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RADIATION-CHEMICAL DEGRADATION OF OXALIC – FORMIC ACID AND THEIR MIXTURE IN AQUEOUS SOLUTIONS

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Abstract: Radiolytic degradation of aqueous oxalic and formic acid solution (1×10^{-2} M) at their various ratios under the γ -irradiation was investigated. With the increasing absorbed dose the total amount of organic substances decreases, and in the case of dominated concentration of oxalic acid, the rate of COD reduction is greater than in the case of converting formic acid concentrations. The initial radiation-chemical yields of H_2O_2 were calculated. The acidity of the solution is decreases with increasing adsorbed dose for all systems.

Keywords: oxalic aid, formic acid, γ -irradiation, liquid radioactive waste, chemical oxygen demand

1. Introduction

Formic and oxalic acid are widely used in radiochemical technologies of processing waste nuclear technology, as a result occur large quantities of liquid radioactive waste [3, 6]. Liquid wastes are very radioactive and continue to emit large amounts of heat. In addition, a mixture of organic and inorganic acids in the wastewaters from industrial enterprises is observed. Formic and oxalic acid is one of these components.

Radiolysis of formic and oxalic acid was investigated in [1-5]. But a comparative study of a mixture of these acids as a waste of nuclear technology has not been sufficiently studied. Therefore, it is of interest to study the radiolysis of aqueous solutions of these acids and their mixtures.

In this study radiolytic degradation of aqueous oxalic and formic acid solution (1×10^{-2} M) at their various ratios under the γ -irradiation was investigated.

Purpose of this work is to study kinetic regularities of aqueous solutions of formic and oxalic acid and their mixtures at different absorbed doses and different ratios of initial concentrations.

2. Methodology

The solutions were irradiated with γ -irradiation from the ^{60}Co isotope, under static conditions, in glass ampules at room temperature. Solutions ($1 \times 10^{-2}M$) were irradiated at different absorbed doses (2-80 kGy) and at different ratios of initial concentration - 1: 7 (5 ml formic + 35 ml oxalic acid); 1: 1 (20 ml formic + 20 ml oxalic acid), 7: 1 (35 ml formic + 5 ml oxalic acid). The total vial volume is 12 ml and 5 ml solution into each vial was poured.

The dose rate was determined by the ferrosulfate dosimetry and was 0.2-0.16 Gy/s. Chemical oxygen demand (COD) and concentration of hydrogen peroxide were determined by the standard method with the titrimetric method [7,8]. The pH was measured by PHS-25.

3. Results and discussion

The kinetics of the COD change on depending absorbed dose in the radiolysis of aqueous

solutions of formic and oxalic acid and their mixture shown in Fig. 1.

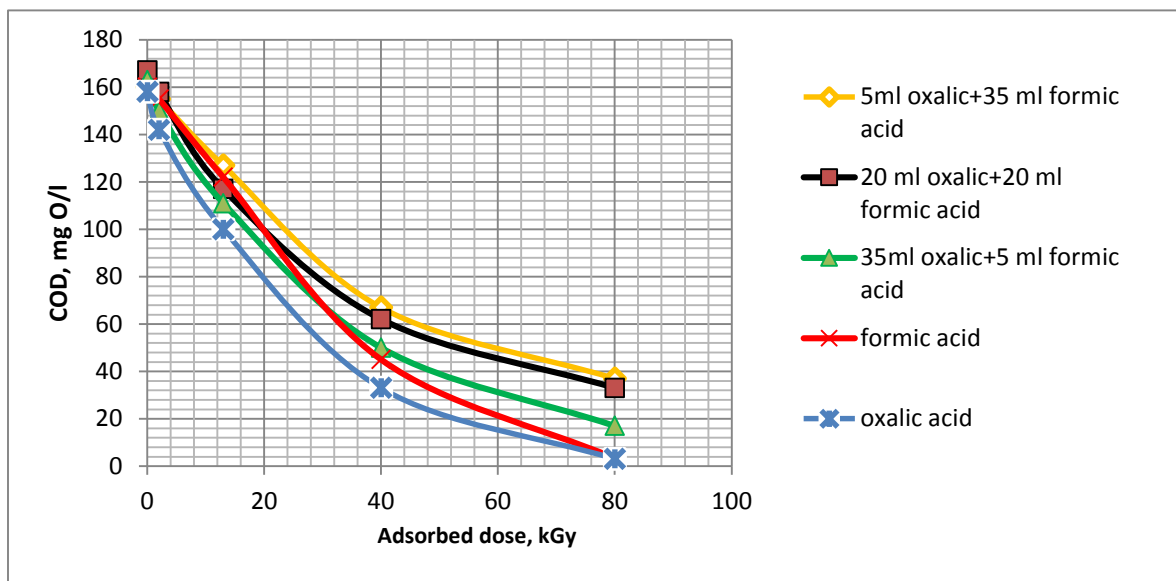


Fig 1. The kinetics of the COD change on depending absorbed dose in the radiolysis of aqueous solutions of formic and oxalic acid and their mixture ($N=1 \times 10^{-2} M$, $P=0,2-0,16 Gy/s$)

As shown from fig.1, with the increasing absorbed dose the total amount of organic substances decreases, and in the case of dominated concentration of oxalic acid, the rate of COD reduction is greater than in the case of converting formic acid concentrations.

The kinetics of the formation hydrogen peroxide in the radiolysis of aqueous solutions of formic and oxalic acid and their mixture on depending absorbed dose is showed in fig.2.

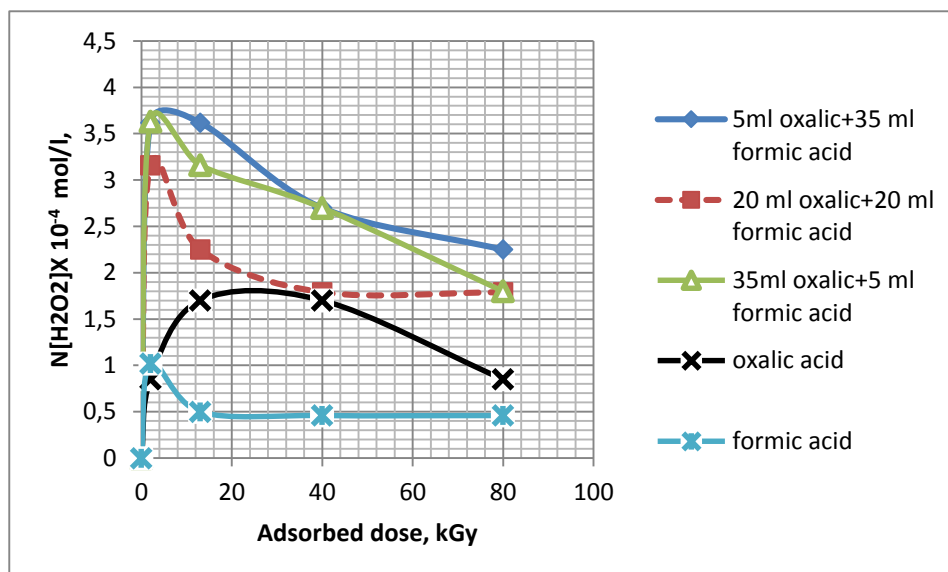


Fig.2. The kinetics of hydrogen peroxide formation on depending absorbed dose in the radiolysis of aqueous solutions of formic and oxalic acid and their mixture ($N=1 \times 10^{-2} M$, $P=0,2-0,16 Gy/s$)

As shown from fig.2 in all cases with increasing adsorbed dose the hydrogen peroxide concentration is increases. Approximately at doses more than 6 kGy concentration of H₂O₂ is decreasing. Calculated initial radiation-chemical yields are given in the following table:

Table 1. Radiation-chemical yields of H₂O₂

System	G (molecul/100 eV)
Oxalic acid	3,2
Formic acid	3,1
5 ml oxalic- 35 ml formic acid	1,7
20 ml oxalic- 20 ml formic acid	1,7
35 ml oxalic- 5 ml formic acid	1,5

The change of acidity of the solution on depending absorbed dose in the radiolysis of aqueous solutions of formic and oxalic acid and their mixture is shown in Fig. 3.

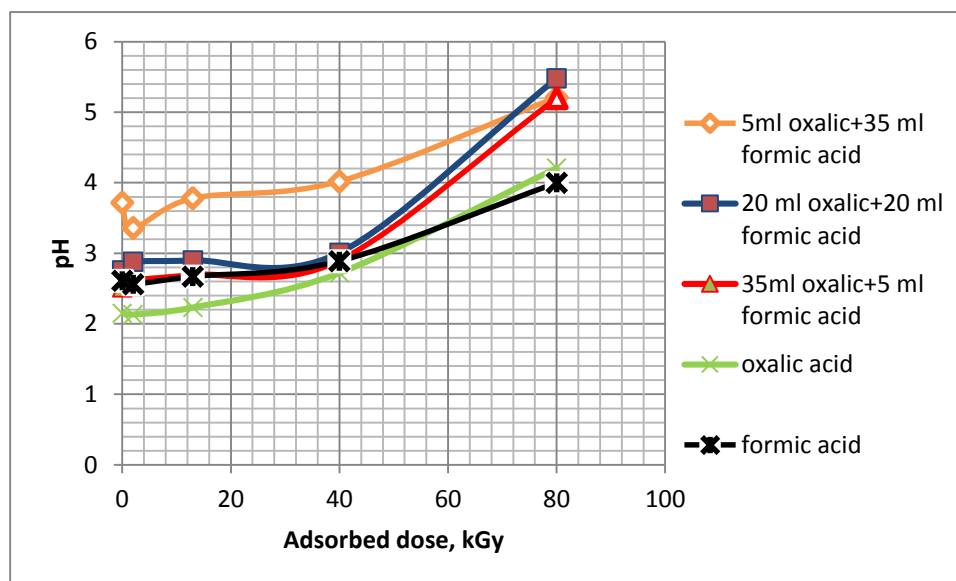
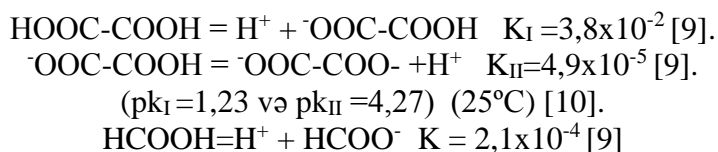


Fig.3. The kinetics of change of acidity of the solution on depending absorbed dose in the radiolysis of aqueous solutions of formic and oxalic acid and their mixture
($N=1 \times 10^{-2}$ M, $P=0,2-0,16$ Gy/s)

As shown from fig.3 with increasing adsorbed dose for all systems the acidity of the solution is decreases. In the aqueous solution of the oxalic and formic acid the acidity increases from 2.1 to 4.2 and 2.6 to 4, respectively, due to destruction of acids in the irradiated solution. With the increasing proportion of oxalic acid in the mixture, the acidity of the initial solution increases. It is explained by the fact that oxalic acid is stronger than formic acid ($pK_I = 1,27$ and $pK_{II} = 4,27$).



At 80 kGy adsorbed dose the pH value being stationary value is about 5.2-5.4.

The obtained results shows, that the rate of oxalic acid oxidation predominate the rate of formic acid oxidation at the radiolysis of aqueous solutions of formic-oxalic acid and their mixtures.

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РАДИАЦИОННО-ХИМИЧЕСКАЯ ДЕГРАДАЦИЯ ЩАВЕЛЕВОЙ И МУРАВЬИНОЙ КИСЛОТ И ИХ СМЕСЕЙ В ВОДНЫХ РАСТВОРАХ

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Резюме: Исследовано радиолитическое разложение щавелевой и муравьиной кислоты в водных растворах (1×10^{-2} М) и при их различных соотношениях под действием γ -излучения. С увеличением поглощенной дозы общее количество органических веществ уменьшается, причем в случае преобладающей концентрации щавелевой кислоты скорость уменьшения ХПК больше, чем в случае преобладающих концентраций муравьиной кислоты. Рассчитаны исходные радиационно-химические выходы для H_2O_2 . С увеличением поглощенной дозы кислотность раствора уменьшается для всех систем.

Ключевые слова: щавелевая кислота, муравьиная кислота, γ -облучения, жидкие радиоактивные отходы, химическое потребление кислорода

**OKSALAT, QARIŞQA TURŞUSU VƏ ONLARIN QARIŞIĞININ SUDA
MƏHLULLARININ RADİASİYA-KİMYƏVİ PARÇALANMASI**

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Xülasə: Oksalat və qarışqa turşularının suda məhlullarının (1×10^{-2} M) müxtəlif nisbətlərdə γ -şüalarının təsiri altında radiolizi prosesi öyrənilmişdir. Udulma dozasının artması ilə üzvi maddələrin ümumi miqdarı azalır, oksalat turşusunun payı çox olan sistemdə OKT-in azalma sürəti qarışqa turşusu ilə müqayisədə daha böyükdür. H_2O_2 üçün ilkin radiasiya-kimyəvi çıxımlar hesablanmışdır. Bütün sistemlərdə udulma dozasının artması ilə məhlulun turşuluğu azalır.

Açar sözlər: oksalat turşusu, qarışqa turşusu, γ -şüalanma, radioaktiv maye tullantılar, oksigenə olan kimyəvi tələbat.