

## Catalytic oxidation of cation exchanger KU-2×8 with an aqueous solution of hydrogen peroxide

© Marina M. Kozlova,<sup>1+</sup> Artem E. Bobylev,<sup>1</sup> Vyacheslav F. Markov,<sup>1,2\*</sup>  
Larisa N. Maskaeva,<sup>1,2</sup> and Maxim I. Smolnikov<sup>2</sup>

<sup>1</sup>Physical and Colloid Chemistry Department. Chemistry and Technology Institute. Ural Federal University named after the first President of Russia B.N. Yeltsin. Mira St., 19. Yekaterinburg, 620002. Sverdlovsk Region. Russia. Phone: +7 (343) 374-39-05. E-mail: boblv@el.ru, v.f.markov@urfu.ru, mln@ural.ru.

<sup>2</sup>Fire Safety in Construction Department. Research Department. Ural State Fire Service Institute of Emergency Ministry of Russia. Mira St., 22. Yekaterinburg. 620022. Sverdlovsk Region. Russia. Phone: +7 (343) 360-80-65. E-mail: smolnikovmi@mail.ru.

\*Supervising author; †Corresponding author

**Keywords:** cation exchange resin KU-2×8, hydrogen peroxide, copper(II) sulfate, kinetic studies, reaction rate constant, activation energy.

### Abstract

During the operation of nuclear power plants, spent ion-exchange resins are formed, which are heterogeneous radioactive low-level waste in the form of particles from a cross-linked organic polymer. Such resins may not always be regenerated. Therefore, the disposal of spent ion exchange resins is currently one of the primary problems at nuclear power plants. Conventional technologies for the processing of waste resins are relatively expensive. In addition, there are difficulties with transportation and storage of waste, and the disposal of spent ion exchange resins is a complex process. In the present study, an attempt has been made to solve the problem of spent ion-exchange resins utilization on example of the sulfonic acid cation exchanger's KU-2×8 oxidative degradation with the Fenton reaction. The decomposition of the cation exchanger was carried out with 20% hydrogen peroxide in the temperature range 323-353 K in the presence of a catalyst – low concentration copper(II) sulfate (0.001-0.009 mmol/l). The influence of process temperature and catalyst concentration on the reaction rate was estimated. When determining the rate of the cation exchanger KU-2×8 heterogeneous oxidation reaction with hydrogen peroxide in the presence of a catalytic additive, the spherical shape of the sorbent granules, the surface area of which changed during reaction, was taken into account. It was shown that with a reaction temperature increasing from 323 to 353 K, the rate constant of cation exchanger's oxidative decomposition have increased by a factor of 20-37. The activation energy values of the sulfonic acid cation exchanger's KU-2×8 decomposition with hydrogen peroxide in the presence of copper(II) sulfate are 89.7-115.2 kJ/mol, which indicates that the process is in the kinetic mode. It was established with electron-microscopic studies that the beads of the cation exchanger KU-2×8, when decomposed in H<sub>2</sub>O<sub>2</sub> solution in the presence of a catalyst can stick together, change their shape and volume, and their surface becomes covered with cracks. The studies performed showed almost complete catalytic decomposition of cation exchanger KU-2×8 in a hydrogen peroxide solution at 323-353 K after 420-220 minutes, which allows accelerating the oxidation at relatively low temperatures.

### References

- [1] M.I. Smolnikov, V.F. Markov, L.N. Maskayeva, A.E. Bobylev, and O.A. Mokrousova. Utilization problems of spent ion-exchange resins of nuclear power plants. *Butlerov Communications*. **2017**. Vol.49. No.3. P.119-134. DOI: 10.37952/ROI-jbc-01/17-49-3-119
- [2] J. Wang, Z. Wan. Treatment and disposal of spent radioactive ion-exchange resins produced in the nuclear industry. *Progress in Nuclear Energy*. **2015**. Vol.78. P.47-55.
- [3] I.B. Plecas, R.S. Pavlovic, S.D. Pavlovic. Leaching of <sup>60</sup>Co and <sup>137</sup>Cs from spent ion exchange resins in cement-bentonite clay matrix. *Bulletin of Materials Science*. **2003**. Vol.26. P.699-701.
- [4] J.F. Li, J.L. Wang. Advances in cement solidification technology for waste radioactive ion exchange resins: a review. *Journal of Hazardous Material*. **2006**. Vol.135. P.443-448.
- [5] C. Arsene, D. Negoiu. Degradation products of ion-exchange resin during the bituminization process of spent resins. *Revista de Chimie*. **2002**. Vol.53. P.118-121.

- [6] C. Arsene, D. Negoiu. The  $^{60}\text{Co}$ ,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  losses during the leaching test from the conditioned ion exchange block. *Revista de Chimie*. **2004**. Vol.55. P.308-310.
- [7] I.A. Sobolev, S.A. Dmitriev, F.A. Lifanov, S.V. Stefanovsky, M.I. Ojovan. Vitrification processes for low, intermediate radioactive and mixed wastes. *Glass Technology*. **2005**. Vol.46. P.28-35.
- [8] O.J. McGann, P.A. Bingham, N.C. Hyatt. Systematic development of alkaline-earth borosilicate glasses for caesium loaded ion exchange resin vitrification. *Ceramic Transactions*. **2013**. Vol.241. P.69-80.
- [9] M.S. Bortnikova, O.K. Karlina, G.Yu. Pavlova, K.N. Semenov, S.A. Dmitriev. Conditioning of slag formed during thermochemical processing of spent ion exchange resins. *Atomic Energy*. **2008**. Vol.105. No.5. P.274-278. (russian)
- [10] H.C. Yang, S.Y. Lee, Y.C. Choi, I.H. Yang, D.Y. Chung. Thermokinetic analysis of spent ion-exchange resins for the optimization of carbonization reactor condition. *Journal of Thermal Analysis and Calorimetry*. **2017**. Vol.127. P.587-595.
- [11] G. Brähler, R. Slametschka. Pyrolysis of spent ion exchange resins. *ATW – Internationale Zeitschrift für Kernenergie*. **2011**. Vol.56. P.404-406.
- [12] V. Luca, H.L. Bianchi, F. Allevatto, J.O. Vaccaro, A. Alvarado. Low temperature pyrolysis of simulated spent anion exchange resins. *Journal of Environmental Chemical Engineering*. **2017**. Vol.5. P.4165-4172.
- [13] K. Kim, S.H. Son, K.S. Kim, J.H. Han, K.D. Han, S.H. Do. Treatment of radioactive ionic exchange resins by super- and sub-critical water oxidation (SCWO). *Nuclear Engineering and Design*. **2010**. Vol.240. P.3654-3659.
- [14] A. Leybros, A. Roubaud, P. Guichardon, O. Boutin. Ion exchange resins destruction in a stirred supercritical water oxidation reactor. *Journal of Supercritical Fluids*. **2010**. Vol.51. P.369-375.
- [15] C. Cheng, H. Tong, W. Lan, S. Geng, H. Zhu. Design and experimental analysis of thermal plasma processing system for simulative radioactive resin waste. *Gaodiyana Jishu/High Voltage Engineering*. **2013**. Vol.39(7). P.1584-1589.
- [16] H.A. Castro, V. Luca, H.L. Bianchi. Study of plasma off-gas treatment from spent ion exchange resin pyrolysis. *Environmental Science and Pollution Research*. **2018**. Vol.25. P.21403-21410.
- [17] A.E. Kuznetsov, O.V. Knyazev, I.Yu. Mareev, M.N. Manakov. Biotechnological destruction of ion exchange resins. *Biotechnology*. **2000**. No.1. P.66-77. (russian)
- [18] H.S. Wu, T.H. Wu. Degradation of radioactive ion-exchange resin using  $\text{H}_2\text{O}_2$ . *Journal of the Chinese Institute of Chemical Engineers*. **2003**. Vol.34. P.263-274.
- [19] Z.R. Liang, Y.S. Wu, X.J. Liu. Pre-treatment of radioactive spent ion exchange resin by Fenton process. *Journal of Nuclear and Radiochemistry*. **2007**. Vol.29. P.71-74.
- [20] M. Zahorodna, R. Bogoczek, E. Oliveros, A.M. Braun. Application of the Fenton process to the dissolution and mineralization of ion exchange resins. *Catalysis Today*. **2007**. Vol.129. P.200-206.
- [21] T.L. Gunale, V.V. Mahajani, P.K. Watal, C. Srinivas. Studies in liquid phase mineralization of cation exchange resin by a hybrid process of Fenton dissolution followed by wet oxidation. *Chemical Engineering Journal*. **2009**. Vol.148. P.371-377.
- [22] Z. Wan, L. Xu, J. Wang. Disintegration and dissolution of spent radioactive cationic exchange resins using Fenton-like oxidation process. *Nuclear Engineering and Design*. **2015**. Vol.291. P.101-108.
- [23] Z. Wan, L. Xu, J. Wang. Treatment of spent radioactive anionic exchange resins using Fenton-like oxidation process. *Chemical Engineering Journal*. **2016**. Vol.284. P.733-740.
- [24] L. Xu, X. Meng, M. Li, J. Wang, J. Yang. Dissolution and degradation of nuclear grade cationic exchange resin by Fenton oxidation combining experimental results and DFT calculations. *Chemical Engineering Journal*. **2018**. Vol.361. P.1511-1523.
- [25] A.V. Zhelovitskaya, E.A. Ermolaeva, A.F. Dresvyannikov. Oxidation of organic compounds using a hydroxide radical generated in solutions by chemical and electrochemical methods. *Herald of Kazan Technological University*. **2008**. No.6. P.211-229. (russian)
- [26] M.M. Kozlova, A.E. Bobylev, V.F. Markov, L.N. Maskaeva, and M.I. Smolnikov. The kinetics of the sulfonic acid cation exchanger KU-2×8 oxidative decomposition with an aqueous solution of  $\text{H}_2\text{O}_2$ . *Butlerov Communications*. **2018**. Vol.56. No.12. P.102-110. DOI: 10.37952/ROI-jbc-01/18-56-12-102
- [27] A.N. Dyachenko, V.V. Shagalov. Chemical kinetics of heterogeneous processes: a training manual. *Tomsk: Publishing house of Tomsk Polytechnic University*. **2014**. 102p. (russian)