

Oxidative destruction of anionite AV-17×8 using the Fenton reaction

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Abstract

The kinetic studies of AV-17×8 strongly basic anionite's oxidative destruction using the Fenton reaction have been carried out. The effect of the process's temperature and the concentration of catalysts of iron(II) sulfate or copper(II) sulfate on the oxidation of anion-exchange resin with hydrogen peroxide is estimated. With an increase in temperature in the range of 323–348 K, a regular increase in the effective rate constant of oxidative anionite destruction is observed when using iron(II) sulfate by 1.5 times, and when using copper(II) sulfate – by 22 times. It was found that the obtained values of the activation energy of the anion exchanger's oxidation with the addition of copper(II) sulfate are 124.3–115.7 kJ/mol and are characteristic of the process proceeding in the kinetic region. The nature of the change in the surface morphology of the anionite granules in the process of oxidative decomposition has been revealed.

Keywords

anion exchanger AV-17×8
hydrogen peroxide
Fenton process
process rate constant
activation energy

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1. Introduction

The ion exchange resins are widely used in the field of waste and wash water treatment at the nuclear power plants. As a result, the spent ion-exchange resins are formed, which are low-activity heterogeneous waste in the form of spherical granules from a cross-linked organic polymer. Over the years, the significant amounts of waste resins have accumulated at nuclear power plants, which subsequently cannot be regenerated [1]. Thus, an effective technology is needed for the disposal of the spent ion-exchange resins in order to reduce their negative impact on the environment.

At present, such technologies as immobilization (cementation, bitumization, vitrification) or incineration, pyrolysis, thermal vacuum drying, and supercritical water oxidation are used to dispose of waste resins [1, 2]. However, regular recycling technologies are characterized by significant economic costs, also there are difficulties with the transportation and storage of wastes that can be accompanied by the formation of explosive products associated with the radiolysis of organic substances and water.

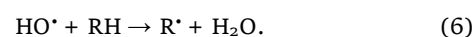
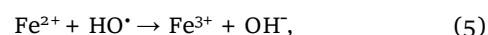
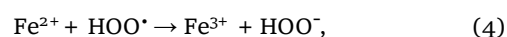
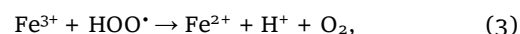
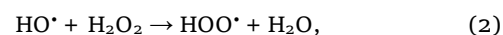
An effective way of the spent ion-exchange resins removal can be oxidative destruction, which significantly reduces the concentration of organic substances. A prom-

ising method is the Fenton process, based on the oxidation of organic compounds under the action of hydrogen peroxide. The catalytic additive can be ions of divalent transition metals, for example, iron(II) sulfate or copper(II) sulfate. The Fenton process is characterized by the formation of free hydroxyl radicals HO• in the system, which have minimal selectivity to various organic substances. HO• radicals are characterized by a high potential (2.80 V), and, therefore, have high oxidizing capacity [3].

The main mechanism of the classical Fenton process can be represented in the form of a redox reaction with the ferrous ions [3]:



As a result of chain reactions and an increase in the concentration of chemically active particles, a complex organic compound RH decomposes into small fragments [3]:



The Fenton process is characterized by a high reactivity, a deep oxidation state, and sufficiently mild operating conditions. The reaction efficiency is influenced by such factors as temperature, pH of the medium, concentration of hydrogen peroxide and catalyst.

The oxidation of sulfonic acid cation exchangers with hydrogen peroxide, as well as strongly basic anion exchangers with tertiary trimethylammonium groups in the presence of catalytic additions of transition metal salts, was described in [4–14]. Thus, in the study [4], the complete decomposition of domestic brand anionite AV-17×8 was achieved by the action of a 30% solution of hydrogen peroxide with the addition of an iron(II) salt in the temperature range 363–373 K. The works of the authors [5–14] are aimed at choosing the optimal conditions for the oxidative destruction of ion exchange resins of some foreign brands. The research [9] is devoted to the complete decomposition of a foreign brand of anion-exchange resin Amberlite INR78 by exposure to a 30% hydrogen peroxide solution with the addition of a copper (II) salt at a temperature of 368 K. In the above mentioned works the individual aspects of the influence such as the concentration of the oxidizing agent, the temperature of the solution, and the concentration of catalytic additives on the Fenton process were studied.

However, there is currently no information on kinetics of the ion-exchange resins oxidative destruction using the Fenton process. Previously, the studies were carried out on the oxidation of hydrogen peroxide using the Fenton reaction of the highly acidic universal cation exchanger KU-2-8 [15]. This works object is to the study of the kinetics of catalytic oxidative destruction of the domestic anionite AV-17×8 using the Fenton process.

2. Experimental

The object of the study was the strongly basic anion exchanger AV-17×8 (GOST 20301-74), the crosslinked copolymer of styrene and divinylbenzene. The diameters of spherical resin granules are in range of 315–1250 μm, the content of the working fraction is not less than 95%, the uniformity coefficient is 1.6, and the specific volume is $3.0 \pm 0.3 \text{ cm}^3/\text{g}$. For the oxidation of the AV-17×8 anionite, we used an environmentally friendly oxidizing agent – hydrogen peroxide H_2O_2 , the concentration of which was determined by permanganometry [16]. The preparation of 0.1 M catalyst solutions was carried out using salts of iron(II) sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and copper(II) sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

In all experiments, the amount of anion-exchange resin was constant and was 0.5 g based on the weight of the air-dry mass. To study the catalytic oxidation, a weighed portion of the AV-17×8 anionite was introduced into the reactors, then 10 ml of a hydrogen peroxide solution with an H_2O_2 concentration of 20 vol.%, then 0.001–0.005 mol/L FeSO_4 or CuSO_4 was added.

The reactors were placed in the thermostat of the brand LOIP LT-105a. The process was carried out in the temperature range of 323–348 K. Each reactor was removed from the thermostat after a certain time. The remaining AV-17×8 anionite in the reactors was thoroughly washed, filtered, dried in air for a week at room conditions, then heated in a PM-1.0-7 electric furnace for 2.5 h at the temperature of $377 \pm 1 \text{ K}$. After that, it was weighed on an analytical balance VIBRA HTR-220CE with a readability of $\pm 0.0001 \text{ g}$.

The study of the surface morphology of the granules of the anionite AV-17×8 was carried out by scanning electron microscopy using a JEOL JSM-6390 LA microscope.

3. Results and discussion

To explain the physicochemical process of AV-17×8 anionite oxidation, it is necessary to consider the patterns of the process in time, depending on the mechanism of the chemical reaction and on thermodynamic factors - the temperature and concentration of the catalyst. Let us consider the effect of temperature as a parameter that has the most significant impact on the rate of anion exchanger oxidative destruction.

The kinetic studies of the AV-17×8 anionite catalytic oxidation with hydrogen peroxide were carried out with the addition of 0.001–0.005 mol/L iron(II) sulfate and copper(II) sulfate. The dependences of the relative weight loss of the anion exchange resin on the exposure time of 20 vol.% hydrogen peroxide with the addition of 0.002 mol/L FeSO_4 at temperatures from 323 to 343 K are shown in Fig. 1a. It is observed that the process of the anionite destruction by hydrogen peroxide with iron(II) sulfate proceeds relatively slowly, and with a decrease in the reaction temperature, the longer induction period occurs. So, at 343 K in 360 min, only 36% of the anion exchanger was dissolved. The lowering of the temperature to 333 K leads to the decomposition of 17% of resin within 210 min. At 323 K, 10% of the anion exchanger is oxidized in 270 min.

With the use of copper(II) sulfate as a catalytic additive at the temperatures in range of 323–348 K, the complete oxidation of the AV-17×8 anionite was achieved (Fig. 1b). The graph shows how the duration of the induction period decreases with increasing temperature. At 348 K the intense oxidation of the anion exchange resin is observed during the first 24 min. The decrease in the working temperature of the solution to 343 and 333 K leads to the complete decomposition of the resin after 35 and 110 min, respectively. At 323 K after 270 min, the resin mass loss was ~92%.

Thus, an increase in the process temperature from 323 K to 348 K significantly influences the rate of anion exchange resin decomposition. It should be noted that increasing the catalyst concentration that is iron(II) sulfate or copper(II) sulfate at a given temperature does not significantly accelerate the decomposition of the AV-17×8 anionite.

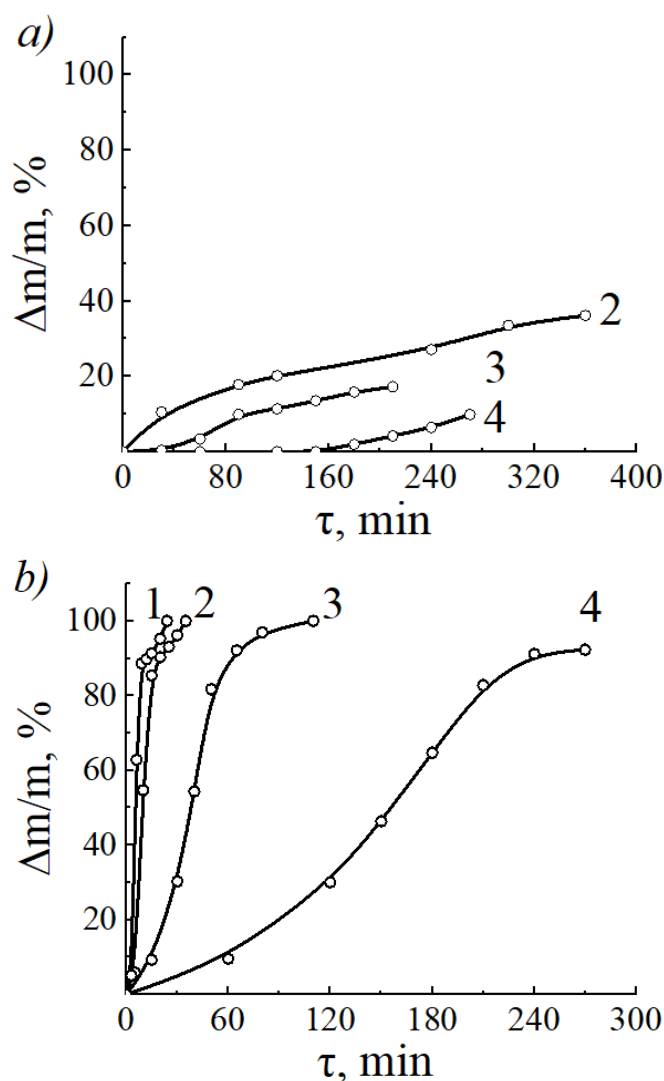


Fig. 1 Kinetic curves of the AV-17x8 anionite relative weight loss in 20% H₂O₂ with the addition of 0.002 mol/L FeSO₄ (a) and 0.003 CuSO₄ mol/L (b) at a temperature, K: 348 (1), 343 (2), 333 (3), 323 (4)

The effect of catalytic additions of copper and iron salts, according to studies [6–9, 11, 14], is based on an increase in the concentration of active oxygen during the decomposition of hydrogen peroxide, which promotes more active resin oxidative destruction. In the works [6, 9], the activities of catalytic additives in the Fe²⁺/H₂O₂ and Cu²⁺/H₂O₂ solutions have been compared and it is concluded that copper(II) ions have a stronger catalytic effect in the process of the anion exchanger oxidation compared to iron(II) ions.

To determine the rate of the heterogeneous process in the "anionite-solution" system, it is necessary to take into account the interfacial area that changes during oxidative destruction, as well as the geometry of the spherical particles of the anion-exchange resin. The reaction rate, that is, the loss of anionite's mass, can be determined according to the equation:

$$-\frac{dm}{d\tau} = kFC \tag{7}$$

where *m* is the mass of the anionite AV-17x8 granule at the time *τ*, *F* is its surface area, *C* is the concentration of H₂O₂, *k* is the rate constant of the oxidation reaction.

By transforming Eq. (7), it is possible to obtain the dependence of the change in the mass of the anion resin granule on the duration of the process of its oxidation "*m*^{1/3} - *τ*" [17]. The processing of the experimental results, carried out in coordinates "*m*^{1/3} - *τ*", allows taking into account the heterogeneous nature of the oxidation reaction and the spherical shape of the anionite AV-17x8 granules.

The effective rate constant of the process *k* was determined from the slope of the obtained straight line in the coordinates "*m*^{1/3} - *τ*". Table 1 shows the calculated values of the effective rate constants of the anion exchanger oxidative destruction process depending on the temperature and the concentration of catalytic additives. From the calculated values with the addition of 0.002 mol/L FeSO₄ catalyst, it shows that an increase in the process temperature from 323 to 343 K leads to an increase in the rate constant by a factor of 1.5. With an increase in the content of the catalytic additive from 0.001 to 0.005 mol/L, the rate constant of the process increases by a factor of 1.2.

According to the obtained values of the process effective rate constant with the addition of 0.002 mol/L CuSO₄, and with increase in the process temperature from 323 to 348 K the rate constant is increasing by a factor of 23. At 0.003, 0.004, and 0.005 mol/L CuSO₄, the effective rate constant of the process increases by a factor of 22. With a decrease in the concentration of the catalytic additive to 0.001 mol/L CuSO₄, an increase in the rate constant by a factor of 18 is observed. An increase in the concentration of the CuSO₄ catalyst from 0.001 to 0.005 mol/L slows down the increase in the process rate constant, increasing it by no more than 1.3–2.2 times.

Table 1 Effective process rate constant (*k*×10³, g^{1/3} min⁻¹) oxidative destruction of the anionite AV-17x8, depending on the temperature and concentration of catalytic additives when using 20 vol.% hydrogen peroxide

<i>T</i> , K	[FeSO ₄], mol/L					[CuSO ₄], mol/L				
	0.001	0.002	0.003	0.004	0.005	0.001	0.002	0.003	0.004	0.005
323	-	0.23	0.25	0.34	0.35	2.15	2.71	2.93	3.20	3.25
333	0.20	0.24	0.25	-	-	5.82	7.88	9.13	10.29	12.67
343	0.27	0.34	-	-	-	32.07	33.49	35.99	42.13	41.83
348	-	-	-	-	-	38.41	63.73	65.96	70.67	72.75

Using the calculated values of the effective rate constants, the activation energy E_a of the process of the anionite oxidative destruction was determined by the graphical solution of the Arrhenius equation in the coordinates " $\ln k - 10^3/T$ ". According to the data presented in Table 2, the activation energies of the anionite oxidation process with the addition of the CuSO_4 catalyst are in the range from 124.3 to 115.7 kJ/mol, which indicates that the process is of the kinetic type.

Table 2 Activation energy of the process of oxidative destruction of the AV-17×8 anionite in 20% hydrogen peroxide at various concentrations of the CuSO_4 catalyst

$[\text{CuSO}_4]$, mol/L	0.001	0.002	0.003	0.004	0.005
E_a , kJ/mol	124.3	118.1	116.4	115.7	116.2

The surface of the anionite AV-17×8 granules in the process of catalytic oxidative destruction has been investigated. For comparison, Fig. 2a shows a relatively smooth and practically undeformed surface of granules before oxidation. Fig. 2b shows an electron microscopic image of a surface of granules after 2.5 h of contact at the temperature of 343 K with a 20 vol.% aqueous solution of hydrogen peroxide containing 0.002 mol/L FeSO_4 , which corresponds to a loss of 20% of granule's mass. Fig. 2c shows a surface of anionite granules after exposure to a 20 vol.% aqueous solution of H_2O_2 containing 0.005 mol/L CuSO_4 . As a result of contact for 10 min at the temperature of 343 K, the weight loss of the anionite was 85%. In Fig. 2(b, c), the local changes can be observed on the resin surface. At the same time, the sorbent granule changed its shape, volume, and its surface was covered with cracks, which may indicate the destruction of the crosslinks of the AV-17×8 anionite in the process of oxidative destruction and a decrease in its mechanical strength.

4. Conclusions

Thus, the kinetic studies of the AV-17×8 anionite catalytic oxidative destruction by hydrogen peroxide showed that the introduction of 0.001–0.005 mol/L of the copper(II) sulfate catalyst significantly increases the intensity of the oxidation process as compared to the addition of 0.001–0.005 mol/L of iron(II) sulfate. It was found that in the presence of 0.002 mol/L catalytic additives in a 20% aqueous solution of hydrogen peroxide in the temperature range 323–348 K the rate constant of the oxidative decomposition of the anion exchanger increases by a factor of 1.5 when using iron(II) sulfate at an operating temperature of 343 K, and with the introduction of copper(II) sulfate at 348 K – by a factor of 23. The calculated activation energies of the process of oxidative destruction of the AV-17×8 anionite by hydrogen peroxide with the addition of copper(II) sulfate are in the range 124.3–115.7 kJ/mol, which is typical for the kinetic type process.

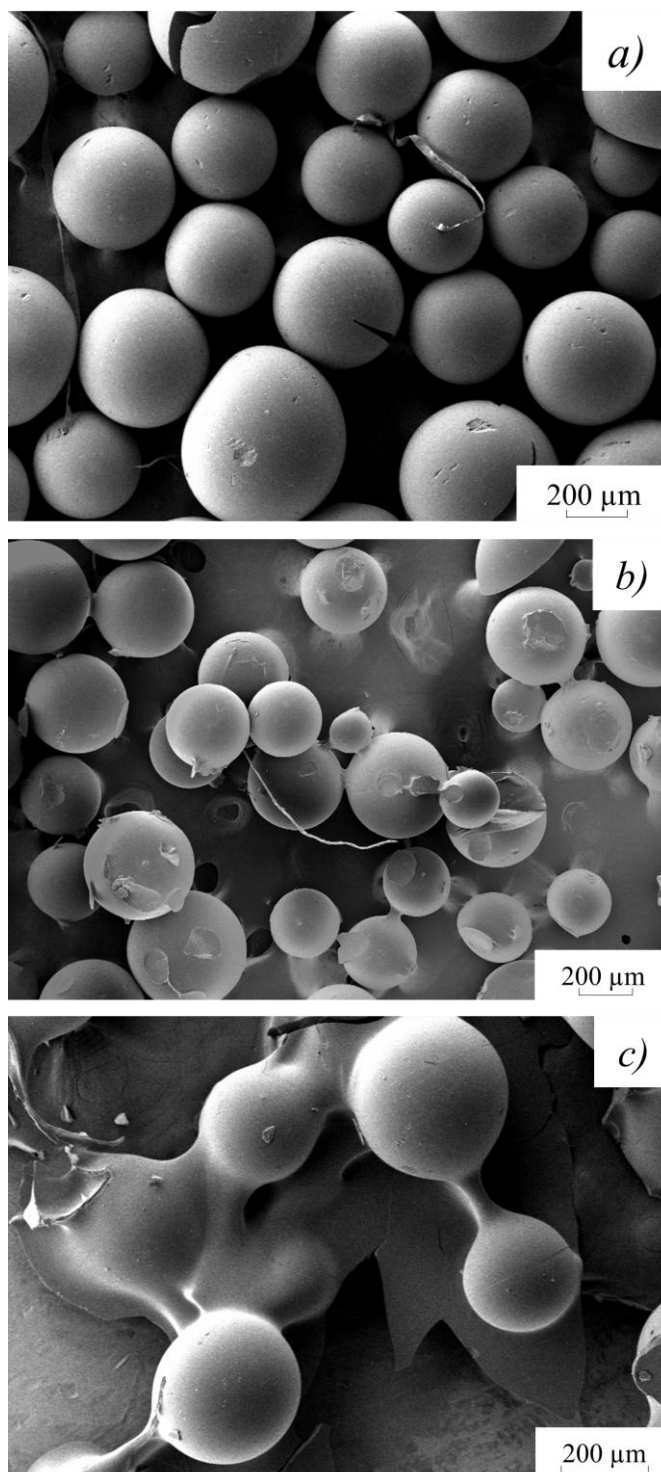


Fig. 2 Electron microscopic images of the surface of the anionite AV-17×8 before oxidation (a), after exposure to 20% H_2O_2 with the addition of FeSO_4 (b) and with the addition of CuSO_4 (c)

References

- Smolnikov MI, Markov VF, Maskaeva LN, Bobylev AE, Mokrousova OA. Utilization problems of spent ion-exchange resins of nuclear power plants. *Butlerov Commun.* 2017;49(3):119–134. doi:[jbc-01/17-49-3-119](https://doi.org/10.1016/j.pnucene.2014.08.003)
- Wang J, Wan Z. Treatment and disposal of spent radioactive ion-exchange resins produced in the nuclear industry. *Prog Nucl Energy.* 2015;78:47–55. doi:[10.1016/j.pnucene.2014.08.003](https://doi.org/10.1016/j.pnucene.2014.08.003)
- Babuponnusami A., Muthukumar K. A review on Fenton and improvements to the Fenton process for wastewater treat-

- ment. *J Environ Chem Eng*. 2014;2(1):557–572. doi:[10.1016/j.jece.2013.10.011](https://doi.org/10.1016/j.jece.2013.10.011)
4. Kuznetsov AE, Knyazev OV, Maraev IY, Manakov MN. Biotechnological destruction of ion exchange resins. *Biotechnol*. 2000;16(1):66–77.
 5. Zahorodna M, Bogoczek R, Oliveros E, Braun AM. Application of the Fenton process to the dissolution and mineralization of ion exchange resins. *Catal Today*. 2007;129(1–2):200–206. doi:[10.1016/j.cattod.2007.08.014](https://doi.org/10.1016/j.cattod.2007.08.014)
 6. Gunale TL, Mahajani VV, Wattal PK, Srinivas C. Liquid phase mineralization of gel-type anion exchange resin by a hybrid process of Fenton dissolution followed by sonication and wet air oxidation. *Asia-Pacific J Chem Eng*. 2009;4(1):90–98. doi:[10.1002/apj.214](https://doi.org/10.1002/apj.214)
 7. Gunale TL, Mahajani VV, Wattal PK, Srinivas C. Studies in liquid phase mineralization of cation exchange resin by a hybrid process of Fenton dissolution followed by wet oxidation. *Chem Eng J*. 2009;148(2–3):371–377. doi:[10.1016/j.cej.2008.09.018](https://doi.org/10.1016/j.cej.2008.09.018)
 8. Wan Z, Xu L, Wang J. Disintegration and dissolution of spent radioactive cationic exchange resins using Fenton-like oxidation process. *Nucl Eng Des*. 2015;291:101–108. doi:[10.1016/j.nucengdes.2015.05.009](https://doi.org/10.1016/j.nucengdes.2015.05.009)
 9. Wan Z, Xu L, Wang J. Treatment of spent radioactive anionic exchange resins using Fenton-like oxidation process. *Chem Eng J*. 2016;284:733–740. doi:[10.1016/j.cej.2015.09.004](https://doi.org/10.1016/j.cej.2015.09.004)
 10. de Araujo LG, Marumo JT. Reaction of ion exchange resins with fenton's reagent. *Environments – MDPI*. 2018;5(11):1–10. doi:[10.3390/environments5110123](https://doi.org/10.3390/environments5110123)
 11. Xu L, Meng X, Li M, Li W, Sui Z, Wang J, Yang J. Dissolution and degradation of nuclear grade cationic exchange resin by Fenton oxidation combining experimental results and DFT calculations. *Chem Eng J*. 2019;361:1511–1523. doi:[10.1016/j.cej.2018.09.169](https://doi.org/10.1016/j.cej.2018.09.169)
 12. Huang CP, Tsai MT, Li YJ, Huang YH, Chung TY. Oxidative dissolution of cation ion exchange resin by the Fenton process using a fluidized bed reactor. *Prog Nucl Energy*. 2020;125:1–8. doi:[10.1016/j.pnucene.2020.103377](https://doi.org/10.1016/j.pnucene.2020.103377)
 13. Feng W, Li J, An H, Wang Y. Degradation of spent radioactive ion exchange resins and its mechanisms by fenton process. *J Renew Mater*. 2020;8(10):1283–1293. doi:[10.32604/jrm.2020.011000](https://doi.org/10.32604/jrm.2020.011000)
 14. Hafeez MA, Jeon J, Hong S, Hyatt N, Heo J, Um W. Fenton-like treatment for reduction of simulated carbon-14 spent resin. *J Environ Chem Eng*. 2021;9(1):1–9. doi:[10.1016/j.jece.2020.104740](https://doi.org/10.1016/j.jece.2020.104740)
 15. Kozlova MM, Markov VF, Maskaeva LN, Smol'nikov MI, Savinykh SD. Kinetics of the Oxidative Degradation of KU-2×8 Cation-Exchange Resin Using Hydrogen Peroxide. *Russ J Phys Chem A*. 2020;94(12):2450–2458. doi:[10.1134/S0036024420120146](https://doi.org/10.1134/S0036024420120146)
 16. Pilipenko AT, Pyatnitsky IV. *Analiticheskaya khimiya* [Analytical chemistry]. Moscow: Chemistry, 1990. 480 p. Russian.
 17. Dyachenko AN, Shagalov VV. *Khimicheskaya kinetika geterogennykh protsessov* [Chemical kinetics heterogeneous processes]. Tomsk: Tomsk Poly Technical University, 2014. 102 p. Russian.