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Influence of the Complex of Natural Mineral Sorbents on Microbiological and Qualitative Measures of Water

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ABSTRACT

Background: Nowadays in Kazakhstan the technologies directed on improving and health maintenance of the population with use of natural medical resources are more and more developed and supported. During this research work we have done complex researches including studying of spread of microbiological pollution of natural water, and also its secondary pollution in water supply systems. It is proved that the technology of water treatment does not cope with the problem of getting quality drinking water. This is the reason why the most part of the population uses drinking water which does not meet the requirements of sanitary standards and rules. **The purpose** of work consisted in an experimental assessment of the efficiency of using a complex of natural mineral sorbents for microbiological water purification. **Results:** In this work the hygienic assessment of efficiency of the available and prospective means and ways of purification of economic drinking water is given. Domestic and foreign experience of application in the processes of water purification and water treatment of natural mineral adsorbents as effective way of removal of pollution is generalized.

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INTRODUCTION

Water intended for drinking and everyday use should not contain any pathogenic agents transmitted through water. Providing safe drinking water supply depends on using either high quality underground waters at good sanitary control, or on the right choice and reliable work of water treatment facilities enabling to reduce the content of pathogenic and other polluting agents till the levels safe for health of a person. The processes preceding the final disinfecting must provide water supply of high microbiological quality, so that this final stage will become a guarantee of proper quality of water (Novikov, *et al.*, 1998).

In the distributive network the bacteriological indices of water can worsen. If water contains significant amounts of digestible organic carbon or ammonia, the appropriate residual levels of residual chlorine are not kept.

If such water mains are not blown through (off/down) and not cleared rather often, there can be a growth of bacteria and other organisms. Pollution of water in distributive networks is caused by infiltration of ground and surface water and repair works on water mains. Local pressure drop in the networks leads to return suction of polluted waters (Gildenscold, *et al.*, 1993).

Besides, microbiological pollution can happen because of growth of bacteria on the construction materials contacting to water (paddings, pipes and plastic covers used in water pipes and cranes) (Mol, 1999).

Therefore equipment of local post-treatment of water must delete microbic pollution from water effectively.

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The purpose of work consisted in an experimental assessment of the efficiency of using a complex of natural mineral sorbents for microbiological water purification.

For achievement of this purpose it is necessary to solve the following **problems**:

1. To estimate the efficiency of a complex of natural mineral sorbents in the processes of purification drinking and sewage waters from microbiological pollution.
2. To study toxic-hygienic indices of the water which was purified with natural mineral sorbents (NMS).
3. To study biological effect of the water which was purified with PMS.
4. To estimate possibility of using PMS for individual and collective post treatment of drinking water.

MATERIALS AND METHODS

Analyses for existence of organisms-indicators of fecal pollution remain the most reliable and concrete way of assessment of hygienic quality of water. To receive adequate results bacteria-indicators of fecal pollution must meet certain requirements. They have to be present widely at excrements of humans and warm-blooded animals, be found quickly by simple methods and not develop in natural water. Moreover it is necessary that their persistence in water and the extent of their removal at water purification were similar to the same indices for pathogens of water origin (Tymoshenko, Klimenko, 1990, Novikov, Melzer, 2000).

Although none of organisms meet *all* the requirements described above for an ideal fecal index, E.coli meets the majority of them, therefore this bacteria was chosen for the research.

As bacteria spores are much immune against effect of disinfecting agents than E.coli cells, absence of the latter in water is not a guarantee of spores absence. As the indices indicating presence of spores bacteria in water we chose the anaerobic spore-forming organism *C. perfringens*, and the aerobic spore-forming bacterium *B. subtilis*. These bacteria differ with location of spores in a cell (Makhorin, 1998). As their spores are able to exist in water much longer, than coliform bacteria, they are immune against disinfecting and therefore serve as indices of old pollution and defects in filtering technology at waterworks (Antonyuk, 1997).

The results of studying the efficiency of PMS relative to removal of E. coli cells, and also *B.subtilis* and *C. perfringens* spores from water are given in tables 1÷3.

The results given in tables 1÷3 show that all studied PMS and also their complex remove effectively microbic pollution from water at concentration of bacterial suspension $(1,2\div 3,5) \times 10^3$ g/ml, not being worse than AU filter.

At much increase of concentration of bacterial suspension [up to $(3,1\div 3,2) \times 10^4$ g/ml] in the seeding from filtrate colonies of bacteria can be found. Their number decreases in comparison with initial one in $(4\div 5) \times 10^3$ times — for “Complex” and AC filters. The efficiency of decrease in microbic pollution by zeolite is lower for sure, than in control and is $(2 \div 2,8) \times 10^3$ of times.

Table 1: The number of microorganisms E.coli ($X \pm x$) in water before and after filtering through filters (n = 5).

The number of microorganisms, g/ml					
Initial	Type of filter				
	Schungite	Zeolite	Bentonite	“Complex” filter	AC
$(1,2 \pm 0,1) \times 10^3$	0	0	0	0	0
$(3,5 \pm 0,2) \times 10^3$	0	0	0	0	0
$(3,2 \pm 0,2) \times 10^3$	$(0,8 \pm 0,1) \times 10^3$	$(1,5 \pm 0,3) \times 10^3$	$(0,7 \pm 0,05) \times 10^3$	$(0,8 \pm 0,05) \times 10^3$	$(0,6 \pm 0,03) \times 10^3$

Notes: 1. Filter - complex zeolite, bentonite, chungite and diatomite;

2. AC- filter with absorbent carbon — control;

3. * *italics* — difference with control is correct.

Table 2: The number of microorganisms B. subtilis ($X \pm x$) in water before and after filtering through filters (n = 5).

The number of microorganisms, g/ml					
Initial	Type of filter				
	Schungite	Zeolite	Bentonite	“Complex” filter	AC
$(1,5 \pm 0,1) \times 10^3$	0	0	0	0	0
$(3,4 \pm 0,2) \times 10^3$	0	0	0	0	0
$(3,2 \pm 0,1) \times 10^4$	$(0,7 \pm 0,1) \times 10^1$	<i>$(1,5 \pm 0,1) \times 10^1$</i>	$(0,7 \pm 0,02) \times 10^1$	$(0,8 \pm 0,02) \times 10^1$	$(0,8 \pm 0,01) \times 10^1$

Notes: 1. Filter - complex zeolite, bentonite, chungite and diatomite;

2. AC- filter with absorbent carbon- control;

3. * *italics* — difference with control is correct.

It should be noted that in practice in distributive networks, and also at water withdrawal from a natural water source, we face less strong microbiological pollution. The equipment for disinfecting of water in field conditions and made on the principle of ultra-violet bactericidal radiation is intended for coli index not more than 5×10^3 kg/l (Klimenko, Koganovsky, 1998).

As the water containing microorganisms cells $(1\div 3)\times 10^3$ g/ml in number is characterized as very dirty (Tarasovich, 1998, Distanov, Konyukhov, 1999) (corresponds to coli index more than 1×10^6), it is possible to conclude that these increased levels of microbiological pollution are effectively removed used in work by PMS.

Table 3: The number of microorganisms *C. perfringens* ($X\pm x$) in water before and after filtering through filters ($n = 5$).

Initial	The number of microorganisms, g/ml				
	Type of filter				
	Schungite	Zeolite	Bentonite	"Complex" filter	AC
$(1,3\pm 0,1)\times 10^3$	0	0	0	0	0
$(3,2\pm 0,2)\times 10^3$	0	0	0	0	0
$(3,1\pm 0,2)\times 10^4$	$(0,6\pm 0,01)\times 10^1$	$(1,6\pm 0,1)*\times 10^1$	$(0,8\pm 0,04)\times 10^1$	$(0,7\pm 0,03)\times 10^1$	$(0,7\pm 0,05)\times 10^1$

Notes: 1. Filter - complex zeolite, bentonite, chungite and diatomite;

2. AC- filter with absorbent carbon — control;

3. * *italics* — difference with control is correct.

As a result of the conducted microbiological researches it was found out that PMS have the expressed sorption features relative to *E.coli* bacteria, *B. subtilis* and *C. perfringens* spores. The greatest efficiency at removal of microorganisms cells from water was shown by chungite and glauconitic limestone, being in this relation not worse than AC.

Toxic-hygienic assessment of water which was filtered through the filters with PMS:

Determination of toxicity of water samples containing chemical toxicants (phenol, sulfate copper) before and after filtering through PMS filters was done with use of *Daphnia magna* crustaceans and *Chlorella vulgaris* microseaweed.

The data from table 4 show that water before filtering through filters with PMS had toxic effect on crustaceans (the percent of death of crustaceans in both cases exceeded 50%). After passing of water through filters with PMS there was no toxic effect on water fleas in all cases, and the percent of their death practically did not differ from control one, except the case with bentonite at concentration of 1,5 mg/l when the death was 11%.

Table 4: Influence of PMS on death of *Daphnia magna* (% to control) in water samples containing toxicants ($n = 5$).

Content of toxicants, mg/l	Initial water	Type of filter				
		Schungite	Zeolite	Bentonite	"Complex" filter	AC
10,0	$85,5\pm 5,0$	$5,0\pm 0,5$	$4,0\pm 0,2$	$3,0\pm 0,2$	$4,0\pm 0,1$	$5,0\pm 0,2$
CuSO ₄						
5,0	$59,0\pm 3,0$	$4,0\pm 0,2$	$3,0\pm 0,1$	$3,0\pm 0,2$	$3,0\pm 0,2$	$4,0\pm 0,2$
1,5	$73,0\pm 2,5$	$3,0\pm 0,2$	$11,0\pm 0,5$	$4,0\pm 0,3$	$3,5\pm 0,1$	$3,5\pm 0,2$
Phenol						
0,05	$57,0\pm 1,5$	$2,5\pm 0,1$	$3,0\pm 0,2$	$3,0\pm 0,1$	$4,0\pm 0,2$	$4,0\pm 0,3$

Notes: 1. In control (water for cultivation) there were no deaths;

2. Duration of cultivation of *Daphnia magna* in water samples - 96 hours;

3. After filtering through filters pH water in all options of the experiment was established within $7,0 \div 7,2$. Water was aerated within 1 hour;

4. Filter - complex zeolite, bentonite, chungit and diatomite;

5. AU — a filter with absorbent carbon.

Similar results were received at determination of water toxicity with use of *chlorella* microseaweed (tab. 5).

Table 5: Values of toxicity index (S_f) of water samples ($n = 5$) (c.u., $X\pm x$) for *Chlorella vulgaris*.

Content of toxicants, mg/l	Initial water	Type of filter				
		Schungite	Zeolite	Bentonite	"Complex" filter	AC
10,0	$95,0\pm 5,0$	$7,0\pm 0,4$	$4,5\pm 0,4$	$5,0\pm 0,5$	$6,0\pm 0,3$	$6,5\pm 0,5$
CuSO ₄						
5,0	$64,0\pm 3,0$	$4,5\pm 0,5$	$3,0\pm 0,3$	$5,5\pm 0,4$	$5,0\pm 0,5$	$7,0\pm 0,4$
1,5	$75,0\pm 5,0$	$3,0\pm 0,2$	$18,0\pm 1,5$	$7,0\pm 0,6$	$4,5\pm 0,2$	$6,0\pm 0,3$
Фенол						
0,5	$56,0\pm 3,0$	$3,5\pm 0,3$	$9,0\pm 0,6$	$4,5\pm 0,5$	$3,5\pm 0,3$	$5,5\pm 0,5$

Note: 1. Control was water from vessels where the *chlorella* was cultivated;

2. After filtering through filters pH waters in all options of the experiment were established within $7,0 \div 7,2$;

3. Filter - complex zeolite, bentonite, chungit and diatomite;

4. AU - a filter with absorbent carbon.

This research showed that water before purification with PMS filters had toxic effect on test objects, and its expressiveness correlated with the concentration of chemicals in water (values of toxicity index S_f are 95 and 64 at the content of copper in water in concentration of 10 mg/l respectively; the S_f index was 75 and 56 at the content of phenol 1,5 and 0,05 of mg/l). As the result of the conducted processing of water the value of the index S_f considerably decreased in all cases. Only at initial concentration of phenol in water of 1,5 mg/l the

water after filtering through a filter with zeolite had the index Sf 18 and was characterized as "slightly toxic". In all other options of the experiment the water which was filtered through filters was characterized as non-toxic ($S_f < 10$).

We determined some indices of quality of tap water (Taldykorgan, the Republic of Kazakhstan) before and after filtering through filter complex containing a complex from four PMS studied at work (zeolite, bentonite, shungit and diatomite). The results of the analyses are given in Table 6.

The received results show that after filtering of tap water through filter complex zeolite, bentonite, schungit and diatomite there were essential changes in its structure. Its organoleptic indices improved considerably; in particular, the smell and taste of water began to correspond to the standards of SanPiN.

The content of iron in water decreased by 9,5 times and began to meet the standards of the SanPiN.

Considerable reduction of the content of heavy metals and organic pollutants in water was also noted. It should be noted that though concentration of these toxicants does not reach in the researched tap water samples the values of maximum concentration limit, but their continuous presence makes negative impact on a human body (Kuznetsov, 1985).

In the filtered water the content of pH, calcium, magnesium, silicon, hydrocarbonate ions, and also general hardness and solid residue raised. This fact should be estimated positively as it is known that tap water in notable for low content of these essential elements, increased softness and general low content of salts (Sokolova, *et al.*, 1984).

It is proved that use of water with insufficient content of ions of calcium and magnesium leads to some pathologies. So, people consuming soft water are amenable to hypertension, ischemia, osteochondrosis, osteoporosis, teeth caries and allergic diseases (Barchtold, 1999, Voronov, Skorik, 1999).

Besides it should be noted ability of calcium to compete with heavy metals for specific protein. Therefore, deficiency of calcium can be the factor assisting increasing of absorption of heavy metals (cadmium, mercury, lead, aluminum etc.) (Gorstein, *et al.*, 1980, Sementovsky, 1998, Novikov, *et al.*, 1990).

Table 6: Indices of quality of tap water before and after filtering through the Complex filter ($X \pm x$) ($n = 5$).

Indices, unit of measurement	In the initial water	In the purified water	PDK
Smell, point	$3 \pm 0^{**}$	0*	2
Taste, point	$3 \pm 0^{**}$	0*	2
Coloration, °	15 ± 1	0*	20
Turbidity, EM	$1,7 \pm 0,1$	0*	2,6
pH	$6,2 \pm 0,2$	$7,1 \pm 0,1^*$	$6 \div 9$
Silicon, mg/l	$< 0,1$	$1,3 \pm 0,2^*$	nn
Aluminum, mg/l	$0,4 \pm 0,02$	$< 0,005^*$	0,5
Iron, mg/l	$0,48 \pm 0,05$	$< 0,05^*$	0,3
Manganese, mg/l	$0,04 \pm 0,01$	$< 0,001^*$	0,1
Copper, mg/l	$0,1 \pm 0,01$	$< 0,001^*$	1,0
Cadmium, mg/l	$0,0008 \pm 0,0001$	$< 0,0001^*$	0,001
Zinc, mg/l	$0,18 \pm 0,05$	$< 0,001^*$	5,0
Lead, mg/l	$0,02 \pm 0,001$	$< 0,001^*$	0,03
Calcium, mg/l	$9,5 \pm 0,5$	$30,0 \pm 2,5^*$	nn
Magnesium, mg/l	$2,1 \pm 0,1$	$4,6 \pm 0,2^*$	nn
Nitrates, mg/l	$0,8 \pm 0,04$	$0,4 \pm 0,02^*$	45,0
Nitrites, mg/l	$0,01 \pm 0,001$	$< 0,001^*$	0,3
Hydrocarbonates, mg/l	$0,5 \pm 0,02$	$4,5 \pm 0,1^*$	nn
Chlorides, mg/l	$33,0 \pm 1,5$	$19,0 \pm 0,5^*$	350
Sulphates, mg/l	$21,5 \pm 0,5$	$19,5 \pm 1,0$	500
Phenol, mg/l	$0,003 \pm 0,0005$	$< 0,001^*$	0,001
Benzol, mg/l	$0,004 \pm 0,0005$	$< 0,0001^*$	0,01
Chloroform, mg/l	$0,02 \pm 0,005$	$< 0,0003^*$	0,02
Toluol, mg/l	$0,0007 \pm 0,0001$	$< 0,00002^*$	0,5
Solid residue, mg/l	$86,0 \pm 0,5$	$300,5 \pm 11,5^*$	1000
General hardness, mg-equ/l	$1,1 \pm 0,1$	$4,2 \pm 0,2^*$	7

Notes: 1. * — indices of quality of initial and cleared water differ considerably;

2. nn — the index is not rated;

3. ** — value is reliable above maximum concentration limit.

It is known also that bioavailability of calcium contained in water is much higher, than calcium of dairy products. The role of water containing calcium in food of people suffering from deficiency of digestive enzymes (Zvyagintseva, 1991, Rakhmanin, *et al.*, 1998) is especially important.

Silicon is also an element necessary for a live organism. It assists in collagen biosynthesis, forming and calcification of bone tissue. Besides, silicon participates in phosphorus metabolism, in lipidic exchange and has an impact on content of calcium in an organism. The daily need for silicon is 20÷30 mg/l. At deficiency in silicon there can be diseases of the lymphatic system, rachitis, malignant diseases.

The specified elements come to water during filtration from the available in the filter complex zeolite, bentonite, shungit and diatomite of natural minerals. Thus PMS presented in the filter do purification of tap water and its conditioning (correction of salt structure).

Biological effect of water activated by zeolite:

In literature they describe different phenomena indicating existence of biological activity in the water activated by zeolite (WAZ).

The results of studying the influence of WAZ on viability of peas and oat seeds are given in Table 7.

Couching the seeds in WAZ considerably accelerated the germination process and increased the percent of seeds viability. For oat this increase is 1,7 times, for peas - 1,4 times.

Activization of seeds germination can be explained with influence of microcomponent composition of water infused on crushed zeolite.

Table 7: Influence of WAZ on seeds germinability ($\bar{X} \pm x$) (n = 3).

Plant	The number of the spired seeds for the observation period, in days					
	WAZ			Control		
	1	2	3	1	2	3
Oat	15 ± 2	54 ± 3	93 ± 6	0	25 ± 1	53 ± 2
Peas	22 ± 2	75 ± 4	98 ± 1	5 ± 2	35 ± 3	68 ± 1

Note: 1. Control was the seeds of corresponding plants couching in the raw tap water;

2. The number of seeds in each option — 100 pieces.

The similar stimulating effect of zeolite on biochemical activity of bifidus bacteria was observed in the experiment at preparation of nutrient medium on the water infused on crushed zeolite. At their growth in the nutrient medium containing an extract from zeolite (which consists of micro amounts of potassium, sodium, calcium, barium, iodine and other cations and anions in a balanced ratio), the increase in growth speed of bifidus bacteria population and more intensive accumulation of products of a metabolism — acetate, lactate, ethanol, extracellular proteases was noted.

The results:

On the basis of the analysis of technical and economic indices for experimental studying the mineral sorbents of the different nature having a domestic raw materials source were chosen: zeolite, bentonite, schungite and diatomite.

The conditions of PMS activation were chosen experimentally. PMS activity increased most considerably (35-57%) after acid processing with a mixture (1:1) of 10 % of oxalic acid and peroxide of hydrogen.

In model experiments on use of natural mineral sorbents in the processes of water purification from microbiological pollution we revealed the essential distinctions in efficiency of the considered sorbents determined by their mineral structure, microstructure, sorption capacity and existence of catalytic activity.

The results of the conducted sanitary and microbiological researches showed that PMS have the expressed sorption features relative to E.coli bacteria strain K12, and also B.subtilis and C.perfringes spores. All studied PMS and their combination in the complex filter zeolite, bentonite, schungite and diatomite delete efficiently microbic pollution from water at initial concentration (1,2÷3,5) of $\times 10^3$ g/ml, without being not worse than the AU filter. At increase of concentration up to (3,1÷3,5) $\times 10^4$ kl/ml the complex zeolite, bentonite, schungite and diatomite worked more efficiently than AC. Studying of biological effect of the water activated by zeolite for germination of plants seeds showed that as a result of preseeding processing the germination process is considerably accelerated and the percent of germiability of seeds raises in 1,4÷1,7 times. Activization of seeds germination is explained by stimulating effect of the water infused on crushed zeolite which has the balanced macro and microcomponent structure.

Natural sorbents have the expressed sorption features relative to E.coli bacteria strain K12, and B.subtilis and C.perfringes spores. PMS is more efficiently at removal of microorganisms cells from water than AU.

The water processed by PMS improved its biological features due to deep purification from chemical pollution, decrease in toxicity, and also enrichment with essential macro and microelements.

Recognition:

The work is done on the basis of grant financing of scientific researches in the Republic of Kazakhstan. 5. Intellectual potential of the country. 5.1 Fundamental researches in the field of natural sciences. No. 161 of 20.09.2012.

The studied PMS are prospective for using in the systems and means of improving water quality in public water supply.

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