радиолитического разложения фенола в водных растворах под действием  $\gamma$ -излучения (при дозах в диапазоне 1.4–18 кГр) в присутствии и в отсутствие катализатора нано- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> при наличии образующегося *in situ* реактива Фентона. Установлено, что добавление в систему нанокатализатора приводит к повышению скорости разложения фенола и увеличению радиационно-химического выхода радиолитического превращения. На реальных пробах промышленных и коммунально-бытовых сточных вод показана возможность их биохимической очистки под действием  $\gamma$ -излучения в присутствии нанокатализатора и компонента реактива Фентона. Облучение образцов сточных вод нефтеперерабатывающего завода привело к улучшению качества

воды и к заметному улучшению бактериологических параметров (показателей *E. coli* и общего микробного числа).

*Ключевые слова:* радиационная очистка воды, гамма-излучение, нанокатализатор, фенол, радиолитическое разложение, реактив Фентона.

## INTRODUCTION

Treatment of wastewater generated by industrial plants of different types and wastewater of domestic origin is an urgent environmental problem all over the world. In the Caspian countries, this problem is of particular importance, since, ultimately, wastewater enters the Caspian Sea, therefore, poor treatment can cause a serious seawater pollution.

Currently, there are many methods for treating industrial and municipal effluents, while radiation-assisted technologies for the treatment of wastewater from toxic components, specifically with the help of ionizing radiation sources have been increasingly used [1–3], including gamma-radiation treatment [4, 5]. In developed countries, pilot and industrial installations for radiation-assisted treatment of contaminated aqueous media are coming into use. The advantages of this technology are due to its ability to perform combined water purification from chemical and biological pollution and improve water quality [6]. Barriers to the wider application of this kind of technology are limitations associated with the levels of concentration of pollutants, since this technology is cost effective only at low concentrations of toxic components due to the insufficient efficiency of using ionizing radiation energy. In order to increase the efficiency of radiation treatment, it was proposed to use catalysts with nanoscaled particle size, the effect of which is apparently due to the additional reaction of charges stabilized on the surface of the particles with molecules of toxic compounds [7]. On the other hand, it is known that an effective purification of water from highly toxic chemical pollutants can be carried out by oxidation procedures, for example, using Fenton's reagent [8, 9].

Accordingly, the aim of this work was to study the kinetics of the radiolytic degradation of model pollutant in aqueous solutions, as well as to explore the possibility of biological wastewater treatment in the presence of the nano- $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst and Fenton's reagent under the action of  $\gamma$ -radiation.

## EXPERIMENTAL PART

Radiological decomposition was studied on samples of aqueous solutions of phenol as a model pollutant ( $\text{C}_6\text{H}_6\text{O}$ , CAS No. 108-95-2, Aldrich, USA, 99% purity). Phenol is a toxic chemical compound and belongs to highly hazardous substances (hazard class II).

Phenol solutions with a concentration of  $5 \cdot 10^{-3}$  M were prepared. For the preparation of solutions, distilled water was taken. To simulate the action of Fenton's reagent under  $\gamma$ -radiation conditions, iron(II) sulfate heptahydrate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was used (Aldrich, USA, 99.5% purity). In this case, iron(II) sulfate acted as a precursor of one of the components of the Fenton's reagent system. It is known that irradiation of aqueous solutions leads to generation of  $\text{OH}^\bullet$ -radicals reacting further with divalent iron ions, which results in the formation of trivalent iron ions [10, 11].

A nano- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.1 g) and FeSO<sub>4</sub> (0.2 g) were introduced in the samples of phenol aqueous solutions. The resulting samples were used as suspensions of solid particles. The nano- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is based on alumina in the form of its crystalline  $\gamma$ -modification. It was purchased from Skyspring Nanomaterials Inc. (USA). The main characteristics of the catalyst are presented in Table 1.

**Table 1.** Basic characteristics of the nano- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

Parameter	Value
Purity	99.99%
Appearance	White nanopowder
Particle size, D <sub>20</sub>	20 nm
Specific surface area	262.09 m <sup>2</sup> /g
Content of $\gamma$ -phase	99.32%
Water content	0.317%
Impurities	Ca: 8.25 mg/kg Fe: 7.967 mg/kg K: 6.3 mg/kg Na: 4.707 mg/kg Si: 9.71 mg/kg

Phenol concentrations in the solutions were determined by the photometric method using a UV Carry-50 UV spectrophotometer (SEM-AZ, official representative of Agilent technologies in Azerbaijan). Current concentrations were calculated using a calibration curve. In the UV spectra, phenol was determined at  $\lambda = 510$  nm. The yields of gaseous products were measured by Gasochrome-3101 chromatograph (column with activated carbon AG-3, carrier gas – air, Manometer Plant, Russia).

The samples were irradiated under the action of  $\gamma$ -radiation generated from a <sup>60</sup>Co source under static conditions at room temperature at doses in the range of 1.4–18 kGy.

The procedure of isolating and estimating the number of coliform bacteria and *E. coli* was carried out as described in the Methodological Instructions 4.2.1884-0403.2004 [12] and in ISO 9308-2 (2012) standard [13].

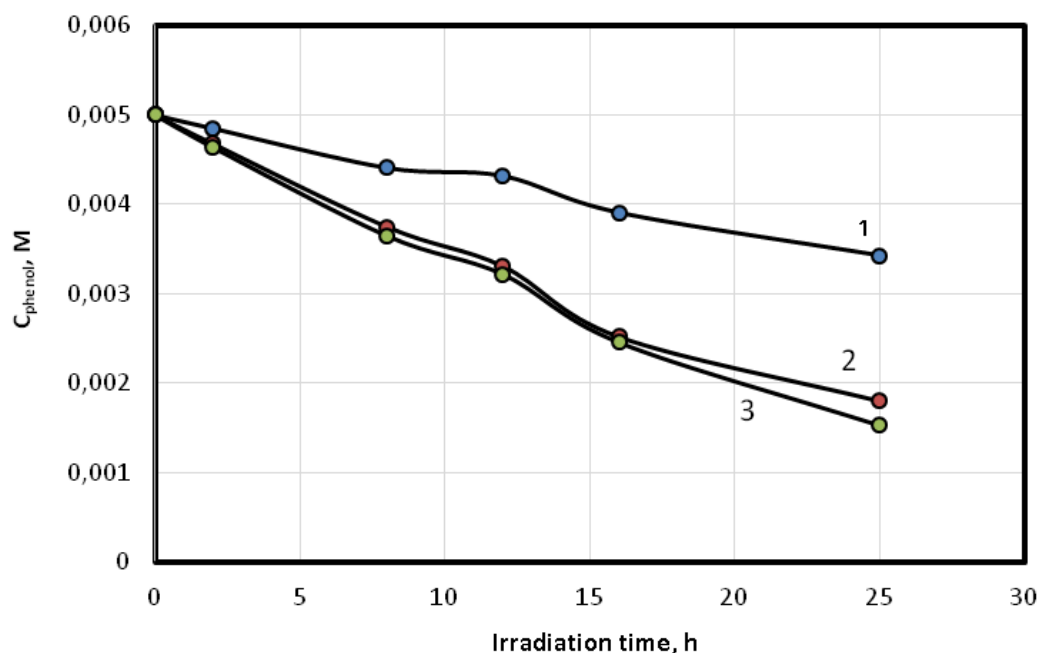
*E. coli* is a thermotolerant coliform bacterium that generates indole formation from tryptophan at a temperature of  $44 \pm 0.5^\circ\text{C}$ , gives a positive test result in the methyl-red test, does not promote formation of acetylmethylcarbinol (a negative reaction in the Voges-Proskauer test), and is also able to use citrate as the sole source of carbon. The number of coliforms in *E. coli* is expressed as the ‘most probable number’ [13].

The total microbial number in aqueous solutions of the examined samples was measured according to the procedure for determining the number of colony forming units (CFU) of microorganisms in 1 cm<sup>3</sup> of water sample in an approximate manner [14].

## RESULTS AND DISCUSSION

*Kinetics of radiolytic decomposition of phenol in model aqueous solutions in the presence of the nanocatalyst*

Radiolytic decomposition of phenol was studied by analyzing changes in the phenol concentration depending on the absorbed dose of  $\gamma$ -radiation in the water-phenol systems at an initial phenol concentration of  $5 \cdot 10^{-3}$  M in the absence and presence of the nano- $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst and  $\text{FeSO}_4$  (0.2 g) The results are summarized in Figures 1–3. Fig. 1 shows the changes in phenol concentration depending on irradiation time at the dose rate of 0.2 Gy/s.

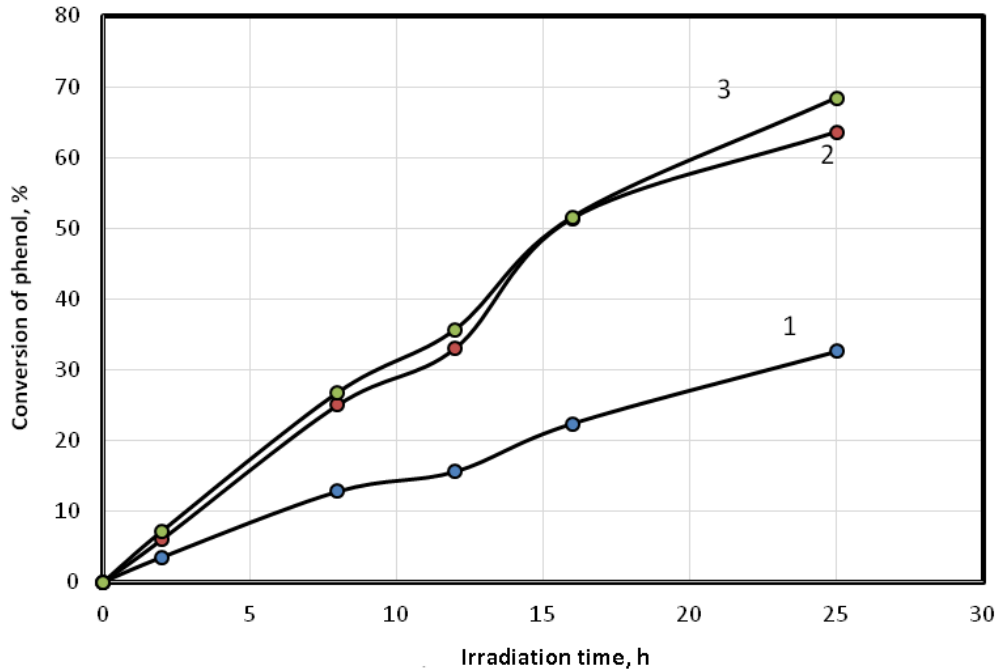


**Fig. 1.** Dependence of phenol concentration on  $\gamma$ -irradiation time at absorbed dose rate of 0.2 Gy/s for systems: (1) phenol-water, (2) phenol-water-nano- $\gamma$ - $\text{Al}_2\text{O}_3$ , (3) phenol-water- $\text{FeSO}_4$ .

As can be seen from Fig. 1, an increase in the  $\gamma$ -irradiation time leads to a monotonic decrease in the phenol concentration; moreover, when the catalyst is added, the observed decrease in concentration occurs faster. Basing on the initial rate of decrease in phenol concentration, the radiation-chemical yields were calculated for phenol radiolytic degradation reaction, which amounted to 0.5 and  $\sim 1.8$  molecules/100 eV for the aqueous phenol solution in the absence and in the presence of nanocatalyst, respectively.

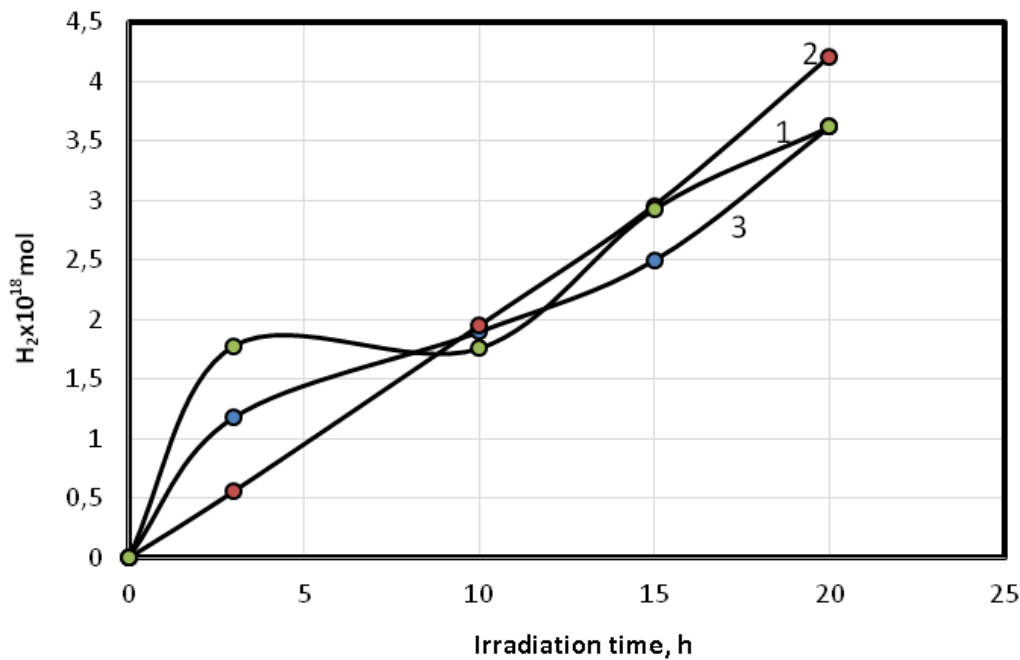
Figure 2 shows data on the changes in the degree of phenol conversion during  $\gamma$ -radiolysis of the systems studied.

As can be seen from Fig. 2, an increase in the  $\gamma$ -irradiation time results in an increase in the degree of phenol conversion; the conversion degree values are  $\sim 32\%$  and  $\sim 65\text{--}70\%$  for the systems phenol-water and phenol-water-catalyst at the absorbed dose of  $\sim 18$  kGy, respectively (irradiation exposure time is 25 h).



**Fig. 2.** Dependence of degree of phenol conversion on  $\gamma$ -irradiation time at absorbed dose rate of 0.2 Gy/s for systems: (1) phenol-water, (2) phenol-water-nano- $\gamma$ - $\text{Al}_2\text{O}_3$ , (3) phenol-water- $\text{FeSO}_4$ .

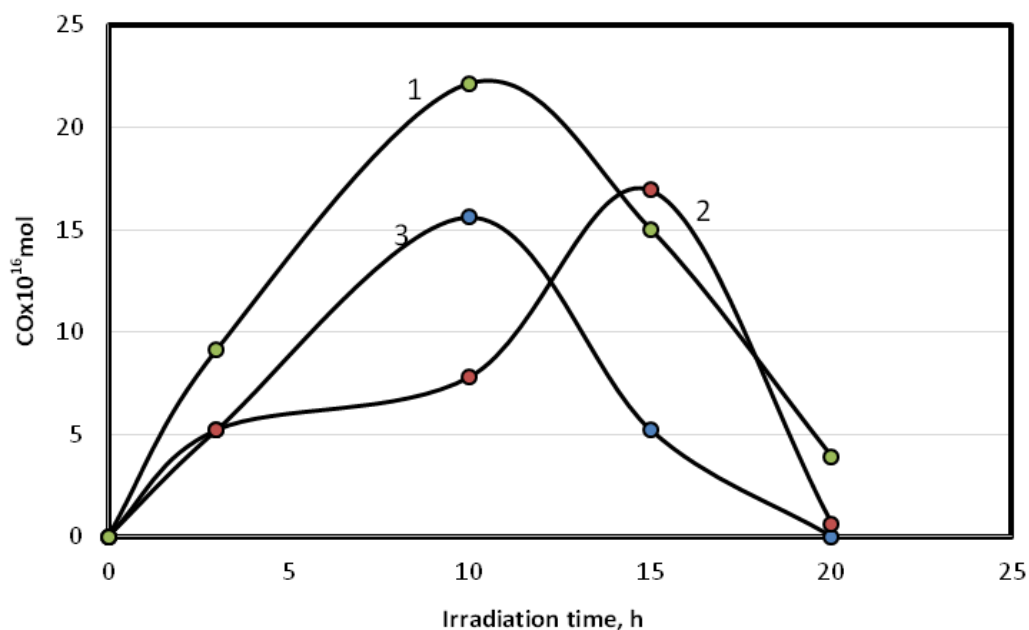
Hydrogen and carbon monoxide were identified in gaseous form as the radiolytic degradation products for these systems. The results of the analysis of radiolysis products are presented in Figures 3 and 4.



**Fig. 3.** Dependence of hydrogen concentration on  $\gamma$ -irradiation time at absorbed dose rate of 0.2 Gy/s for systems: (1) phenol-water, (2) phenol-water-nano- $\gamma$ - $\text{Al}_2\text{O}_3$ , (3) phenol-water- $\text{FeSO}_4$ .

As can be seen from Fig. 3, the introduction of the catalyst leads to an initial decrease in the rate of hydrogen production, although with an increase in the irradiation dose, the amount of hydrogen in all cases increases (data not shown). In all cases, a decrease in the rate of hydrogen formation is especially noticeable when the nano- $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst is added to the aqueous phenol solution.

Changes in the concentration of carbon monoxide formed during  $\gamma$ -radiolysis depending on the absorbed dose are shown in Figure 4.



**Fig. 4.** Changes in concentration of carbon monoxide depending on  $\gamma$ -irradiation time at absorbed dose rate of 0.2 Gy/s for systems: (1) phenol-water, (2) phenol-water-nano- $\gamma$ - $\text{Al}_2\text{O}_3$ , (3) phenol-water- $\text{FeSO}_4$ .

The results obtained for changes in the concentration of carbon monoxide depending on the absorbed dose indicate the extreme character of the kinetic curves. Initially, the concentration of carbon monoxide increases with the increasing dose reaching a maximum value, then, a further increase in the dose level leads to a decrease in the concentration of carbon monoxide formed in the phenol degradation reaction. The highest rate of carbon monoxide formation is observed during radiolysis of aqueous phenol solutions without additives. The addition of the catalyst results in a decrease in the rate of formation of carbon monoxide. In this case, when irradiated with a dose of 14 kGy, the formation of carbon monoxide is not observed.

#### ***Biochemical wastewater treatment under the influence of $\gamma$ -radiation***

A series of experiments was conducted on biochemical treatment of real-life wastewater samples from an oil refining plant in Baku under the influence of  $\gamma$ -radiation. Table 2 shows the results obtained in terms of the total number of coliform bacteria, *E. coli* test value, the total microbial number at 22°C, the total microbial number at 37°C for the initial samples taken from household wastewater of the plant

(1), industrial wastewater, and (2) and mixtures thereof (3). Mixed industrial and household wastewater from the plant is usually directed to biological treatment step.

**Table 2.** Bacteriological parameters of initial samples taken from domestic wastewater (1), industrial wastewater (2) and mixtures thereof (3) of oil refining plant

Bacteriological parameters	Sample	Water	Water	Water
	Point #	1	2	3
	Unit			
The total number of coliform bacteria	CFU/100 ml	< 1	1	< 1
<i>E. coli</i>	CFU/100 ml	< 1	< 1	< 1
Total microbial count at 22°C	CFU/1 ml	800	2200	2000
Total microbial count at 37°C	CFU/1 ml	633	1835	1670

As can be seen from Tab. 2, the presence of microbes was detected in all three types of wastewater samples. The values of other bacteriological parameters are below the sensitivity limit of the measuring procedures.

Table 3 shows the values of bacteriological parameters during exposure of ZDVWHZDWHUVDPSOHVWR-radiation dose of 17, 17, and 50 kGy.

**Таблица 3.** Bacteriological parameters of wastewater samples of oil refining plant after  $\gamma$ -irradiation at dose of 17 kGy and 50 kGy

Bacteriological parameters	Sample	Water	Water	Water	Water	Water	Water
	'RVHN*\	1					
	Unit						
Total number of coliform bacteria	CFU /100 ml	< 1	< 1	< 1	< 1	< 1	< 1
<i>E. coli</i>	CFU /100 ml	< 1	< 1	< 1	< 1	< 1	< 1
Total microbial count at 22°C	CFU /1ml	9	< 1	< 1	< 1	300	< 1
Total microbial count at 37°C	CFU / 1 ml	<1	<1	<1	<1	<1	<1

As can be seen from the table, irradiation of the wastewater samples at the dose of 17 kGy leads to the complete destruction of coliform bacteria and *E. coli*. At the dose of 50 kGy, the total microbial number decreases to ~1 CFU/ml. These results indicate a possibility of chemical and biological wastewater treatment.

## CONCLUSION

Thus, the influence of the nanocatalyst and Fenton's reagent system on the radiation-assisted treatment of wastewater under the action of  $\gamma$ -radiation was studied

on model aqueous solutions of phenol. It was revealed that the addition of the nano- $\gamma$ - $\text{Al}_2\text{O}_3$  to the reaction system results in an increase in the phenol decomposition rate and an increase in the radiation-chemical yield of the radiolytic transformation. The radiation-chemical yields of phenol degradation were determined during the  $\gamma$ -radiolysis of its aqueous solutions in the presence of the nanocatalyst.

Samples of industrial and domestic wastewater, as well as its mixtures generated by the Baku oil refining plant were used for the investigations. It was found that  $\gamma$ -radiation exposure in the presence of the nanocatalyst and Fenton's reagent component led to a noticeable improvement in bacteriological parameters of the examined wastewater samples which indicates a good potential of using radiation-assisted technology for wastewater treatment.

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