Influence of Water Treatment Plants on the Ecological Situation in Industrialized Regions

O I Volkova\textsuperscript{a}, N A Zolotukhina\textsuperscript{b}, V M Zolotukhin\textsuperscript{c}, M Y Yazevich\textsuperscript{d}

Kuzbass State Technical University named T.F. Gorbachev, Kemerovo, Russian Federation

E-mail: \textsuperscript{a}olvolkova94@mail.ru, \textsuperscript{b}zna.htnv@kuzstu.ru, \textsuperscript{c}zvm64@mail.ru, \textsuperscript{d}maria762003@list.ru

Abstract. The article investigates the most effective methods of water purification necessary for its application in power generating systems. The need for this is due to the need for water purification, bringing it to a quality state that allows it to be used in industry. The most effective modern method of purification is the method of using of ion-exchange resins, since water purified from the mineral elements contained in it (desalting) is mainly used. One of the effective methods of desalting, from an ecological and economic point of view, is ion exchange, based on the removal of inorganic substances, heavy metal ions and other substances from the water. The essence of this method is the ability, with the help of ion-exchange resins, to sorb unwanted elements and their compounds from water. This technology allows to achieve water quality which corresponds to standards (technical norms) in various spheres of consumption. The authors show the influence of various parameters on the efficiency of the ion exchange process in order to improve the quality of desalination and reduction of wastewater. The stages of desalination of process water are considered in order to determine the state of wastewater at different stages. Proposed alternatives is economically and environmentally beneficial solutions to problem with wastewater and analysed ways of regeneration, as well as advantages and disadvantages of switching from once-through regeneration in countercurrent. In the presented designs, when using filters with different regeneration options, positive characteristics of monodisperse resins necessary for water purification in accordance with the requirements of environmental standards are determined.

Introduction

Water resources of any state are national property, preservation and rational use of which affects economic [1], social and demographic [2] and other processes. First of all, we are talking about effective water resources management and biodiversity conservation in the industrial use of water resources and in the search for effective water treatment at various water objects including quarries [3] at coal enterprises. This problem is relevant for Kuzbass as an industrially developed region within the framework of preserving the ecological balance, including the use of innovative chemical technologies [4]. Preservation of ecological balance is important for ensuring safe living conditions of the population, transformation of socio-cultural values and improvement of the "quality of life" [5]. According to the state report "On the state and use of water resources of the Russian Federation in 2017" for the Kemerovo region is characterized by a situation where the water supply per inhabitant is 15.9 thousand cubic meters per year with a population of 2717.2 thousand people. Per inhabitant of the Siberian Federal district, an average of 102.3 thousand cubic meters per year, with a population of 19320.6 thousand people. Water resources are respectively 43.2 and 1975.7 cubic km per year [6, p. 13]. According to the total water intake, in 2010 Kemerovo region took the 10th place, and in 2017 – the 11th among various subjects of the Russian Federation. In terms of fresh water use in 2010 – 11th, and in 2017 – 10th place [6, pp. 167-168]. In terms of discharge of normative-treated water into surface natural reservoirs in 2010 24th place (21.43 million cubic meters) and in 2017 – 1st (165.94 million cubic meters) [7, p. 169]. In large cities of the Kemerovo region, wastewater discharge into surface natural reservoirs for the city Kemerovo was in 2009 – 111.6 million cubic meters, and in 2017 – 100.32 million cubic meters. For the city...
Novokuznetsk: in 2009 – 205.8 million cubic meters, and in 2017 – 69.6 million cubic meters [6, p. 165].

**Results and Discussion**

Water resources are actively used in various spheres of activity: domestic, industrial and agricultural, from the point of view of the fact that water is a raw commodity resource. Water purified from mineral elements contained in it (desalting) is mainly used. A variety of purification systems based on adsorption, ion exchange and reverse osmosis methods are currently on the market. However, so far the best method for desalting is the method of application of ion-exchange resins. The effectiveness of this method is due to the possibility of preparing water and its qualitative characteristics for use in power generating systems.

When preparing water of appropriate quality, various filters are used, the main purpose of which is to select the most acceptable (physicochemical, technological, economic, etc.) components for water purification. Filters that implement purification using the reverse osmosis method, effectively purify water of any mineralization from cations, are very effective, but have a disadvantage—a sufficient water pressure is required, which makes it difficult to widely use it.

Ion exchange filters are connected to a water tap and are quite effective, can work with a small water pressure. A significant advantage over reverse osmosis filters is a more affordable price, the disadvantage is the need to regenerate ion-exchange resins with acid and alkali solutions. The average efficiency of these filters is 90-98% [7].

The operation of water treatment plants (WTP) is accompanied by the formation of wastewater, which contains various impurities that have a negative environmental impact on their rational use in industry. For its further use, there are maximum permissible concentrations (MPC) of contaminants (Table 1). Allow them to be classified according to the degree of suitability for industry, as well as provide grounds for the development of methods and technologies for the treatment of these waters.

**Table 1. Maximum permissible concentrations of contaminants**

| The name of the substance | Unit of measure | Maximum permissible concentration of the substance |
|--------------------------|----------------|--------------------------------------------------|
| Suspended solids         | mg/dm³         | 300                                              |
| Chemically absorbed      | mg/dm³         | 500                                              |
| oxygen (CAO)             |                |                                                  |
| Chlorides                | mg/dm³         | 1000                                             |
| Sulfates                 | mg/dm³         | 1000                                             |
| Aluminium                | mg/dm³         | 5                                                |
| Iron                     | mg/dm³         | 5                                                |
| Manganese                | mg/dm³         | 1                                                |
| pH                       |                | 6-9                                              |

Sampling of wastewater is carried out according to GOST 31861-2012 (State Standard) [8]. To determine the amount of suspended solids used Federal environmental regulations PND F 14.1:2.3.110-97 [9]. The gravimetric method of measuring the mass concentration of suspended solids was used as the research method. The waste water sample is passed through a pre-weighed paper filter, the filter with the residue is weighed again, then dried in a drying cabinet at 105°C to a constant mass.

Determination of chlorides is carried out by Federal environmental regulations PND F 14.1:2.4.111-97 [10]. The mercurimetric method for determining the mass concentration of chlorides is based on the interaction of chlorides with mercury (II) ions to form a low-dissociated compound of mercury chloride. The excess of mercury (II) ions forms with the indicator diphenylcarbazone in an acidic medium a complex compound colored in purple, at the appearance of which the titration is stopped.

For the determination of sulfates in wastewater is used Federal environmental regulations PND F 14.1:2.108-97 [11]. The titrimetric method for determining the mass concentration of sulfates is based on the ability of sulfates to form a slightly soluble precipitate PbSO4 with lead ions. At the equivalence point an excess of lead ions react with dithizone with the formation of complex compounds. In this case, the color of the solution changes from blue-green to red-purple.
Iron in wastewater is defined by Federal environmental regulations PND F 14.1:2:4.50-96 [12]. The photometric method for determining the mass concentration of total iron is based on the formation of sulfosalicylic acid or its sodium salt with iron salts of colored complex compounds, moreover, in a weakly acidic environment, sulfosalicylic acid reacts only with iron (III) salts (red staining), and in a weakly alkaline environment-with iron (II) and iron (III) salts (yellow staining).

Determining the pH of wastewater after regeneration is the most important indicator, so its value is important. The measurement is carried out by Federal environmental regulations PND F 14.1:2:3:4.121-97 [13]. As a method of analysis, a potentiometric method is used, which is based on the electromotive forces of an electrode system consisting of a glass electrode and an auxiliary reference electrode with a known potential.

Using mercurimetric and photometric methods, the amount of substances contained in wastewater was determined (Table 2).

**Table 2. The results of analyses of wastewater**

| The name of the substance | Unit of measure | Maximum permissible concentration of the substance |
|--------------------------|----------------|---------------------------------------------------|
| Suspended solids         | mg/dm³         | 100                                               |
| Chlorides                | mg/dm³         | 30                                                |
| Sulfates                 | mg/dm³         | 150                                               |
| Iron                     | mg/dm³         | 3                                                 |
| pH                       |                | 6.5                                                |

Based on the results, it can be concluded that the substances contained in wastewater are included in the limit of MPC (maximum permissible concentration), are not dangerous for the environment and do not have negative consequences not only for human activities, but also for environmental and economic responsibility [14] and socio-economic risks [15] within the framework of environmental conservation.

Practically for each of the above methods of desalting is characterized, in addition to waste water, the formation of secondary pollution – waste water, precipitation. Insufficiently treated primary wastewater requires secondary neutralization and disposal necessary to preserve the environmental sustainability of water resources in general.

Waste water generated during the operation of the WTP (water treatment plant) depends on the principle of operation of treatment plants that are part of the WTP, which, ultimately, is determined by the technical and economic characteristics of the equipment used [16, 18].

The classical structure of the WTP includes two stages. At the first stage there is a preliminary removal of suspended solids from the treated water. The next step is the purification of colloidal particles and desalination of water.

During pretreatment, wastewater is not aggressive, the pH value is close to neutral (if reagent deposition methods were not used) and is characterized only by increased concentrations of suspended and colloidal particles, and wastewater of the second stage is highly aggressive, since it involves the use of acid and alkaline reagents to restore the ion exchange capacity of filters [17–21].

The second stage of preparation – desalination determines the formation of the following types of wastewater [17]:
- waste regeneration solutions formed during the regeneration of ion-exchange resins are solutions of sulfuric acid and sodium hydroxide;
- washing water, the first portions which are close in concentration to the waste regeneration solution.

The most common solution to the problem with wastewater is dilution with water to the MPC standards and subsequent discharge into the reservoir.

An environmentally friendly option is neutralization with dosing of appropriate reagents, however, during neutralization, secondary pollution – precipitation occurs [18, 22].

Dilution of wastewater is not beneficial from an environmental and economic point of view, as it leads to an increase in the concentration of mineral salts on the surface layers of water bodies. Its neutralization requires solving the issue of utilization of the formed precipitation.
An option to solve the problem with wastewater is to change the technological designs of existing filters. Solutions can be as follows:

- replacement of once-through regeneration to counter-current;
- application of monodisperse ion-exchange resins instead of polydisperse;
- introduction of membrane desalting methods at the last stage of WTP.

Since the use of membrane methods requires a large cost to change the design of the entire enterprise WTP, it is energy-consuming, which is not economically profitable.

An important point in the recovery of ionites is the supply of regenerating solution, in accordance with this regeneration is direct-flow and counter-current [22].

Direct-flow regeneration – the solution is fed top-down, counter-current regeneration – bottom-up.

When compared with direct-flow regeneration of ion-exchange resin, counter-current provides [22] not only a reduction in the consumption of reagents for regeneration (specific consumption), the quality of desalted water increases, which is accompanied by a decrease in water consumption for their own needs.

In direct-flow regeneration, the source water passes from top to bottom sequentially through filters loaded with cationite and anionite. The volume of ion-exchange resin is not more than 60 % of the internal volume of the filter [22–23]. The positive aspects of such a scheme include [23]: the possibility of changing the working volume of the ion-exchange resin; removal of contaminants from the top of the ionite layer, destroyed granules and simplicity of construction. The disadvantage is the insufficient degree of regeneration, since the granules clamped in the layer are poorly regenerated.

In counter-current regeneration, the source water is fed by analogy, as in direct-flow regeneration, passes through the ion-exchange resin layer and is excreted at the bottom. The reagent flow is fed from the bottom-up [24], which allows loosening the entire volume of the ionite. The use of this method allows to completely regenerate it and get rid of impurities inside the ion exchange resin layer, which is the main advantage of the regeneration method.

Due to the homogeneous granulometric composition of monodisperse resins compared with polydisperse can improve the kinetics of the desalting process, as well as increases the surface area of interfacial contact during ion exchange [22–24].

The use of monodisperse ion exchange resins in the WTP allows to reduce the specific consumption of regeneration solutions by 10–20 %, while the quality of the treated water is not reduced and the filter cycle is not reduced [24]. The service life of such ionites is about 12 years, while polydisperse ones are operated for no more than 10 years.

**Conclusion**

Thus, in order to improve the economic and environmental performance of WTP, it is necessary to change the regeneration system of ion-exchange resins from direct-flow to counter-current. It is advisable to switch to the technology of using monodisperse resins in filters, which in their characteristics are superior to polydisperse. This process will improve the efficiency of management in the field of water purification, which depends on the varying degrees of economic impact on activities. Payments for the negative impact on water bodies in 2010 amounted to 1,140 million rubles in the sphere of water supply and sanitation, and 418 million rubles in the sphere of mineral extraction. In 2016, these costs respectively amounted to 1296 and 218 million rubles. [6, p. 213]. The technological solution largely depends on the degree of compliance with water legislation, including the possibility of building unauthorized facilities in water protection zones.

**References**

[1] Grigashkina, S., Galanina, T., Mikhailov, V., Koroleva, T., Trush, E. Environmental and economic efficiency of comprehensive technology of sulfur oxides, nitrogen oxides and mercury removal from flue gases: E3S WEB OF CONFERENCES 2017. C. 02001.

[2] Zolotukhin, V., Bel'kov, A., Stepantsova, E., Kozyreva, M., Tarasenko, A. Demographic and migration policy in the mining region and its impact on the ecological consciousness of the population, 2017. - E3S Web of Conferences, 15,04015

[3] Tyulenev, M., Khoreshok A., Garina E., Litvin O., Litvin Y., Maliukhina E. A Method of effective quarry water purifying using artificial filtering arrays: IOP Conference Series: Earth and Environmental Science Current Problems and Solutions. Cep. "Ecology and Safety in the
Technosphere: Current Problems and Solutions" 2017. C. 012035

[4] Bel’kov, A., Zolotukhin, V., Zolotukhina, N., Sedina, N., Kozyreva, M. The Solution of Environmental Problems and the Dynamics of Demographic Processes in Industrialized Regions E3S Web of Conferences 134, 03005 (2019) SDEMR-2019 https://doi.org/10.1051/e3sconf/201913403005

[5] Zolotukhin, V.M., Zhukova, O.I. Man and Transformation of His Socio-Cultural Values in the Ethnic-National Aspect Smart Innovation, Systems and Technologies. - 2019, T. 139, p. 772-777

[6] State report "On the state and use of water resources of the Russian Federation in 2017". - Moscow: NIA-Priroda, 2018. - 298 p.

[7] Novikova, M. A. Methods of physical-chemical wastewater treatment / M. A. Novikova, A. S. Pacholak, O. N. Romanova // Fundamental and applied studies in the modern world. — 2014. — No. 7. — 83–86 p.

[8] State Standard GOST 31861-2012. Water. General requirements for sampling. - in. 2014 – 01 – 01. - Moscow: STANDARDINFORM, 2013. – 7 p.

[9] Federal environmental regulations PND F 14.1:2.3:110-97. Quantitative chemical analysis of waters. Methods of measuring the mass concentration of suspended solids in samples of natural and wastewater gravimetric method. – 2016 – 09 – 01. – M: Akvatest, 2016. – 5 p.

[10] Federal environmental regulations PND F 14.1:2:4.111-97. Methods of measuring the mass concentration of chlorides in drinking, surface and wastewater mercurimetric method. – 2011 – 03 – 23. – M.: Akvatest, 2011. – 6 p.

[11] Federal environmental regulations PND F 14.1:2.108-97. Technique of execution of measurements of mass concentrations of sulphate in the samples of natural and treated waters by titration with lead salt in the presence of dithizone. – 1997 – 03 – 21. – M.: Akvatest, 2004. – 7 p.

[12] Federal environmental regulations PND F 14.1:2.4:50-96. Method of measurement of total iron mass concentration in drinking, surface and wastewater by photometric method with sulfosalicylic acid. – 2011 – 03 – 23. – M.: Akvatest, 2011. – 6 p.

[13] Federal environmental regulations PND F 14.1:2:3: 121-97. Guidelines for the application of methods of pH measurements in waters potentiometric method. – 1997 – 03 – 04. – M.: Akvatest, 2004. 16 p.

[14] Kovalevsky, S., Ravochkin N., Shchennikov V. Ecological and social-responsibility of coal mining companies E3S Web of Conferences Electronic edition 2018.

[15] Kiseleva T.V., Mikhailov V.G. Management of current environmental costs contributing to reduce eco-economic risk: IOP Conference Series: Earth and Environmental Science. Cep. "International Scientific Conference on Knowledge-based Technologies in Development and Utilization of Mineral Resources" 2018. C. 012050

[16] Kurtukova, L. V. Creation of eco-efficient technology of softening of natural waters with the use of new types of materials // L. V. Kurtukov, V. A. Somyn, L. F. Komarova / Polzunovskii Herald. — 2012. — No. 3-1. — 217–219 p.

[17] Vivek, V. Ranade, Vinay M. Bhandari. Industrial Wastewater Treatment, Recycling and Reuse. – Elsevier Ltd., Publication, 2014. – 577 p.

[18] Krivoshein, D. A. Fundamentals of ecological safety of production / D. A. Krivoshein, V. P. Dmitrenko, N. V. Fedotov // From the LAN. – 2015. – 336 p.

[19] Ebewele, R. O. Polymer science and technology. - CRC Press, 2010. – 544 p.

[20] Liw, Z.S. Preparation of superabsorbent polymer by crosslinking acrylic acid and acrylamide copolymers. - J. Appl. Polym. Sci., 2007. – 64 p.

[21] Pavlov, D. V. Universal system of industrial wastewater treatment / D. V. Pavlov, V. A. Kolesnikov // water Treatment. – 2013. - No. 1. – 12 – 16 p.

[22] Doskina, E. P., Treatment and disposal of municipal wastewater precipitation / E. P. Doskina, Moskvicheva A.V., E. V. Moskvicheva, A. A. Geraschenko // V.: VSTU. – 2018. – 186 p.

[23] Mannanova, G. V. Methods of industrial wastewater treatment / G. V. Mannanova // M.: SINTEG, 2015. – 539 p.

[24] Voronov, Yu. V. Wastewater Disposal and treatment / Yu. V. Voronov, S. V. Yakovlev // M.: publishing house DIA, 2016. – 704 p.