Resource-Efficient Technologies 4 (2020) 1-9





**Resource-Efficient Technologies** 

journal homepage: http://reffit.tech

### **Review Article**

# EFFECTIVE APPROACH TO WATER PURIFICATION FROM MICROBIOLOGICAL CONTAMINATION BASED ON NOVEL SURFACE-MODIFIED ADSORBENTS

Martemianova I.<sup>1</sup>, Tin H. L.<sup>2</sup>, Duong H. H.<sup>3</sup>, Martemianov D.<sup>1</sup>, Plotnikov E. <sup>4\*</sup>

<sup>1</sup>Polytech ltd, Tomsk, Russia <sup>2</sup>Sunny-Eco JSC, Hanoi, Vietnam

<sup>3</sup> Institute for Water and Environment, Vietnam Academy for Water Resources, Hanoi, Vietnam

<sup>4</sup> Mental Health Research Institute, Tomsk National Research Medical Center, Russian Academy

of Sciences, Tomsk, Russia

# Abstract

In this work, we provide a literature review of water treatment techniques and propose a novel resource-efficient solution for the purification of aqueous media from microbiological contamination. **Methods:** Combined filter sorbents were developed and studied based on novel modified nanostructured filter materials. Synthetic and natural zeolite were used as the mineral base. The production technique was optimized to coat minerals with aluminum oxyhydroxide by means of a sol–gel process. Additional treatment with fine zinc particles obtained by electrospark dispersion was applied to modify the sorbent surface and obtain the surface charge required. **Results:** The antibacterial, sorption and physicochemical properties of the samples as well as their surface structures were investigated. According to broad microbiological tests, the possibility of purifying bacterial-contaminated water was demonstrated to an acceptable level by means of adsorption filtration. **Conclusion:** The proposed novel approach for water treatment against bacterial contamination can be considered an alternative to the currently available water treatment technologies.

Keywords: Zeolite, Water purification, Aluminum oxyhydroxide, Escherichia coli, Zinc nanoparticles.

# 1. Introduction

Among the pollutants present in the Earth's hydrosphere, microbiological impurities are especially dangerous to humans [1]. The biological factor of water pollution can be defined as the sum of its biological components. The impact of these components on the environment and humans is related closely to their ability to reproduce under natural or artificial conditions. These components produce biologically active substances that, when released into the environment,

\* Corresponding authors: Dr. Evgenii Plotnikov,

E-mail: plotnikov.e@mail.ru

☆ Peer review under responsibility of Tomsk Polytechnic University. https://doi.org/10.18799/24056537/2020/4/275 have adverse effects on both living organisms and the environment itself. Water sources always contain microorganisms, among which there may be pathogens, some of which cause lethal diseases. The main sources of biological pollution are domestic sewage and wastewater from enterprises (primarily farms, dairy and sugar factories, and meat processing plants) [2].

Notably, pathogens can also be found in groundwater [3]. The pathogenic microorganisms found in water change the environment as well as the water itself over time, causing it to manifest new properties that may cause disease [4]. Statistics show that one of the main causes of illness and death in the world is the use of water containing pathogens [5]. As a result of changes in various factors, such as the socioeconomic, demographic, ecological, or immunological state of a population, there will be a corresponding adaptation of pathogenic microorganisms to new conditions, which represents a significant problem for public health. Despite the development of technology and the level of hygiene in society, a large number of people in the world still live with limited access to clean drinking water [6].

Therefore, in modern water treatment, it is especially important to reliably remove bacterial contaminants from the water being used [7]. In most cases, natural water does not meet the standard hygienic requirements for drinking. Therefore, water must be purified and disinfected before being supplied to consumers. Natural water used for drinking and industrial purposes must be harmless and comply with both sanitary and epidemiological indicators. The standard water treatment includes water filtration and disinfection. When water is purified from microbiological contaminants, impurities contained previously in the source water are removed to a particular degree, depending on the effectiveness of the purification [8]. At present, the treatment of water from microbiological pollutants can be divided into two categories: mechanical water purification and disinfection. Purifying water from microbiological pollutants is a process by which bacteria, viruses, fungi, microalgae, and protozoa are extracted from the aquatic environment. As a rule, disinfection requires the introduction of chemical reagents into the water, and secondary pollution thus occurs. Reagents can react with the impurities contained therein to form more hazardous compounds. The advantage of water disinfection processes is prolonged action and a wide antibacterial and antiviral spectrum [9]. As a result of disinfection, microbiological impurities are not removed from the water but are instead destroyed [10]. However, with disinfection, organic bacterial residues and chemical reagents remain in the treated water and can be toxic and allergenic. In addition, the methods of water disinfection existing in modern water treatment systems cannot achieve 100% efficiency in destroying microorganisms.

Among the various methods to neutralize microbiological contaminants, the most common are ultraviolet sterilization, chemical and thermal treatment (ozonation and chlorination, respectively), and membrane purification.

The ultraviolet sterilization of water is a fairly effective approach for purification [11]. Ultraviolet radiation of a certain wavelength has a detrimental effect on the enzyme systems of bacteria. When water is treated in this way, irreversible damage to the DNA, RNA, and cell membranes of microorganisms occurs as a result of photochemical reactions. However, the UFO method is incapable of disinfecting turbid waters and is quite expensive, while toxins may be formed owing to the decomposition of dead bacteria.

The membrane purification of aqueous media is the most effective method to remove a wide range of inorganic and organic pollutants as well as pathogenic microorganisms from water [12]. According to this method, water molecules pass (are filtered) through the pores of the membrane, while microorganisms (bacteria, viruses, etc.) remain on the surface of the membrane because their size is larger than the pore diameter. Compared with other membrane methods, reverse osmosis is the most effective method and has been used in the water treatment industry since the 1970s. The main disadvantage of the membrane method is the need to create an increased pressure (from 2 to over 20 kgf/cm<sup>2</sup>). In addition, the cleaning membrane quickly becomes clogged with pollutants, and additional water is required to flush it, which then goes down the drain and into the sewer (up to 75 % of the purified water). Sediment formation also occurs on the surface of membranes, reducing the economic performance of the method. As a rule, such membranes are short-lived and need to be replaced after a while. Chemical methods of disinfection are based on the addition of various chemicals (reagents) to water that contribute to the death of the microorganisms it contains. Chlorination is the most widespread and affordable method of chemical water disinfection [13] because of its simplicity, the low cost of liquid or gaseous chlorine, its ease of maintenance, and the high bactericidal properties of chlorine. Liquefied chlorine is used most often in this process, but other reagents, such as bleach, chlorine dioxide, chloramines, calcium, and sodium hypochlorites, are also employed.

The process of ozonating water for disinfection is a method used widely and improves the water quality significantly by killing microorganisms and oxidizing chemical impurities [14]. This method is much more efficient than the chlorination process. However, ozone is unstable and exists for only 30–40 minutes in water, while the products obtained in the process of ozonation of water can affect human health negatively. In addition, ozonation plants have a high cost and high energy consumption.

Although all these purification methods have advantages, they all also have major disadvantages. Therefore, new resource-efficient methods to purify different aqueous media from microbiological pollutants must be discovered urgently. The problem of urban wastewater should also be especially emphasized, as it has grown to a global scale due to the growth of human society. Combining different water treatment methodologies is considered to be a promising solution to recycle wastewater [15].

If followed by disinfection, plain filtration is also effective in achieving discharge standards for wastewater [16]. In this regard, the development of new sorbents that possess bacteriostatic properties could considerably improve this method. Removing disinfection products from drinking water is a problem in itself, and various approaches have been used to solve it. Flexible reverse osmosis is a newly proposed technology to purify and save water simultaneously by recycling brine into inlet water [17]. However, this approach is quite expensive. Nanofiltration is also used to purify drinking water and has been applied increasingly in municipal water treatment plants because it has a high removal rate of organic pollutants, while it simultaneously reserves significant amounts of minerals beneficial for drinking water [18]. Compared with conventional drinking water treatment, membranes efficiently remove color and turbidity, ions (up to 97 %), metals and metalloids (ranging from 80 to 100%) and pharmaceuticals [19].

Increased industrial activity and population growth have led to an acute and permanent shortage of fresh water resources. The purification of industrial wastewater by removing toxic pollutants to make it suitable for agriculture requires an effective approach [20].

It should be noted that, in recent years, the use of sorption technologies has been increasing in the field of water purification. Usually, sorption materials are used for water purification against chemical pollutants, including arsenic [21], iron [22], and other heavy metals [23]. New sorbents have now appeared that can extract microorganisms from aqueous media [24]. This ability is not based on the effect of mechanical filtration (sieve effect), but on the specific sorption properties of the materials. The majority of microorganisms in water are in an electronegative state. The reliable extraction of these impurities from an aqueous medium is possible only with the help of sorbents with a positive electrokinetic potential. Here, we can use the principle of electrokinetic adsorption, according to which negatively charged microorganisms are attracted to the surface of a sorbent with a positive potential. This is a new and highly promising niche in the field of creating modified sorbents [25]. The approach is based on the fact that the new materials represent a different fibrous base, on which the nanofibers of aluminum oxyhydroxide are immobilized in the form of an active component [26]. Surface-modifying agents can be obtained from a variety of starting materials, even concrete [27].

It was discovered previously that aluminum oxyhydroxides can form an electropositive charge in an aqueous medium [28]. However, the magnitude and sign of the charge depend on the reagents used and the method of producing aluminum hydroxides and oxides. A similar effect has been shown for nanosized filter materials [29], such as a non-woven material containing nanosized powders [30]. This material is intended for the filtration of liquid media to extract contaminants, including microorganisms. The effect is achieved by a mixture of alumina nanofibers and secondary fibers arranged in a matrix, creating asymmetric pores with an average size of 5-48 µm. The secondary fibers are microglass fibers, cellulose fibers, and fibrillated cellulose fibers. The most effective samples for tissue filtering nanomaterials show efficiencies in the extraction of bacteria and virus models from aqueous media within a range of 99.9 % for *Escherichia coli* (initial concentration:  $5.9 \times 10^5$ colony-forming units [CFU]/cm<sup>3</sup>) and 99.999 % for bacteriophage MS2 (initial concentration:  $1.1 \times 10^5$  $PFU/cm^{3}$ ).

The disadvantages of these materials are that they cannot be used in standard water treatment equipment and do not have bacteriostatic properties. The common disadvantages of such technologies also include a small working range regarding the pH of the purified medium, the low mechanical strength of fabric filter adsorbents, and the high cost of the materials used.

Considering all the advantages and disadvantages of nanostructured electropositive filter sorbents, we can conclude that they are promising for private and industrial water treatment. However, this would require improving their operational characteristics, reducing their cost, and increasing the overall resource efficiency in production and use.

In this context, we propose and describe in detail a new approach for water treatment using powdered materials as an adsorption base for novel nanomaterials. Powders, as a rule, have a small specific surface area, but high technical and operational properties when used in a variety of water treatment equipment. Obtaining the bacteriostatic properties of these materials is also difficult. Among the known filter sorbents with bacteriostatic and bactericidal characteristics, these properties are imparted by modifying material using silver compounds, which are expensive and not applicable to the mass segment.

Investigations of the physicochemical, filtration, and bactericidal properties of novel nanostructured filter materials with combined surface modifications to achieve supreme sorbent efficacy against bacterial contamination may lead to a novel effective method for water treatment.

# 2. Methodological Section

Natural zeolite from the Kholinsky deposit (LLC "Kholinsky zeolites," Russia) and synthetic zeolite NaX (LLC Molecular Sieve Plant "REAL SORB," Russia) with fraction sizes 0.1–0.5 mm were used as materials for the production and study of novel nanostructured filter sorbents. The structure of Kholinsky zeolite can be represented by a three-dimensional grid of alternating tetrahedra including many chemical elements and saturated with oxygen atoms.

Synthetic zeolite NaX is an artificial mineral and is used for the deep drying and fine purification of gases and liquids, separation of gaseous and liquid mixtures, separation of hydrocarbon mixtures, and air separation. The chemical formula of the zeolite is NaX\*Na<sub>2</sub>O\*Al<sub>2</sub>O<sub>3</sub>\*2.5SiO<sub>2</sub>\*H<sub>2</sub>O. The material has a developed porous structure, with pores that have precisely defined dimensions.

Aluminum oxyhydroxide was obtained from raw materials in the form of food-grade aluminum using a sol–gel process. During this synthesis, nanofibers of aluminum oxyhydroxide were immobilized on a zeolite surface. An aluminum plate was ground using a JET JPSG-0618SD surface grinder (JET, Switzerland). Then, the crushed aluminum was sieved using a laboratory sieve (Vibrotekhnik LLC, Russia) with a mesh size of 0.1 mm. The resulting fraction of aluminum of size less than 0.1 mm was used in the synthesis of the nanostructured filter adsorbent.

Bactericidal properties were realized in the sorbents because of the immobilization of fine particles of zinc compounds on the surface of the carriers. Zinc particles were obtained by electrospark dispersion from zinc granules. To carry out the electrospark dispersion, the installation described in Zhuravkov et al. [31] was assembled. A positive charge was imparted to the surfaces of minerals by immobilizing nanofibers of aluminum oxyhydroxide using the solgel technology described in Martemyanov et al. [32].

To impart the required fractional composition (0.1–0.5 mm) to the carrier, the initial fraction of zeolites was ground in an agate mortar (Xiamen Tob New Energy Technology Co., Ltd., China) and passed through sieves (Vibrotechnik LLC, Russia) with mesh sizes of 0.1 and 0.5 mm.

The morphology of the modified surface of the developed nanostructured filter adsorbents and their individual components was studied by transmission electron microscopy using a JEM-100-CXII electron microscope (JEOL, Japan).

The specific surface area and specific pore volume of the developed filter sorbents as well as their carriers, intermediate products, and active components were determined using the thermal desorption of nitrogen on a Sorbtometer-M specific surface area analyzer (OOO Katakon, Russia).

Measurements of the zeta potential of the studied samples were taken using a Zetasizer Nano ZSP device (Malvern Instruments, Great Britain) in automatic mode, based on the electrophoretic mobility of particles using the dynamic light scattering method. The samples were prepared prior to the zeta potential study. For their preparation, the samples under study were ground in an agate mortar (Xiamen Tob New Energy Technology Co., Ltd., China) and then passed through a sieve (Vibrotechnik LLC, Russia) with a mesh size of 0.1 mm. A sample of material with a particle size less than 0.1 mm was taken and a suspension of the test samples was prepared. A 0.02-g portion of the sample was weighed and suspended in 20 cm<sup>3</sup> of distilled water and subjected to short-term ultrasonic action (~3-4 s), and an aliquot (~1 cm<sup>3</sup>) was taken and placed in a measuring cell. A dynamic mode was used to carry out the study of the filtration properties of the nanostructured materials and their components to extract E. coli bacteria from the model suspension. The installation for the test consisted of a tank with a volume of 250 dm<sup>3</sup>, a peristaltic pump (Calpeda, Italy), a filter module, a receiving tank, and a pipeline connecting all the components. The model bacterial suspension was pumped from the tank through the loading of the filter material, and the filtrate entered the receiving tank. The filter module height was 100 mm and its inner diameter was 42-46 mm. The objects of study for the microbiological testing were natural zeolite from the Kholinsky deposit (fraction 0.1-0.5 mm),

synthetic zeolite NaX (fraction 0.1–0.5 mm), a novel surface-modified sorbent based on Kholinsky zeolite (fraction 0.1–0.5 mm), and a novel surface-modified sorbent based on synthetic zeolite NaX (fraction 0.1–0.5 mm). The surface-modified sorbent was loaded into the filter module at 20 vol. %, while the rest of the volume was natural zeolite (80 vol. %). Viscose fabric (GeoSM, Russia) was placed between the materials in the module to separate them into layers.

A test bacterial suspension was prepared in tap water, which was settled for 24 hours to remove chlorine, and then seeded with *E. coli* ATCC 25922 (Liofilchem, Italy), leading to a final concentration of  $1.7 \times 10^7$  CFU/cm<sup>3</sup>.

*E. coli* strains are used widely to prepare model solutions in microbiological studies. These bacteria have been studied and characterized extensively and are the most convenient and versatile organisms for screening tests.

Filtration studies were conducted at three speed modes at capacities of 10, 20, and 40 dm<sup>3</sup> per hour. In the final stage,  $500 \text{ dm}^3$  was filtered through sorbents, and control probes for microbiological studies were taken every  $50 \text{ dm}^3$ .

Bacteria were counted by the membrane accumulation method. The investigated filtrates and the initial model solution were passed through bacterial concentration membranes (Elema-N LLC, Russia). Then, the membranes were placed on Endo agar in Petri dishes (Petroplast LLC, Russia) and placed in a B6 thermostat (Thermo Fisher Scientific, Germany). The cultures were then incubated at a temperature of  $37^{\circ}$ C  $\pm 1^{\circ}$ C for 24 hours. After 24 hours, a visual count of the colonies was carried out, measured in CFU/cm<sup>3</sup>.

To determine the antibacterial properties of the studied sorbents and their constituents, contact inhibition was used as a diffusion method for E. coli ATCC 25922 (Liofilchem, Italy) on a solid nutrient medium. The technique was as follows. First, a 24-hour culture of E. coli with a concentration of  $1.4 \times 10^7$  CFU/cm<sup>3</sup> was seeded on a Petri dish 90 mm in diameter with meat peptone agar. The cups were dried in air for 10 minutes. On the back surface, the sample application zones were marked. Then, the studied sorbent was weighed in 0.1-g amounts, and the sorbent was placed on a seeded Petri dish in the corresponding marked areas. After 24 hours, the contact suppression of microbial growth was measured in millimeters within the sorbent zones. The transpiration of the inhibition zone (absence of bacterial growth) was assessed visually in transmitted light.

#### 3. Results and Discussion

An analysis of the major surface characteristics of the novel sorption nanomaterials revealed a slight increase in all the parameters studied, in comparison with the initial minerals. In general, the changes observed in characteristics were not critical in improving the sorption properties. The values established for the specific surface area and specific pore volume of the nanostructured filter sorbent samples as well as those of their carriers and active components are presented in Table 1.

Sample	Particle size, mm	Specific surface area, m <sup>2</sup> /g	Specific pore vol- ume, cm <sup>3</sup> /g
Natural zeolite	0.1–0.5	28.84	0.012
Synthetic zeolite	0.1–0.5	340.47	0.146
Aluminum oxyhydroxide	≤0.1	192.68	0.084
Zinc compound particles	≤0.1	21.42	0.009
Modified sorbent based on natural zeolite	0.1–0.5	45.71	0.02
Modified sorbent based on syn- thetic zeolite	0.1–0.5	355.7	0.152

**Table 1.** Specific surface area and specific pore volume ofthe materials studied

The differences among the parameters of natural and synthetic minerals should be noted. From Table 1, it can be seen that the synthetic zeolite had a specific surface area and specific pore volume an order of magnitude larger than those of natural zeolite. Therefore, the modification of the zeolite with active components led to a significant increase in surface characteristics (>50 %). After modifying the minerals, one would expect a sharp increase in surface parameters and a radical increase in the sorption capacity of artificial zeolite. This was not observed when modifying the synthetic zeolite with active components.

An important characteristic of particles is their hydrodynamic radius, which is determined largely by the zeta potential. Table 2 shows the zeta potentials of the nanosorbent samples studied, their individual mineral carriers, and their active components. **Table 2**. Zeta potentials of the sorbents studied and their individual components

Sample	Particle size, mm	Surface zeta potential (3av), mV
Natural zeolite	0.1 - 0.5	-28.00

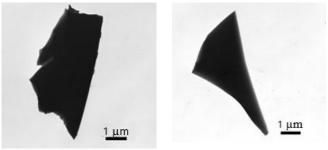
Synthetic zeolite	0.1–0.5	-38.20
Aluminum oxyhydroxide	≤0.1	33.20
Zinc compound particles	≤0.1	8.79
Modified sorbent based on natural zeolite	0.1–0.5	22.4
Modified sorbent based on synthetic zeolite	0.1–0.5	26.1
Modified sorbent based on natural zeolite with bacte- ria	0.1–0.5	-20.00
Modified sorbent based on synthetic zeolite with bacte- ria	0.1–0.5	-31.90

We determined the zeta potentials of the surfaces of the sorption materials obtained, including those with E. coli bacterial culture adsorbed on their surface at a concentration of  $2.8 \times 10^7$  CFU/cm<sup>3</sup>. The modification of mineral surfaces with active components was found to lead to the appearance of a positive charge. As a result, the modified sorbents had a positive surface charge that would interact with microorganisms. The synthetic zeolite had a slightly higher positive surface charge than the sorbents based on natural zeolite. This result can be explained by the fact that the specific surface area of the original synthetic zeolite was significantly higher than that of natural zeolite, and a larger amount of active components (aluminum oxyhydroxide) with a positive charge can be immobilized on a larger surface. The inner surface (closed) with a negative charge barely interacted with the microbiological contaminants. Charged surface could be one of the effective solutions in microbiological water purification.

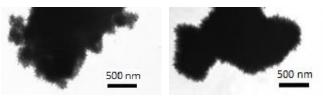
The study of the surface morphology of the samples using transmission electron microscopy revealed the polymorphism of the sorbent particle structures. Figure 1 shows the scanning electron microscopy (SEM) images of the natural and synthetic zeolite at  $7,200 \times$  magnification.

The surfaces of these particles were slim, but they had sharp angles. Neither particle had a spherical shape, and they looked similar to each other (Figure 1).

The surface modification covered the particles with nanofibers of aluminum oxyhydroxide 150–200 nm in length and 2 nm in width (Figure 2). Fine zinc particles are not visible under the nanofibers of aluminum oxyhydroxide. At the same time, the nanoscale coating on the modified sorbents is an even layer, even in difficult and sharp areas. Taking this surface morphology into account, it is assumed that these particles can suppress the growth of bacteria not only by chemical action with zinc ions but also by mechanical damage and dislocation of the bacteria by nanoneedles [33]. Bactericidal surfaces are currently being investigated thoroughly and seem to be a promising alternative to chemical treatment [34]. This interesting phenomenon could be used to develop a new generation of bacteriostatic sorbents. The results of the bacteriological test thus confirm the presence of a weak antibacterial effect in the modified sorbents. The evaluation results of the test samples in suppressing the growth of *E*. *coli* at a concentration of  $1.4 \times$  $10^7$  CFU/cm<sup>3</sup> are presented in Table 3.



**Fig. 1.** SEM photomicrographs of zeolite particles at 7,200× magnification: (a) natural zeolite and (b) synthetic zeolite

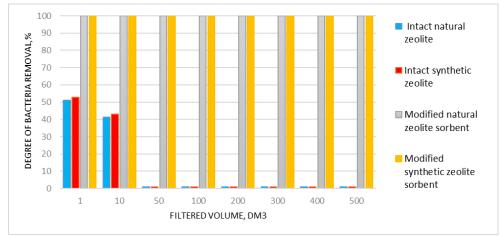


**Fig. 2.** SEM photomicrographs (10,000× magnification) of sorbents based on (a) natural zeolite and (b) synthetic zeolite

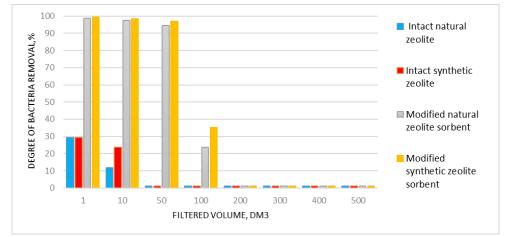
**Table 3.** Determination of bactericidal properties of sorption materials and their individual components

Sample	Zone of inhibition of bacterial growth, mm
Natural zeolite	0
Synthetic zeolite	0
Aluminum oxyhydroxide	5
Zinc compound particles	0
Modified sorbent based on natural zeolite	1
Modified sorbent based on synthetic zeolite	1

Table 3 shows that both the initial minerals and their active component, aluminum oxyhydroxide, did not possess bactericidal properties, as there was a continuous growth of bacteria around and under the sample, and there was no zone of microorganism suppression. The pure fine zinc particles had a large microbial inhibition zone of approximately 5 mm, while the modified sorbents suppressed the growth of microorganisms under a sample of materials and within a radius of 1 mm surrounding them. The very presence of this zone can be considered a desirable property. For this reason, testing the sorption properties of modified materials in relation to microbiological contaminants was of great interest. In the course of the microbiological testing of the samples, the surfacemodified samples were found to have a significant advantage compared with the intact minerals. Testing was carried out at various filtration rates ranging from 10 to 40 dm<sup>3</sup> per hour.



**Fig. 3.** Degree of bacteria removal from the model suspension by intact and modified sorbents at a filtration rate of 10 dm<sup>3</sup> per hour



**Fig. 4.** Degree of bacterial removal from the model suspension by intact and modified sorbents at a filtration rate of 40 dm<sup>3</sup> per hour

Figure 3 shows a comparison of the filtration characteristics of the intact minerals and novel modified sorbents (natural and synthetic zeolites; fraction 0.1-0.5 mm) in the process of extracting *E. coli* from a model solution at a filtration rate of 10 dm<sup>3</sup> per hour. Under these conditions, the intact natural zeolite showed poor filtration of *E. coli*. Some degree of bacterial removal was observed in the first and tenth liters of the filtrate, and the most significant result reached 51.18 % purification based on the initial concentration of bacteria ( $1.7 \times 10^7$  CFU/cm<sup>3</sup>). This value is six orders of magnitude higher than the usual maximum permissible concentration (MPC). The synthetic zeolite had a similar weak performance in filtering *E. coli* from the model solution. On the contrary, high-quality removal of microorganisms from the aqueous medium ranging from 1 to 300 liters of filtrate was observed for the modified sorbent based on natural zeolite (at 10 dm<sup>3</sup> per hour), with complete purification being underway (0 CFU/cm<sup>3</sup>). At 400 liters of filtrate, a small breakthrough of bacteria into the filtrate began (16 CFU/cm<sup>3</sup>). However, this was also higher than the MPC. For modified synthetic zeolite, the recovery of microorganisms from an aqueous medium was also very good from 1 to 300 liters of filtrate, and complete purification was underway (0 CFU/cm<sup>3</sup>). At 400 liters of filtrate, bacterial breakthrough into the filtrate was visible (6 CFU/cm<sup>3</sup>). At 500 liters of filtrate, 95 CFU/cm<sup>3</sup> was observed, which is a relatively low value but is still higher than the MPC.

A significant increase in the filtration rate up to 40 dm<sup>3</sup> per hour led to an unsatisfactory recovery of microorganisms after 50 liters of filtration (Figure 4). At the same time, after 200 liters of filtration, the degree of extraction of microorganisms decreased further, and water purification did not occur for any sorbent type.

However, with a decrease in the rate of transmission of the model solution through the layer of the studied modified sorbent, there was a significant increase in the degree of extraction of microorganisms from the aqueous medium. Thus, an increase in the contact time between the surface of the modified sorbents and the contaminated aqueous medium made it possible to clean the model solution from *E. coli*. The modified sorbents based on synthetic zeolite demonstrated slightly better characteristics for cleaning microorganisms from the model solution than the natural sorbents (Fig. 4).

In this study, large fractions of unmodified minerals had a low extraction of bacteria from the model suspension, thus indicating that they cannot be used for microbiological filtration, even with a slow pump rate. We suppose this is because of the lack of charge

#### References

- Grabow W.O.K. Waterborne diseases: Update on water quality assessment and control. Water SA, 1996, 22, pp. 193–202.
- [2] Slifko T.R., Smith H.V., Rose J.B. Emerging parasite zoonoses associated with water and food. *International Journal for Parasitology*, 2000, vol.30, no.12–13, pp. 1379–1393. doi: 10.1016/S0020-7519(00)00128-4
- [3] The world health report 1997 conquering suffering, enriching humanity. World Health Organization, Geneva, Switzerland, 1997, pp. 127–129. Available at: https://www.who.int/ whr/1997/en/
- [4] Woolhouse M.E.J. Population biology of emerging and reemerging pathogens. *Trends in Microbiology*, 2002, vol.10, no.10, pp. S3–S7. doi: 10.1016/s0966-842x(02)02428-9
- [5] Taylor L.H., Latham S.M., Woolhouse M.E.J. Risk factors for human disease emergence. *Philosophical Transactions* of the Royal Society London – B: Biological Sciences, 2001, vol. 356, no. 1411, pp. 983–989. doi: 10.1098/rstb.2001.0888
- [6] Desselberger U. Emerging and re-emerging infectious diseases. *Journal of Infection*, 2000, vol.40, no.1, pp. 3–15. doi: 10.1053/jinf.1999.0624

on the sorbent surface. Surface-modified nanostructured sorbents have much better characteristics as well as a positive charge, which is key to extracting bacteria from a model suspension. Further development of this approach and extended testing on natural samples of polluted waters are of considerable interest.

### 4. Conclusion

In this study, the combined surface modification of minerals with nanosized aluminum oxyhydroxide and zinc nanoparticles to improve the extraction of microorganisms from aqueous media was developed and analyzed for the first time. The specific surface area and specific pore volume of the studied samples were found to barely affect the degree of sorption of microorganisms, while the presence of a charge on the sorbent surface was a critical parameter. The technique used to modify the surface of minerals could become the basis for a resource-efficient approach to water treatment based on cheap feedstock. This approach can also be considered an alternative to the currently available water treatment technologies.

#### **Conflict of Interest**

The authors declare that there are no conflicts of interests.

- [7] Emerging Issues in Water and Infectious Disease. World Health Organization, Geneva, Switzerland, 2003. Available at: https://www.who.int/water\_sanitation\_health/emerging/emerging.pdf
- [8] Tyrrell S.A., et al. Inactivation of bacterial and viral indicators in secondary sewage effluents, using chlorine and ozone. *Water resources*, 1995, vol. 29, no.11, pp. 2483– 2490. doi: 10.1016/0043-1354(95)00103-R
- [9] Venczel L.V. et al. Inactivation of Cryptosporidium parvum oocysts and Clostridium perfringens spores by a mixed-oxidant disinfectant and by free chlorine. *Applied and Environmental Microbiology*, 1997, vol. 63, no. 4, pp. 1598–1601. doi: 10.1128/aem.63.4.1598-1601.1997
- [10] Ainsworth R.G. Safe piped water: Managing microbial water quality in piped distribution systems. Geneva, World Health Organization, 2004, 147 p.
- [11] Guyader Le F. Use of an RT-PCR internal control to evaluate viral removal. *Water Science and Technology*, 1997, vol. 35, no. 11–12, pp. 461–465.
- [12] Taylor J.S., Wiesner M. Membranes, In: Letterman RD, Water Quality and Treatment. New York, McGraw Hill, Inc, 1999, Chapter 11, pp. 1–71.
- Bryda K., Sellman L. Recent developments in cleanup technology. *Remediation*, 1994, vol. 4, no. 4, pp. 475–489. doi: 10.1002/rem.3440040410

- [14] Singer P.C. Assessing ozonation research needs in water treatment. *Journal American Water Works Association*, 1990, vol.82, no.10, pp. 78–88.
- [15] Li F., Wichmann K., Otterpohl R. Review of the technological approaches for grey water treatment and reuses. *Science Total Environment*, 2009, vol.407, no. 11, pp. 3439–3449. doi: 10.1016/j.scitotenv.2009.02.004
- [16] Karnapa A. A Review on Grey Water Treatment and Reuse. *International Research Journal of Engineering and Technology*, 2016, vol.03, no. 05, pp. 2665–2668.
- [17] Chen B., Zhang C., Wang L., Yang J., Sun Y. Removal of disinfection byproducts in drinking water by flexible reverse osmosis: Efficiency comparison, fates, influencing factors, and mechanisms. *Journal of Hazardous Materials*, 2021, vol. 401, 123408. doi: 10.1016/j.jhazmat.2020.123408
- [18] Wang S., Li, L., Yu S., Dong B., Gao N., Wang X. A review of advances in EDCs and PhACs removal by nanofiltration: Mechanisms, impact factors and the influence of organic matter. *Chemical Engineering Journal*, 2021, vol. 406, 126722. doi: 10.1016/j.cej.2020.126722
- [19] García-Vaquero N., Lee, E., Jiménez Castañeda R., Cho J., López-Ramírez J.A. Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility. *Desalination*, 2014, vol. 347, pp. 94–102. doi: 10.1016/j.desal.2014.05.036
- [20] Raouf M.E.A., Maysour N.E., Farag R.K., et al. Wastewater Treatment Methodologies. *International Journal Environmental & Agricultural Science*, 2019, vol.3, pp. 018.
- [21] Martemyanov D.V., Galanov A.I., Yurmazova T.A. Sorption of As3 +, As5 + ions from aqueous solutions on vermiculite concrete and aerated concrete modified with iron oxyhydroxide. *Proceedings of higher educational institutions. Chemistry and Chemical Technology* (In Rus), 2014, vol. 57, no.11, pp. 30–33.
- [22] Martemianov D.V. et al. Study of Hematite Mineral Samples in Purification of Aqueous Solutions from As<sup>3+</sup> and Fe<sup>3+</sup> Ions. *Key Engineering Materials*, 2016, vol. vol. 712, pp. 295–300. doi: 10.4028/www.scientific.net/KEM.712.295
- [23] Martemianov D. Cellular concrete-supported cost-effective adsorbents for aqueous arsenic and heavy metals abatement. *Journal of Environmental Chemical Engineering*, 2017, vol. 5, no.4, pp. 3930–3941. doi: 10.1016/j.jece.2017.07.063
- [24] Meltzer T.H., Jornitz M.W. Filtration in the Biopharmaceutical Industry. NY, Informa Healthcare, Marcel Dekker Inc. Published, 1998, 926 p.

- [25] Martemyanov D.V., Korotkova E.I., Galanov A.I. Sorption materials of a new generation for purification of aqueous media from microbiological contaminants. *Bulletin of Karaganda University* (In Rus), 2012, vol. 3, no. 67, pp. 61– 64.
- [26] Lozhkomoev A.S. et al. Adsorption of negative ions of eosin, Tannin molecules and latex spheres on nanofibers of aluminum oxyhydroxide nanofibers. *Russian Journal of Applied Chemistry*, 2009, vol. 82, no.4, pp. 581–586. doi: 10.1134/S1070427209040090
- [27] Plotnikov E., Martemianova I., Martemianov D., Zhuravkov S., Kan T., Voronova O. The study of surface parameters and sorption properties of aerated concrete-based sorbents for water purification from E.Coli bacteria. *Journal of Materials and Environmental Science*, 2016, vol. 7, no.11, pp. 3944–3948.
- [28] Pechenyuk S.I., Semushkin V.V., Arkhipov I.V. Acid-base properties of aluminum oxyhydroxide hydrogels. *Proceedings of the Chelyabinsk Scientific Center* (In Rus), 2006, vol. 34, no. 4, pp. 64–68.
- [29] Lerner M.I., Rodkevich N.G., Svarovskaya N.V., Lozhkomoev A.S., Psakhie S.G., Rudensky G.E. Method of obtaining filtering material. RF patent 2297269. Patentee LLC "Aquazon". publ. 20.04.2007. Bul. No. 11.
- [30] Tepper F., Kaledin L. Nonwoven material, including ultrafine or nano-sized powders. RF patent # 2394627. Patentee "Argonide Corporation" publ. 20.07.2010, Bul. No. 20.
- [31] Zhuravkov S.P. et al. Study of sorption properties of aluminium oxides and hydroxides powders obtained by electro-impulse methods. *IOP Conference Series: Materials Science and Engineering*, 2015, vol.81, no. 1, 012057. doi:10.1088/1757-899X/81/1/012057
- [32] Martemyanov D.V., Galanov A.I., Yurmazova T.A. Determination of the sorption characteristics of various minerals in the extraction of As5+, Cr6+, Ni2+ ions from aqueous media. *Fundamental Research*, 2013, vol. 8, no. 3, pp. 666–670.
- [33] Yi G., Riduan S.N., Yuan Y., Zhang Y. Microbicide surface nano-structures. *Critical Reviews in Biotechnology*, 2019, vol.39, no. 7, pp. 964–979. doi: 10.1080/07388551.2019.1641788
- [34] Tripathy A., Sen P., Su B., Briscoe W.H. Natural and bioinspired nanostructured bactericidal surfaces. *Advanced Colloid Interface Science*, 2017, vol.248, pp. 85–104. doi: 10.1016/j.cis.2017.07.030

Received: September 23, 2020