ЕКОЛОГІЯ ТА РЕСУРСОЗБЕРЕЖЕННЯ

UDK 628.16(08)

KRYZHANOVSKA Y. P., PhD student; GOMELYA M. D., Dr. Sc., professor, head of department;
RADOVENCHIK Y. V., Dr. PhD., assistant professor;
SHABLIY T. O., Dr. Sc., professor; MIGRANOVA V. O., mahistrant
National Technical University of Ukraine
«Igor Sikorsky Kyiv Polytechnic Institute»

EVALUATION OF EFFICIENCY OF COAGULANT OBTAINED FROM ELABORATED RED SLUDGE FROM ALUMINA PLANT

In document, the effectiveness of reducing the chromaticity and turbidity of the Dnipro river water was investigated and estimated by means of existing coagulants $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ and synthesized coagulant from the red sludge of alumina plants - SC. During the experimental part of the work in the laboratory, the following optimal dosages of coagulants were chosen, namely, 0, 1, 2, 5, 10 mg/dm^3 based on Al_2O_3 and Fe_2O_3. The volume of samples of the solutions, which were subjected to the study, reached 200 ml. Model solutions of bentonite with a concentration of 100 mg/dm^3, sodium humate with a concentration of 16.8 mg/dm^3, kaolin concentration of 100 mg/dm^3 and natural water of the Dnipro River were used.

Based on the analysis of the experimental data obtained, it was found that the alternative coagulant is not inferior to the existing and widely used coagulants.

During clearing and discoloration of the Dnipro river waters, the SC showed better results. Therefore, it can be said that obtaining "alternative" coagulants from waste products is a very promising and economically viable direction of research and development of new reagents for water purification and water treatment.

Ключові слова: *coagulant, chromaticity, turbidity, filtration, waste sludge, discoloration.*

DOI: 10.20535/2617-9741.3.2020.217905

Formulation of the problem. With the rapid development of industry, national economy and agriculture in Ukraine and in the world as a whole, the qualitative and quantitative composition of natural waters is changing significantly. This is especially noticeable in the industrial areas of our country, where due to anthropogenic pressure the level of water mineralization is constantly increasing and the shortage of drinking water is increasing. Also, the efficiency of treatment facilities in cities is constantly deteriorating due to the use of inefficient coagulants and wear and tear of wastewater treatment systems, which leads to the deterioration of natural reservoirs, where, in fact, discharges occur.

It is necessary to take into account the fact, that nowadays the Dnipro River is the main source of water supply in Ukraine, water in which periodically has high values of chromaticity and turbidity, and used coagulants cannot provide proper lighting and discoloration, which in turn reduces the overall water quality by organoleptic parameters. Therefore, the development of effective, affordable and cost-effective coagulants in our country is an extremely important task.

Analysis of the forefront. These days, water treatment facilities of cities are focused on the removal of organic and inorganic compounds, which determine the chromaticity and turbidity of water. It is known that the processes of drinking water preparation include the process of coagulation [1, 2]. In modern water treatment technologies mainly aluminum and iron-containing coagulants are used [3, 4]. More common are aluminum coagulants, which have a number of advantages over iron salts. The main advantages, in comparison with other reagents, include:

- the possibility of using hydroxoaluminum chloride at low temperatures;
- smaller doses of reagents and low residual concentrations of aluminum in treated water;
- improving water stability indicators;
- increasing the decontaminating effect [5, 6].

Today in Ukraine the main coagulant based on aluminum is aluminum sulfate. Basically, its use is widespread at many water treatment plants in different cities of Ukraine. Aluminum sulfate is a fairly affordable coagulant, cheaper than its counterparts on the market for water treatment chemicals. In this case, its use leads to a significant increase in the number of sulfate ions in water [7, 3].

Another effective coagulant should be mentioned. It is ferric chloride, the neutral salt of ferric iron and hydrochloric acid. Iron chloride has been widely used as a coagulant in the process of industrial and municipal wastewater treatment. Compared to others, namely aluminum-based coagulants, this chemical reagent has an important advantage: ferric chloride is endowed with a high rate of deposition of various impurities. As a result of hydrolysis, sparingly soluble iron hydroxide is formed. In the process of its formation, various organic and inorganic suspended particles are captured, forming visible flakes, which are easily removed by filtration.

There is a problem with the use of iron-containing coagulants in water treatment significant residual iron content after the coagulation process.

The development of alternative ways of obtaining coagulants is quite relevant [7–10]. One such ways is to obtain a coagulant by disposing of red sludge from alumina plant. Complex coagulant based on alumina waste ensures efficient removal of suspended and colloidal substances from water, which is then used for human consumption as drinking water.

The purpose of the article. The purpose of this work was to evaluate the efficiency of natural water treatment coagulant obtained by synthesis from spent red sludge Mykolayiv alumina plant (SC), namely the assessment of the decrease in chromaticity and turbidity of water from the Dnipro River during its purification by settling and further filtration through a sand mechanical filter.

Methods of work. To conduct an experimental work in order to study the reduction of chromaticity and turbidity of the water of the Dnipro River used model solutions bentonite with a concentration of 100 mg/dm^3, sodium humate with a concentration of 16.8 mg/dm^3 and kaolin with a concentration of 100 mg/dm^3 and actually water from the Dnipro River. Such model solutions have been selected: bentonite, kaolin and sodium humate. They it possible to best assess the effectiveness of coagulants, as they have the most similar characteristics with natural pollutants of the Dnipro River.

Synthesized coagulant from red sludge was used for water treatment, which is obtained by treating the sludge with 10% hydrochloric acid (SC). For comparison with the synthesized known coagulants were used: aluminum sulfate ($Al_2(SO_4)_3$*$18H_2O$) and ferric chloride ($FeCl_3$*$6H_2O$).

To reduce the turbidity of the model suspension of bentonite and kaolin suspension, and to reduce the chromaticity of the model suspension of sodium humate to a sample of water, a volume of 200 cm^3 added different doses of coagulant, stirred vigorously for 2-3 minutes, then stood for 2 hours. Doses of coagulants were calculated by Al_2O_3 and Fe_2O_3.

After the settling process, turbidity and chromaticity in the samples were determined. The settled sample was filtered through a sand filter. Filtration, as well as settling, is used to clarify water, ie the retention of suspended particles that are in the water column, which are not always visible to the naked eye. Sand is used as the main filter material. The load capacity of the sand filter was 50 cm^3. After passing each sample, the filter was thoroughly washed. After passing the sample through a mechanical filter, turbidity and chromaticity were determined in the selected sample. Turbidity, expressed in SiO_2 per 1 dm^3 of water, was determined by photocolorimetric method [11], and chromaticity – in degrees of chromato-cobalt scale (CCS) [11].

The main material. The effectiveness of reducing turbidity in the model suspensions and water of the Dnipro River when using SC can be judged by the results shown in table 1.

As can be seen from table 1, all coagulants contribute to the effective reduction of turbidity of the model suspension both after settling and after filtration. It should be noted that the coagulant derived from sludge and existing traditional coagulants have the effect of reducing turbidity at doses > 1 mg/dm^3 to 0. It should be also noted that after filtration, all coagulants used in the study have a high efficiency of reducing turbidity.

To compare the turbidity reduction efficiency, another model suspension was used, namely a kaolin suspension with a concentration of 100 mg/dm^3. The use of these coagulants also gave good results, which can be seen from table 2.

As you can see, when using ferric chloride from the initial turbidity of the kaolin suspension 122 mg/dm^3 after treatment with coagulants turbidity is reduced to 2 mg/dm^3 at a dose of 10 mg/dm^3, and when using SC and aluminum sulfate we have turbidity values at 0 at similar doses of coagulant, which is a very positive indicator.

To determine the effectiveness of coagulants in water decolorization, a model solution of sodium humate with a concentration of 16.8 mg/dm^3 was used. The results of the study of water decolorization processes are shown in table 3.

As can be seen from table 3, the use of coagulant $FeCl_3 \cdot 6H_2O$ was ineffective. After settling, the chromaticity of the solution did not change significantly, but after filtration at the level of 20 degrees CCS. It is possible that such significant values of chromaticity are due to the high content of ferric sulfate, which in itself gives a yellowish-red hue. It should be emphasized that the use of two other coagulants: SC and $Al_2(SO_4)_3 \cdot 18H_2O$ was more effective.

Table 1 – The effect of coagulants SC, $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ on the effectiveness of reducing turbidity in a model solution of bentonite with a concentration of 100 mg/dm^3 after settling (2 hours) and filtration

Coagulant	Coagulant doze, mg/dm^3 by Al_2O_3 and Fe_2O_3	Turbidity, mg/dm^3		
		primary	after settling	after filtration
SC	0	78	76	30
	1	78	43	11
	2	78	43	0
	5	78	52	0
	10	78	47,5	0
$Al_2(SO_4)_3 \cdot 18H_2O$	0	97,5	73	27
	1	97,5	39	0
	2	97,5	33	0
	5	97,5	26	0
	10	97,5	26	0
$FeCl_3 \cdot 6H_2O$	0	97,5	28	6,5
	1	97,5	60,5	2
	2	97,5	52	0
	5	97,5	52	0
	10	97,5	25,5	0

Table 2 – The effect of coagulants SC, $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ on the efficiency of reducing turbidity in a model solution of kaolin with a concentration of 100 mg/dm^3 after settling (2 hours) and filtration

Coagulant	Coagulant doze, mg/dm^3 by Al_2O_3 and Fe_2O_3	Turbidity, mg/dm^3		
		primary	after settling	after filtration
SC	0	122	120	19
	1	122	62	15
	2	122	56,5	12,5
	5	122	26	8
	10	122	6	0
$Al_2(SO_4)_3 \cdot 18H_2O$	0	120	100	2,5
	1	120	39	0
	2	120	11	0
	5	120	8	0
	10	120	6,5	0
$FeCl_3 \cdot 6H_2O$	0	170	150	30
	1	170	117,5	50
	2	170	107,5	42,5
	5	170	87,5	4
	10	170	62,5	2

Thus, after filtration at doses of 10 mg/dm^3, the chromaticity was at the level of 5-7 degrees CCS, which is a very positive result. Also, it can be noted that the chromaticity in all cases decreased with increasing dose of coagulants during filtration.

The results obtained using these coagulants in the treatment of water from the Dnipro River are shown in table 4.

Speaking of chromaticity, the best result was obtained with the use of SC, at a dose of coagulant 10 mg/dm^3 chromaticity was 14 degrees CCS. This is the best result among all coagulants studied. When using $Al_2(SO_4)_3 \cdot 18H_2O$ the chromaticity was 22 degrees CCS, and when using $FeCl_3 \cdot 6H_2O$ – 71, which is not effective enough.

Table 3 – The effect of coagulants on the effectiveness of decolorization of a model solution of sodium humate with a concentration of 16.8 mg/dm^3 after settling (2 hours) and filtration

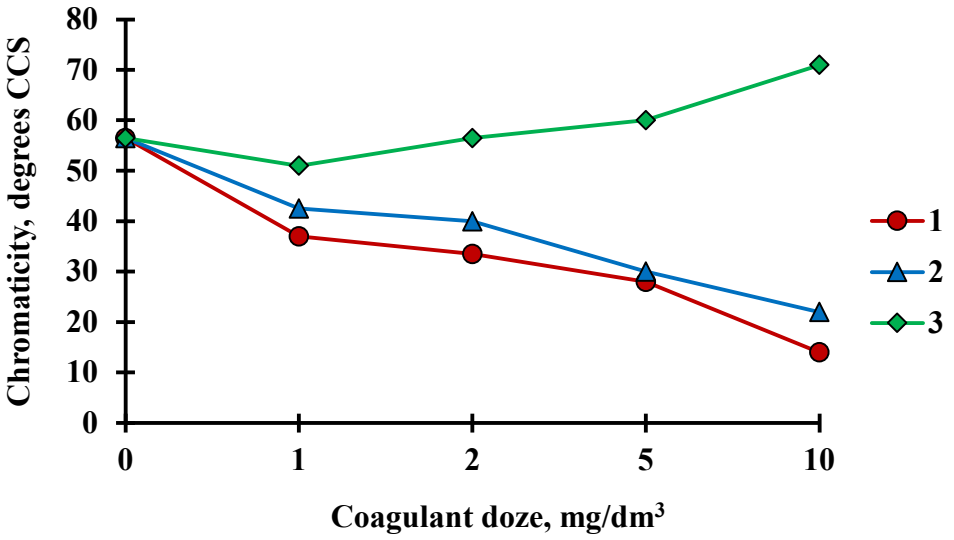
Coagulant	Coagulant doze, mg/dm^3 by Al_2O_3 and Fe_2O_3	Chromaticity, degrees		
		primary	after settling	after filtration
SC	0	180	180	96
	1	180	180	42,5
	2	180	180	17
	5	180	180	15
	10	180	169	7
$Al_2(SO_4)_3 \cdot 18H_2O$	0	180	180	68
	1	180	180	56
	2	180	180	20
	5	180	180	8,5
	10	180	173	0
$FeCl_3 \cdot 6H_2O$	0	190	188	92
	1	190	188	168
	2	190	187	160
	5	190	160	23
	10	190	159	20

Table 4 – Influence of coagulants on the efficiency of reducing turbidity and chromaticity of water in the Dnipro River after settling (2 hours) and filtration (Primary turbidity=15 mg/dm^3, Primary chromaticity=97 CCS)

Coagulant	Coagulant doze, mg/dm^3, by Al_2O_3 and Fe_2O_3	Turbidity, mg/dm^3			Chromaticity, degrees		
		primary	after settling	after filtration	primary	after settling	after filtration
SC	0	15	6	0	97	95	56,5
	1	15	6	0	97	56,5	37
	2	15	6	0	97	63,5	33,5
	5	15	11	0	97	79	28
	10	15	26	0	97	73	14
$Al_2(SO_4)_3 \cdot 18H_2O$	0	15	13	0	97	95	53,5
	1	15	7,5	0	97	90	42,5
	2	15	7	0	97	90	40
	5	15	15	0	97	95	30
	10	15	15	0	97	90	22
$FeCl_3 6H_2O$	0	15	2	0	97	95	56,5
	1	15	2	0	97	90,5	51
	2	15	7,5	0	97	102	56,5
	5	15	11	0	97	255	60
	10	15	26	0	97	386	71

After 2 hours of standing, the turbidity decreased, but it should be noted that with increasing the dose of all three coagulants, the turbidity increased slightly. After filtration, the turbidity was reduced to 0 (at a primary value of 15 mg/dm^3) for all types of coagulants.

Evaluating the obtained results, we can say that the use of SC in comparison with $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ is the most appropriate and effective (Fig. 1).



1 – SC; 2 – $Al_2(SO_4)_3 \cdot 18H_2O$; 3 – $FeCl_3 \cdot 6H_2O$

Fig. 1 – Dependence of residual chromaticity on the dose of coagulant after filtration (water in the Dnipro River: primary turbidity=15 mg/dm^3, primary chromaticity=97 CCS)

As can be seen from Fig. 1, the use of SC is the most effective, as when using SC at a dose of 10 mg/dm^3 chromaticity decreased to 14 degrees CCS, which is the best result. The use of $FeCl_3 \cdot 6H_2O$ to reduce chromaticity is generally ineffective.

Conclusions. During the research, the processes of reducing turbidity of bentonite and kaolin model suspensions, processes of decolorization of sodium humate model solution, as well as the effectiveness of reducing turbidity and chromaticity of the Dnipro River water by coagulation were studied. Coagulant synthesized from red sludge (SC), aluminum sulfate and iron (III) chloride were investigated.

It is shown that SC is not inferior to existing and widely used coagulants, and in the case of Dnipro water treatment gives even better results.

Prospects for further research. During the analysis of the obtained data, it was found that obtaining "alternative" coagulants from waste, namely red sludge from the alumina plant, is a very promising and cost-effective direction of further research and development of water treatment reagents.

Referenses

1. Manash Kamal Dutta. (2020), “Energy and water conservation by coagulant change over from aluminum sulfate to poly aluminum chloride (PAC) at a conventional water treatment plant”, *Petroleum and Chemical Industry International*, 3 (1), pp. 6–9.
2. Tong Zhen-gong, Kang Cai-xia. (2013), “Optimization of coagulant for raw water in Ganjiang River in winter”, *Desalination and Water Treatment*, 51 (16-18), pp. 3257–3262.
3. Ivanenko, O., Shabliy, T., Nosachova, Y. (2020), “Application of potassium ferrate in water treatment processes”, *Journal of Ecological Engineering*, 21 (7), pp. 134–140.

4. Radovenchik, V. M., Glynyana, S. V., Radovenchik, Y. V., Kalinichenko, N.D. (2014), "Aluminium coagulants efficiency evaluation for natural water clarification", *Eastern-European Journal of Enterprise Technologies*, 2 (10), pp. 17–20. (In Ukrainian)
5. Shabliy, T.O. (2012), "Synthesis of coagulants to intensify processes of water clarification", *Eastern-European Journal of Enterprise Technologies*, 6(59), pp. 23–28. (In Ukrainian)
6. Shabliy, T.O. (2012), "Development of affordable coagulant for intensification lighting natural waters", *Eastern-European Journal of Enterprise Technologies*, 6 (60), pp. 6–11. (In Ukrainian)
7. Gomelja, M.D., Krysenko, T.V., Trohymenko, G.G. (2017), "Evaluation of efficiency of coaguluanes synthesized from waste manufactured by aluminum at water treatment", *Integrated Technologies and Energy Conservation*, 4, pp. 80–86. (In Ukrainian)
8. Iqbala, A., Zahra, N. (2018), "Coagulation efficiency comparison of natural and its blended coagulant with alum in water treatment", *Desalination and Water Treatment*, 109, pp.188–192.
9. Janna, H. (2016), "Effectiveness of using natural materials as a coagulant for reduction of water turbidity in water treatment", *World Journal of Engineering and Technology*, 4, pp. 505-516.
10. Nutiu, E. (2015), "Waste Water Treatment Using a New Type of Coagulant", *Procedia Technology*, 19, pp. 479–482.
11. Lurie, J.J., Rybnikova, A.I. (1974), Khymycheskyi analyz proyzvodstvenykh stochnykh vod. M.: «Khymyia», 336 p. (In Russian).

Надійшла до редакції 23.10.2020

Крижановська Я. П., Гомеля М. Д., Радовенчик Я. В., Шаблій Т. О., Мігранова В. О.

ОЦІНКА ЕФЕКТИВНОСТІ КОАГУЛЯНТУ ОТРИМАНОГО З ВІДПРАЦЬОВАНОГО ЧЕРВОГО ШЛАМУ ГЛИНОЗЕМНОГО ЗАВОДУ

В роботі досліджено ефективність зниження кольоровості та каламутності води річки Дніпро за допомогою існуючих коагулянтів $Al_2(SO_4)_3 \cdot 18\ H_2O$ та $FeCl_3 \cdot 6\ H_2O$ та синтезованого коагулянту із червоного шламу глиноземних заводів (ШК). При проведенні експериментальної частини роботи у лабораторних умовах використовували такі оптимальні дози коагулянтів: 0, 1, 2, 5, 10 мг/дм^3 з розрахунку по Al_2O_3 та Fe_2O_3. Об'єм проб, що піддавались дослідженням, сягали 200 дм^3. Для моделювання забруднень використовували модельні розчини бентоніту з концентрацією 100 мг/дм^3, гумату натрію з концентрацією 16,8 мг/дм^3, каоліну з концентрацією 100 мг/дм^3 та природну воду річки Дніпро.
На підставі аналізу отриманих експериментальних даних встановлено, що ШК нічим не поступається існуючим та широко використовуваним коагулянтам.
При очищенні та знебарвленні води річки Дніпро ШК показав кращі результати. Тому, можемо сказати, що отримання «альтернативних» коагулянтів із відпрацьованих відходів є цілком перспективним та економічно вигідним напрямком дослідження та розробок нових реагентів водоочищення та водопідготовки.

Ключові слова: *коагулянт, кольоровість, каламутність, фільтрування, відпрацьований шлам, знебарвлення*

Список використаної літератури

1. Manash Kamal Dutta. Energy and water conservation by coagulant change over from aluminum sulfate to poly aluminum chloride (PAC) at a conventional water treatment plant // Petroleum and Chemical Industry International. 2020. 3 (1). P. 6–9.
2. Tong Zhen-gong, Kang Cai-xia. Optimization of coagulant for raw water in Ganjiang River in winter // Desalination and Water Treatment. 2013. 51 (16–18), 3257–3262.
3. Ivanenko O., Shabliy T., Nosachova Yu. Application of potassium ferrate in water treatment processes // Journal of Ecological Engineering. 2020. 21 (7). P. 134–140.
4. Радовенчик В.М., Глиняна С.В., Радовенчик Я.В., Калініченко Н.В. Оцінка ефективності алюмінійвмістких коагулянтів в процесах освітлення природних вод // Східно-Європейський журнал передових технологій. 2014. 2 (10), P. 17-20.

5. Шаблій Т.О. Синтез коагулянтів для інтенсифікації процесів освітлення води // Восточно-Европейский журнал передових технологий. 2012. 6 (59), С. 23–28.
6. Шаблій Т.О. Розробка доступних коагулянтів для інтенсифікації освітлення природних вод // Восточно-Европейский журнал передових технологий. 2012. 6 (60), С. 6–11.
7. Гомеля М.Д., Крисенко Т.В., Трохименко Г.Г. Оцінка ефективності коагулянтів, синтезованих із відходів виробництв алюмінію, при очищенні води // Интегрированные технологии и энергосбережение: Збірник наукових праць за матеріалами XVII Міжнародної науково-практичної конференції. 2017. 4. С. 80 – 84.
8. Iqbala A., Zahra N. Coagulation efficiency comparison of natural and its blended coagulant with alum in water treatment // Desalination and Water Treatment. 2018. 109. P. 188–192.
9. Janna H. Effectiveness of using natural materials as a coagulant for reduction of water turbidity in water treatment // World Journal of Engineering and Technology. 2016. 4. P. 505-516.
10. Nutiu E. Waste Water Treatment Using a New Type of Coagulant // Procedia Technology. 2015. 19. P. 479–482.
11. Лурье Ю.Ю., Рыбникова А.И. Химический анализ производственных сточных вод. М.: «Химия», 1974. 336 с.

УДК 628.161.2:546.71

ГОМЕЛЯ М.Д., д.т.н.,професор; ТВЕРДОХЛІБ М.М., к.т.н., асистент; ВОЗНА І.П., магістрант
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»

МЕХАНІЗМ СОРБЦІЙНО-КАТАЛІТИЧНОГО ОЧИЩЕННЯ ВОДИ ВІД ІОНІВ МАРГАНЦЮ

В роботі представлені результати по вивченню процесів очищення води від іонів Mn^{2+} при використанні іонного обміну та каталітичного окислення. Показано, що сильнокислотні катіоніти добре сорбують іони марганцю в кислій та сольовій (Na^+) формі, задовільно сорбують марганець в Ca^{2+} формі. При використанні катіоніту модифікованого магнетитом видалення іонів Mn^{2+} із водних розчинів відбувається як за рахунок іонного обміну, незалежно від форми іоніту, так і за рахунок окислення на каталізаторі (магнетиті) в присутності розчиненого в воді кисню.

Ключові слова: *іони марганцю, магнетит, сорбент, катіоніт, каталізатор, оксид марганцю.*

DOI: 10.20535/2617-9741.3.2020.217906

Постановка проблеми. На сьогодні в Україні залишилося дуже мало джерел водопостачання, які можна віднести до першої категорії за якістю води. Це стосується і підземних вод, включаючи артезіанські свердловини. Особливо часто води з артезіанських свердловин забруднені нітратами, іонами заліза та марганцю [1]. І якщо від нітратів воду легко очищати методом іонного обміну [2], від іонів заліза методом каталітичного окислення [3], то при очищенні води від іонів марганцю існують певні проблеми. Насамперед іони Mn^{2+} окислюються лише за високих значень pH середовища в присутності специфічних каталізаторів. Іонообмінне їх вилучення мало ефективне в присутності іонів жорсткості, коли концентрація останніх значно переважає вміст іонів марганцю. Вміст іонів марганцю в артезіанських водах сягає 0,5-10 мг/дм^3 (0,01-0,21 мг-екв/дм^3), тоді як жорсткість таких вод може сягати 3-10 мг-екв/дм^3[1]. Тому створення та вдосконалення існуючих методів очищення води від іонів марганцю є складною проблемою.

Аналіз попередніх досліджень. Якщо судити по літературним даним, то проблемі очищення води від марганцю приділяється значна увага [4-6]. Частіше за все використовують фільтрувальні завантаження із нанесеним на поверхню зерен каталізатором. Дуже часто активним компонентом каталізатора є оксид