THE USE OF COAGULANTS FROM INDUSTRIAL WASTE IN WATER TREATMENT PROCESSES

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ABSTRACT

Today, the problem of providing the population with high-quality drinking water is becoming increasingly important, as it determines the social, environmental and economic situation in the country. This problem is complicated by anthropogenic interference, degradation of surface and groundwater sources, as well as imperfections in the technological solution of drinking water treatment. The efficiency of reducing the color and turbidity of the Dnieper and Desna rivers, which are the main waterways of Kyiv, was studied using known coagulants (($Al_2(SO_4)_3 \times 18H_2O$, $FeCl_3 \times 6H_2O$, Polvak) and synthesized coagulants from red sludge formed on alumina plant (RM). The processes of clarification and decolorization of water by coagulants on the example of model solutions of bentonite, kaolin and sodium humate depending on the dose of coagulant during settling and filtration have been studied. Based on the analysis of the obtained experimental data, it was found that the RM coagulant is not inferior to existing widely used coagulants. Therefore, obtaining coagulants from industrial waste is a very promising and cost-effective area of research and development of new reagents for purification and water treatment.

Keywords: *coagulant, filtration, waste sludge, bentonite, kaolin, sodium humate, chromaticity, turbidity.*

INTRODUCTION

Natural water treatment is a very important environmental problem of household and national economy of each country. Neglecting of this problem can lead to significant negative consequences. Providing the population and industry with high-quality water is one of the important factors determining the economic development of the country and its social and environmental condition [1 - 3].

Worldwide as well as in Ukraine, there is a deterioration in the qualitative and quantitative composition of natural waters due to the activities of industry and agriculture [4 - 6]. Today, much of the world's population suffers from water shortages or poor water quality [7 - 10]. This is especially noticeable in the industrial regions of Ukraine, where due to anthropogenic pressure the level of water mineralization is constantly increasing, which leads to an increase in the shortage of quality drinking water [11, 12]. In addition, due to the use of outdated technologies, most treatment plants are characterized by a low level of treatment efficiency and the discharge of contaminated mineralized water into natural reservoirs [13 - 15]. As a result, they lose their water management purpose [16 - 19]. The use of ineffective coagulants is also a problem that needs to be addressed urgently [20]. Therefore, the latest cleaning technologies, equipment and cleaning methods must be used to address these issues.

Recently, despite the restrictions on wastewater discharge, there has been a deterioration in quality of surface water. Today, the Dnieper river is the main source of water supply in Ukraine but water there periodically has high values of color and turbidity. Used coagulants cannot provide proper clarification and discoloration, which in turn reduces the overall water quality by organoleptic characteristics [21, 22]. In winter, the chromaticity is 20° - 40°, but sometimes there is a sharp increase to 75° - 80°. This exacerbates an already difficult situation. Therefore, the development of effective, affordable and cost-effective coagulants is an extremely important task [23 - 25].

The chemical composition and properties of natural water and consumer requirements determine the choice of water treatment methods [26, 27]. Urban water treatment facilities are focused on the removal of organic and inorganic compounds that determine the color and turbidity of water.

According to the European Union Directive 75/440 / EC, when using Class 1 water to obtain drinking water, it is sufficient to use a simple physical treatment and disinfection - rapid filtration and disinfection [28]. For water of the 2nd class it is necessary to apply physical and chemical treatment and disinfection - primary chlorination, coagulation, flocculation, clarification, filtration and secondary chlorination. Class 3 water requires intensive physical and chemical treatment methods - primary chlorination or chlorination in a specific place of the technological scheme, coagulation, flocculation, lighting, filtration, ozonation, adsorption on activated carbon and disinfection. Most water sources now belong to classes 2 or 3.

One of the main technological processes of natural water purification is coagulation [29 - 31]. This is due to its sufficient efficiency and relative cheapness. Modern water treatment technologies mainly use various coagulants. Inorganic one, mainly salts of polyvalent metals of aluminum and iron - aluminum sulfate, polyaluminum chloride, iron chloride, iron salts of iron (II and III), mixed coagulant-based and mixed coagulants. More common are aluminum coagulants, which have several advantages over iron salts, namely: the possibility of using hydroxoaluminum chloride at low temperatures; lower doses of reagents and low residual concentrations of aluminum in purified water; improving water stability and increasing the disinfectant effect [32 - 35].

The main disadvantage using aluminum sulfate is significant increase in the concentration of sulfate ions in water. However, today in Ukraine this coagulant is widely used due to its low cost compared to other analogues [36, 37].

The use of ferric chloride as a coagulant in wastewater treatment is quite widespread due to its high efficiency, high rate of deposition of various impurities. Hydrolysis produces insoluble iron hydroxide. In the process of its formation, various organic and inorganic suspended solids are captured, forming flakes that are easily removed by filtration. However, the disadvantage of using iron-containing coagulants in water treatment is a significant residual iron content after the coagulation process [38, 39].

Improving existing and introducing new promising cost-effective water treatment technologies using highly efficient methods that can reliably purify water to the appropriate degree is currently extremely important [40].

The development of alternative methods of obtaining coagulants is quite relevant. Such a method is to obtain a coagulant by disposing of red sludge from an alumina plant. Coagulant based on alumina waste provides effective removal of suspended and colloidal substances from water, which is then used as drinking water.

The aim of this work was to evaluate the effectiveness of natural water treatment with coagulant obtained by synthesis from red sludge of Mykolayiv Alumina Plant, to reduce the color and turbidity of natural water during its purification by settling and subsequent filtration through a sand mechanical filter.

EXPERIMENTAL

Model solutions of bentonite and kaolin with a concentration of 100 mg dm^{-3}, sodium humate with a concentration of 14.3 mg dm^{-3} (150°), water from the Dnieper and Desna rivers were used. These concentrations were chosen because they have the most similar characteristics to natural pollutants of the Dnieper and Desna rivers (Table 1).

Synthesized coagulant from red sludge was used for water treatment, which is obtained by treating sludge with 10 % hydrochloric acid (contains aluminum hydroxochlorides) RM-1 and sulfuric acid (contains aluminum and iron sulfates) RM-2. Aluminum sulfate $Al_2(SO_4)_3 \times 18H_2O$, iron chloride ($FeCl_3 \times 6H_2O$) and Polvak were used for comparison with the synthesized one.

To reduce the turbidity of the model suspension of bentonite and kaolin and to reduce the color of the sodium humate suspension, to a water sample of 200 cm^3 the calculated dose of coagulant for Al_2O_3 and Fe_2O_3 was added, water was stirred vigorously for 3 minutes, then left for 2 hours and further analyzed. The settled water was filtered through a sand filter

Table 1. Water quality indicators of the Dnipro and Desna rivers.

Indicator	Units of measurement	Dnipro river	Desna river
Chromaticity,	° CCS	40 - 60	20 - 30
Turbidity	mg dm^{-3}	5.0 - 10.0	2.0 - 7.0
pH		7.8 - 8.0	7.7 - 7.9
Alkalinity	mg-eq dm^{-3}	2.8 - 3.0	4.8 - 5.0

with a loading volume of 50 cm^3. After passing each sample, the filter was thoroughly washed. Residual turbidity, filtrate color, residual aluminum and iron concentrations were determined in each sample.

Turbidity, expressed in mg SiO_2 per 1 dm^3 of water, was determined by photocolorimetric method, chromaticity in degrees of chromato-cobalt scale. The parameters were determined with the photocolorimetric method using a photocolorimeter KFK-2 at 20ºC at wavelength 670 nm (red) [41]. The solution was placed in a 50 mm cuvette. The sample is measured relative to distilled water. The obtained results are determined according to the schedule. The dilution of sample is also taking into account on the calibration graph.

The degree of clarification (Z) was calculated by the formula:

$$Z = \frac{M_b - M_z}{M_z} \cdot 100\%$$

where: Mb - turbidity of the initial suspension, mg dm^{-3}, Mz - residual turbidity of water, mg dm^{-3}.

RESULTS AND DISCUSSION

Polvak, aluminum sulfate and iron chloride were used for comparison. Polvak is a coagulant produced in Ukraine, it contains 2/3 and 1/3 of aluminum hydroxochlorides. When decolorizing water, model solutions of sodium humate with a chromaticity of 145 degrees on the chromato-cobalt scale (CCS) were used to evaluate the effectiveness of coagulants. The effectiveness of decolorization of solutions from the dose of coagulant (within two hours) is given in Table 2.

Treatment of the model solution with RM-2 coagulant was ineffective. When increasing the dose of coagulant to 20 mg dm^{-3} during settling, the color of the solution did not change. After settling and filtration, the color of the solution decreased to 61.9^0, which is insufficient. Because RM-2 was treated with sulfuric acid, such high chromaticity values are observed due to the high content of $Fe(SO_4)_3$ in the coagulant. As the dose of coagulant increases, the remnants of colloidal particles or ions with iron may cause an increase in the color of the solution. However, coagulant RM-1, which also contains iron ions, was quite effective in decolorizing water. He reduced the color from 145 to 14.3 degrees CCS at a coagulant dose of 2.5 mg dm^{-3}. When the dose was increased to 10 and 20 mg dm^{-3}, the chromaticity was 7.1 and 5.9, respectively.

The use of $Al_2(SO_4)_3$ in water purification by settling and filtration allowed to reduce the color of water to 11.3 at a coagulant dose of 2.5 mg dm^{-3}. Further increasing the dose of coagulant can reduce the color of the water.

The use of $FeCl_3 \times 6H_2O$ coagulant was ineffective. After settling, the chromaticity of the solution does not change significantly, but after filtration it is possible to reduce the chromaticity at the level of 20 degrees CCS at a coagulant dose of 2.5 - 20.0 mg dm^{-3}. Perhaps such significant chromaticity values are due to the high content of ferrous sulfate (III), which itself gives a yellowish-red color.

Therefore, coagulant RM-1 was not inferior in efficiency to aluminum sulfate and coagulant Polvak. It provided a reduction in chromaticity to values less than 20.0 degrees CCS that meets the requirements for drinking water quality (Table 3).

As the dose of coagulants increases, the color of the solutions decreases, both during settling and filtration. The reason for this is not only the coagulating action of the reagents, but also in lowering the pH of the solutions. This causes, in turn, a decrease in the solubility of humic acids in water.

To compare the effectiveness of reducing turbidity used different models of suspension - based on bentonite and kaolin.

As can be seen from Table 4, all coagulants

Table 2. Efficacy of chromaticity reduction in model solution of sodium humate by coagulants after sedimentation (I) and after sedimentation and filtration (II).

Coagulant	Dose coagulant (for Al_2O_3, Fe_2O_3), mg dm^{-3}	Degree of discoloration, Z, %	
		I	II
-	-	0.0	53.0
RM-1	1	0.0	25.3
	2.5	0.0	90.1
	5.0	0.0	90.8
	10.0	57.2	95.1
	20.0	63.3	95.9
RM-2	1	0.0	2.9
	2.5	0.0	17.4
	5.0	0.0	33.3
	10.0	0.0	52.2
	20.0	3.3	57.3
$Al_2(SO_4)_3$	1	0.0	65.0
	2.5	0.0	92.2
	5.0	0.0	95.1
	10.0	28.8	99.2
	20.0	67.9	99.5
$FeCl_3 \cdot 6H_2O$	1	0.0	5.3
	2.5	0.0	9.7
	5.0	11.6	87.3
	10.0	13.5	91.1
	20.0	27.8	92.7
Polvak	1	0.0	5.1
	2.5	0.0	11.7
	5.0	0.0	33.5
	10.0	25.2	78.1
	20.0	59.6	91.1

Table 3. Requirements for regulatory documents on water quality.

Water quality indicator	Requirements for water quality according to DSanPin 2.2.4-171-10	WHO Standards for drinking water
Turbidity, mg dm^{-3}	20.0 (35.0)	15.0
Chromaticity, ° CCS	0.5 (1.5)	5.0

Table 4. Efficacy of turbidity reduction in model solution of bentonite and kaolin by coagulants after settling (I) and after settling and filtration (II).

Coagulant	Dose coagulant (for Al_2O_3, Fe_2O_3), mg dm^{-3}	Degree of clarification, Z, %			
		bentonite		kaolin	
		I	II	I	II
-	-	37.1	61.5	22.5	86.7
RM-1	1	50.5	85.1	47.6	87.1
	2.5	58.9	95.5	52.6	90.5
	5.0	73.5	98.8	77.5	94.8
	10.0	79.6	99.9	83.6	99.1
	20.0	86.7	100.0	89.5	99.7
RM-2	1	21.5	92.8	20.7	85.4
	2.5	33.5	95.6	28.5	89.6
	5.0	37.4	96.7	34.5	93.9
	10.0	59.7	98.7	52.6	98.5
	20.0	63.8	99.3	61.5	99.3
$Al_2(SO_4)_3$	1	43.1	95.8	45.7	97.1
	2.5	57.3	97.9	82.1	99.3
	5.0	57.5	99.1	85.9	99.5
	10.0	61.8	100.0	93.5	100.0
	20.0	74.5	100.0	95.8	100.0
$FeCl_3 \times 6H_2O$	1	34.2	96.1	28.6	31.5
	2.5	47.6	99.3	36.8	34.9
	5.0	49.6	99.5	47.9	98.7
	10.0	65.9	99.7	61.5	99.3
	20.0	74.5	99.9	69.4	99.5
Polvak	1	43.7	84.5	41.5	81.5
	2.5	59.9	93.8	58.4	92.5
	5.0	64.2	96.3	63.4	97.1
	10.0	67.1	98.9	65.8	98.4
	20.0	69.5	99.9	63.5	99.6

contribute to the effective reduction of turbidity of the model suspension of bentonite and kaolin during settling. When settling and filtering, there is an increase in clarification efficiency. At doses > 1 mg dm^{-3}, all coagulants show a high effect of reducing turbidity.

The results obtained using these coagulants were used for water purification of the Dnipro and Desna rivers (Table 5). If we talk about chromaticity, the best result was obtained when using coagulants RM-1, RM-2 and $Al_2(SO_4)_3$. At a dose of coagulants 10 - 20 mg dm^{-3}, the normative values were achieved. After settling, the turbidity decreased, but with increasing dose of coagulants there was a slight increase. After filtration, the turbidity was reduced to 0 for all types of coagulants.

As the dose of coagulants increases, there is an increase in the residual content of aluminum or iron. However, their concentration did not exceed 0.2 mg dm^{-3}. When using coagulants RM-1 and Polvak residual

Table 5. Influence of coagulants on the efficiency of reducing turbidity and color in the Dnieper and Desna rivers with coagulants after settling (I) and after settling and filtering (II).

Coagulant	Dose coagulant (for Al_2O_3, Fe_2O_3), mg dm^{-3}	Residual turbidity, mg dm^{-3}				Filtrate color, degrees on the CCS			
		Dnieper river		Desna river		Dnieper river		Desna river	
		I	II	I	II	I	II	I	II
-	-	6.9	0.0	3.4	0.0	58.0	43.1	29.3	23.5
RM-1	1	6.7	0.0	2.9	0.0	35.4	31.1	22.3	21.2
	2.5	6.1	0.0	2.3	0.0	39.5	29.8	23.7	20.1
	5.0	9.3	0.0	4.9	0.0	42.5	27.3	24.5	17.7
	10.0	10.7	0.0	5.1	0.0	45.2	9.7	24.9	8.7
	20.0	17.1	0.0	6.3	0.0	47.1	9.3	25.1	8.5
RM-2	1	6.3	0.0	3.1	0.0	38.9	35.8	22.9	22.3
	2.5	5.8	0.0	3.0	0.0	39.6	34.6	23.1	20.5
	5.0	8.4	0.0	4.5	0.0	43.9	29.8	24.1	18.6
	10.0	9.9	0.0	4.7	0.0	46.8	12.5	24.9	9.5
	20.0	10.2	0.0	5.2	0.0	49.5	11.1	26.5	8.8
$Al_2(SO_4)_3$	1	6.9	0.0	3.7	0.0	58.6	31.3	28.6	23.9
	2.5	5.8	0.0	3.5	0.0	57.4	27.5	29.4	23.5
	5.0	11.8	0.0	4.9	0.0	56.5	25.4	27.6	22.2
	10.0	12.1	0.0	5.1	0.0	53.8	21.8	27.9	20.3
	20.0	12.3	0.0	5.4	0.0	55.9	20.1	26.7	19.1
$FeCl_3 \times 6H_2O$	1	2.3	0.0	1.9	0.0	59.5	31.9	29.7	20.9
	2.5	1.7	0.0	1.6	0.0	71.5	34.6	39.7	22.6
	5.0	6.5	0.0	3.5	0.0	132.5	38.9	71.9	23.7
	10.0	9.7	0.0	5.7	0.0	210.6	43.5	115.6	24.6
	20.0	21.3	0.0	9.7	0.0	329.5	47.5	198.6	24.9
Polvak	1	7.5	0.0	4.1	0.0	44.1	37.8	27.5	24.8
	2.5	6.2	0.0	3.5	0.0	43.9	35.6	26.8	24.5
	5.0	8.9	0.0	4.6	0.0	39.6	29.6	26.1	22.9
	10.0	10.2	0.0	5.1	0.0	35.6	21.9	25.1	20.6
	20.0	15.2	0.0	5.9	0.0	33.2	20.5	24.9	19.3

metal concentrations did not exceed 0.07 mg dm^{-3}, and in some cases - 0.03 mg dm^{-3}.

After evaluation of the results, we can say that the use of coagulants based on sludge is the most appropriate and effective, as it solves the problem of disposal of these sludges and provide water purification to the required requirements.

CONCLUSIONS

The processes of reducing turbidity of model suspensions of bentonite and kaolin during treatment with known and synthesized coagulants have been studied. It is shown that coagulant RM-1 is quite effective in the processes of water clarification during sedimentation and filtration.

Coagulant RM-1, which contains aluminum hydroxochlorides and aluminum sulfate, was found to be effective in decolorizing sodium humate solutions at doses less than 2.5 mg dm^{-3} during sedimentation and filtration. Iron chloride and Polvak effectively decolorized the solution at significantly higher doses of 10.0 and 20.0 mg dm^{-3}, respectively.

It was found that the residual content of aluminum and iron in the clarification and decolorization of water with the use of known and new coagulants did not exceed 0.2 mg dm^{-3}.

Clarification and discoloration of natural waters from the Dnipro and Desna rivers have been studied, it has been shown that the synthesized coagulants are not only not inferior, but give even better results than known.

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