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THE USE OF EFFECTIVE COAGULANTS AND FLOCCULANTS TO INTENSIFY THE PROCESS OF WATER PURIFICATION AT COKE PLANTS

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Abstract

The paper proposes a reagent method of water purification at the Kharkiv Coke Plant when using the phenolic wastewater in the water-circulating system, which corresponds to industry standards, together with coagulant (aluminum sulfate, aluminum hydroxychloride Pro-AQUA-18) and flocculant treatment (Extraflock and Besfloc). The use of cationic flocculants in water treatment has shown a high degree of efficiency in the removal of suspended substances compared with the Pro-AQUA-18 coagulant at a dose of 50 mg/dm3 or flocculant – 2-4 mg/dm3; it does not lead to the secondary pollution of the water and does not increase its corrosive activity. The purification of the clarified water was carried out using a filtration unit with a filtering load from a layer of quartz sand. The use of the proposed reagent method of water purification will allow it to be used for the technical purposes of the enterprise, reduce the consumption of fresh water, and eliminate the discharge of phenolic wastewater into the municipal sewer network.

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Key words

- Reagent treatment,
- Coagulant,
- Flocculant,
- Circulating water supply,
- Coke plant.

1 INTRODUCTION

One of the most important issues of environmental protection is the protection of water basins from pollution. Therefore, the main focus of the environmental policy of enterprises is resource conservation, i.e., repeated or consistent use of all categories of wastewater. The tightening of requirements for the protection of an air basin from pollution increases the requirements for the quality of the wastewater treatment (Stanko and Škultétyová, 2018). The process of the wet quenching of coke contributes to the pollution of the atmosphere by even using processed water for quenching coke (Bargieł et al., 2018).

The relevance of the chosen topic is due to the need for a substantial intensification of the water purification process at coke-chemical plants, provided that coke-plant water resources are used rationally. Suspended mechanical impurities impede the use of water in industrial processes and are deposited on equipment and in pipelines and structures (Bargieł et al., 2018; Pavlov et al., 2010; Parimal and Ramesh, 2014; Popova and Christov, 2006). Therefore, the improvement of the processes of reagent water treatment at coke-chemical plants is the main factor in the preparation of water for its use in water-cooling systems.

The problem of wastewater treatment of coke-chemical production is solved by a complex of physical, chemical, mechanical and biochemical methods that are used to treat local effluents and total phenolic effluents in biochemical plants. The choice of methods and the effectiveness of treatment are largely determined by how the treated wastewater is used. At most operating coke plants, treated wastewater is used to extinguish coke (Pavlov et al., 2010; Parimal and Ramesh, 2014).

Foreign experience in the purification of phenolic wastewater at coke plants shows that purification is carried out by an extraction method and that their purification is biological. At some plants, quartz filters are installed; resinous substances are effectively removed from over-resinated water and flotation plants for sewage treatment, as well as biological installations for the disposal of wastewater. Recently, the post-treatment of wastewater has become topical, because only one biochemical treatment of industrial wastewater in some cases is not enough.

Sewage from coke production contains the following streams (Voytenko et al., 2004):

– sludge water from the preparation of coal and dust collection at coal preparation and coke plants;
– phenolic wastewater – phenol content 0.02 g/l. In addition to vapor-volatile monohydric phenols, the wastewater contains nonvolatile dihydric phenols (pyrocatechol, resorcinol)
– polluted stormwater runoff.

The largest amount of polluted wastewater is phenolic wastewater. In a plant-wide stock of coke production, the contents of the main carriers of carcinogenic substances (benzopyrene) are as follows: phenols, ammonia, hydrogen sulfide, cyanides, benzenes, and resins.

At coke plants with wet quenching of coke, there are the following categories of polluted wastewater (Voytenko et al., 2004; Grigoruk and Pushkarev, 1987):

1. Phenolic wastewater in the amount of 150-250 m^3/h. They are used for the purpose of the wet quenching of coke.
2. Industrial rainfall in the amount of 20-150 m^3/h (periods of no precipitation and snowmelt) and less than 1000 m^3/h (during rainy periods). They come from, i.e., surface rainfall runoff from the territory of the coke plant, overflow from different recycling cycles, drainage wastewater, and sometimes a small amount of domestic wastewater.
3. Domestic and fecal waste water in the amount of 20-100 m^3/h.

Depending on the nature and concentration of the pollutants contained in wastewater, as well as in the directions for use of these waters, wastewater from coke plants requires different preparations (Liu and Tian, 2005; Parimal and Ramesh, 2014).

Typically, the preparation of phenolic wastewater is carried out in the following order:

– cleaning of mechanical impurities, resins and oils in the settling tanks;
– biochemical purification from phenols, ammonia, rhodanides, and cyanide in the airtanks;
– after-treatment on filters with granular loading;
– stabilization treatment with substances – corrosion inhibitors and inhibitors of the formation of dense salt deposits.

In plants with wet coke quenching, purified phenolic wastewater is used to quench coke. Wastewater from the wet quenching of coke is in a closed loop with cleaning in sumps.

The stable operation of biochemical purification in coke plants and the high activity of bacteria are possible, provided that the oils and resins are sufficiently complete prior to removal; they have a detrimental effect on phenol oxide cultures.

Therefore, the first stage of purification is the lighting, i.e., the separation of insoluble impurities (suspended solids, resins and oils) in the settling tanks. Coagulants are used to improve the treatment of the wastewater from resins and oils.

The main disadvantage of closed systems is the need to purge the system and fill it with fresh water. However, existing methods of intensifying water treatment at coke plants when using phenolic wastewater as a wake-up water are not always acceptable, since they lead to an increase in the content of suspended solids, biological growth, and water purification at coke plants with subsequent purifications. An analysis of phenolic wastewater treatment methods and the experience of coke plants has shown the need to intensify the water purification process when using effective flocculating coagulants and the need for additional purification of water by filtration.

Thus, the development and justification of the intensification of the water purification process to improve its quality for reuse in water-cooling systems at coke plants when using effective reagents is relevant.

The purpose of this study is to substantiate the method of water purification at coke plants with vicariously sensitive coagulants and flocculants to improve the quality of recycled water for reuse in the system.

2 MATERIALS AND METHODS

Experimental studies were carried out at the Kharkiv Coke Plant. The facilities of the biochemical plant installation provide:

- Mechanical sewage treatment using filters with loading from the coke breeze;
- Physical and chemical cleaning – using a composite coagulant and settling equipment;
- Biochemical purification – in aeration tanks and mechanical vacuum filters on sand-loaded filters.

Water pollution in circulating water supply systems occurs in the process of its production, as well as in open coolers upon contact with the atmospheric air. Suspended mechanical impurities impede the use of water in industrial processes; they are deposited on equipment and in pipelines and structures. At the same time, they are types of carbonate salt concentration centers, which accelerate the precipitation of salt (Privalov et al., 1973; Vinarskii and Papkov, 1978).

The amount of suspended particles at the Kharkiv Coke Plant is 500-600 mg/dm^3. This indicates corrosion in the treated water, as well as entrainment of slurries from the biological purification system and the coke shop.

The purification of water from mechanical impurities (clarification) is carried out in horizontal sumps and in clarifiers with a suspended layer of sediment in open hydrocyclones and filters. Physical and chemical methods of industrial wastewater treatment using coagulants and flocculants can remove up to 97-98% of colloidal and highly dispersed impurities from wastewater and are among the most effective methods used today (Draginskiy and Alekseeva, 2005; Getmantsev et al., 2008; Veytser and Mints, 1984; Linevich and Getmantsev, 2007; Gandurina, 2000).

The investigation of the corrosion processes in the circulating water supply system at the Kharkiv Coke Plant showed that, despite the operation of the wastewater treatment plants at the plant, the degree of their purification does not meet the established standards for discharge not only for water bodies, but also for urban sewage systems. On that basis, the best option is to use the biologically treated phenolic wastewater at the plant in the water-cooling systems.

We propose using one of the methods for the preparation of water for the removal of suspended substances, i.e., the coagulation method, for treatment with effective coagulants and flocculants and to carry out post-treatment on filters with a granular load (sandy).

2.1 Justification of the choice of reagent for clarifying phenolic wastewater

As coagulants for water purification, salts of aluminum sulfate $Al_2(SO_4)_3$ (alumina), iron sulfate $FeSO_4$ (vitriol), and ferric chloride $FeCl_2$ (Draginskiy and Alekseeva, 2005; Get`mantsev et al., 2008) have become widely used. Iron sulfate is recommended as a coagulant for the purification of phenolic waters since, simultaneously with the manifestation of the coagulating properties of iron salts, cyanides are mixed in the phenolic waters for non-toxic biochemical purification of ferrocyanides. With the introduction of the ferrous sulfate into water, slightly soluble iron hydroxides are formed:

$$FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2 + H_2SO_4, \quad (1)$$

Since it is not hydroxide (II) $Fe(OH)_2$, but iron (III) hydroxide $Fe(OH)_3$, which has a coagulative effect (flakes), it must be oxidized to the trivalent, when using ferrous iron:

$$4Fe(OH)_2 + O_2 + H_2O \rightarrow 4Fe(OH)_3, \quad (2)$$

The optimal temperature of wastewater during coagulation with iron sulfate is 30-40°C with a pH of 8-10. At low pH values, the alkalization of water is necessary. It is initially necessary to attribute the intensive mixing of the water at the initial stage for a uniform distribution of the coagulant solution. At the next stage, during agglomeration of the particles, the mixing of the water should be moderate, since the macrophase formed has a low-strength structure that can collapse.

The presence of organic matter in the water requires an increase in the dosage of the coagulant. Typically, the flocculation process should be completed in 5-10 minutes. With various deviations, in particular when the pH of the water is excessive, the duration of the flocculation process may increase to 20 minutes.

Our experience of using reagents in the process of preparing wastewater from coke plants shows that its use is associated with certain difficulties, i.e., the preparation of reagents requires special equipment; production areas are needed; raw materials are necessary; reagents are needed for correlation of the pH of the medium caused by corrosion, etc.

Therefore, methods that can intensify water treatment with reagents with modern coagulants or flocculants, for example, aluminum hydroxychloride Proaqua, Besfloc, Extraflock, etc., are currently becoming more common.

The correct choice of coagulant is one of the conditions for an effective coagulation process. The optimal dose of the coagulant and the minimum amount at which full clarification of water is provided depends on the physicochemical properties of any contaminants, the temperature, the pH, and the salt composition of the water. Due to the lack of sufficiently reasonable patterns to calculate the optimal dose of a coagulant, it should be determined by the trial coagulation method.

2.2 Research Methods

Studies assessing the effect of coagulant and flocculant additives and determining their optimal dosage were carried out according to the generally accepted method of trial coagulation (Get`mantsev et al., 2008; Veytser and Mints, 1984; Gandurina, 2000). Preparation of the coagulant solutions investigated (aluminum sulfate $Al_2(SO_4)_3$, aluminum hydroxychloride Pro-AQUA-18 $Al_2Cl(OH)_5$) and the flocculants Extraflock and Besfloc (South Korea, manufactured by Kolon Life Science Inc. and Pology Chemical Plant COAGULANT ALC, Zaporizhia region, Ukraine) were carried out in laboratory conditions.

The effectiveness of the use of the coagulant was determined by the hydraulic size (U_0), which is a measure of kinetic stability equal to the deposition rate (emersion) of particles, which can be calculated by the following formula (Draginskiy and Alekseeva, 2005; Get`mantsev et al., 2008; Nesterenko et al., 2013):

$$U_0 = \frac{h}{t}, \text{ мм/с}, \quad (3)$$

where h is the height of the settling zone, mm;

t – duration of settling, sec.

The relative percentage of suspensions:

$$E = \frac{C \cdot 100}{C_0}, \%. \quad (4)$$

With decreasing sizes of particles, their resistance to sedimentation increases. The effectiveness of wastewater treatment with coagulants and flocculants is determined not only by the aggregative and kinetic stability of the dispersed contaminants, but also by the chemical characteristics of the dispersed phase and the dissolved organic and inorganic contaminants.

The studies were carried out in laboratory conditions on the model and the recycled water of the Kharkiv Coke Plant according to the standard method, i.e., the test coagulation method. The trial coagulation method was performed as follows:

The source water was poured into several cylinders (up to 10) with a capacity of 0.5 or 1 liter; then a solution of a coagulant of a certain concentration and volume calculated for a specific range of reagent doses was introduced into the cylinders. The coagulant was mixed with water by stirring the water with a glass rod. A visual observation of the process of the formation of flakes, the efficiency of the sedimentation, the size of the flakes, and the height of the formation of the sediment was conducted in some cases on the basis of visual observation. The required dose of the coagulant was then selected. However, for a more accurate determination of the coagulant dose, the separated water was filtered through previously prepared paper filters washed with hot distilled water. The pH was measured in the settled water. The research results are expressed as the dependence of the optical density, turbidity, or chromaticity on the dosage of the coagulant.

The optimal dose of coagulant is that dose at which the quality of the purified water is almost independent of the dose of the reagent injected and when the monitored indicators correspond to the requirements of the standard.

If necessary, the introduction of service reagents, i.e., lime or soda, during the test coagulation of these reagents is introduced into the water. When monitoring the effectiveness of the water purification process, the timing of their introduction is determined, i.e., before or after the coagulant, as well as the dose when performing the coagulation test.

To improve the efficiency of the water clarification during the coagulation, the flocculant is introduced into the water. The determination of the required dose of flocculant is also carried out during the trial coagulation. Various doses are introduced into the treated water with the optimal dose of the coagulant after 1-2 minutes.

The trial coagulation should be carried out at a constant water temperature that corresponds to the temperature of the water in the circulating water system. The conditions of the test coagulation may vary, depending on the technology and mode of water purification in specific enterprises. The results of the test coagulation data are refined and adjusted when used in production conditions, taking into account the operating experience of the sewage treatment plant. In each case, the optimal dose will be the one at which all the controlled indicators reach the standard values.

3 RESULTS AND DISCUSSION

At coke plants, reagents are mainly used for local wastewater treatment from suspended solids, resins and oils. The use of ferrous sulfate $FeSO_4$ (with a dose of 30-70 mg/dm^3) at the Kharkiv Coke Plant makes it possible to reduce a residual content of the suspended substances, resins and oils by 50 % compared to non-reagent sedimentation or flotation.

However, for the physico-chemical purification of phenolic wastewater, the plant periodically uses a composite coagulant (0.1% solution of $FeSO_4$: $AlCl_3$ in the ratio of 3.4: 1), followed by settling in the sewage regulator. The use of this type of coagulant (during a flood period) has its drawbacks. The required dose is large (the average value is 70 mg/dm^3); therefore, from an economic point of view, its application requires additional consideration. Also, the addition of such a composite coagulant to water leads to a decrease in the pH and alkalinity of the water and requires adjusting the pH to 7-8.5 units. It therefore leads to an increase in the corrosion rate.

The existing water treatment with coagulants given above is inefficient and significantly reduces the pH of the water. Since the use of certain coagulants, especially in large doses, leads to the acidification of the wastewater, it is necessary to additionally adjust the pH with alkaline reagents.

The research study of the effect of the additives of coagulant and flocculant solutions was carried out under laboratory conditions on the model water and the circulating water of the Kharkiv Coke Plant.

3.1 Influence of coagulants and flocculants on the clarification of the model water

In this work, polyoxychloride aluminum Pro-AQUA-18 and Extraflock and Besfloc-type flocculants were used as coagulants. The effectiveness of the Extraflock and Besfloc flocculants for sewage treatment at coke plants was investigated.

At the first stage, the model water was prepared. A standard technique was applied, which involves the use of an aqueous extract of peat and a settling kaolin suspension within 2 hours. A peat extract was prepared from a peat briquette; it was steamed in hot water (t = 80° C) for a day, and then the resulting concentrate was filtered through a dense cloth. The pH of the concentrate was adjusted to 7 by introducing a Na_2CO_3 solution into it. The pooled concentrate was placed in a hydraulic mixer, diluted to the value of the chromaticity (estimated to be 5–6 times greater, and then was metered into tap water in the required ratio.

To research the physicochemical purification of phenolic water with various coagulants and flocculants under laboratory conditions, model solutions were prepared with pollutants. Model waters (artificially prepared water samples) simulate the composition of circulating phenolic waters with their typical coking plant pollution. The approximate concentrations of pollutants in the model solution are as follows: phenol concentration – 4 mg/dm^3; total hardness – 30 mg/dm^3; the content of suspended substances – 48-700 mg/dm^3.

Preparation of the reagents in laboratory conditions was the next stage. For the research the following reagents were used:

– flocculants (Besfloc, Extraflack) cationic. Flocculants belong to the class of low-toxic substances (Tab. 1) with solution concentrations of 0.1-0.2%;
– coagulants (aluminum sulfate $Al_2(SO_4)_3$, Pro-AQUA-18 aluminum hydroxychloride).

Preparing the solution took 60 minutes. Preparation of the solution was carried out in stainless steel or plastic containers. The temperature of the working solution was 15-30°C.

Flocculants consist of high molecular weight anionic, non-ionic and cationic polymers. They are used to increase the efficiency of the precipitation, illumination, filtration and centrifugal processes in most wastewater treatment processes. Colloidal particles are particles with a size of less than one micron that perform Brownian motion. The energy of this movement is sufficient to prevent the particles from being precipitated by gravity, and such particles remain in limbo for long periods of time.

When using flocculants, bridges are formed between the individual particles. The formation of such bridges occurs when the segments of the polymer chain are absorbed at different lobes and grown together. Flocculants carry the active groups that serve as a counterweight to the charge of the particles. Flocculants are absorbed by the particles that cause destabilization, either through the formation of bridges or by neutralizing the charge.

In the treated water (model or circulating) the test portion of the flocculant solutions should be added to each laboratory glass in cups of 500 or 1000 ml. The resulting solution is then preserved in magnetic mixers for 1-3 minutes at a speed of 30-70 revolutions per minute. At the same time the time required for the formation of the flocs should be determined and the following indicators should be recorded:

– the time required for the formation of the flocs;
– the size of the floccules and their strength (small, large, etc.; loose, dense, etc.);
– the deposition rate compared to the test in the cylinder.

The studies were conducted under laboratory conditions at a temperature of 25° C and a pH of 7.1. A 0.1% solution of the flocculants was added to the water with a dose of 0.5-10 mg/dm^3. The research

Tab. 1 *Characteristics of the flocculants*

Appearance	**White granular powder**
The size of the granules	0.1 mm <95% <1 mm
Ionity of the connection	High Active Cation
Viscosity of 0.5% at 25°C	50 - 70 cps
pH of a 0.2% solution	3.0 - 5.0

Tab. 2 *Results of the laboratory studies of the effect of flocculant solutions on the clarifying of model water*

N of sample	0	1	2	3	4	5	6	7
Volume of solution, W, ml	-	0.1	0.2	0.6	0.8	1.2	1.6	2.0
Dose of flocculant, mg/dm^3	-	0.5	1	3	4	6	8	10
Optical density, D (before stagnation)	0.8							
0.1% cationic flocculant solution of Besfloc								
Optical density, D (after stagnation)	0.6	0.11	0.095	0.065	0.065	**0.05**	0.055	0.075
Time of subsidence, min	20	18	15	13	14	**3**	6	7
0.1 % cationic flocculant solution of Extraflock								
Optical density, D (after stagnation)	0.35	0.19	**0.14**	0.16	0.18	0.22	0.25	0.28
Time of subsidence, min	20	20	**5**	6	9	10	12	13

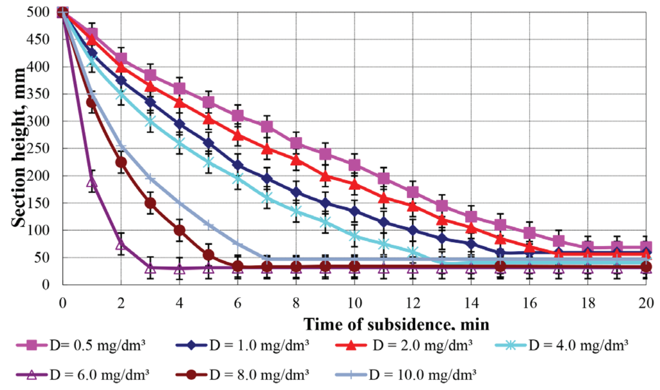

Fig. 1 *Kinetics of the stagnation of the model water using different coagulants and a 0.1% cationic flocculant solution of Besfloc*

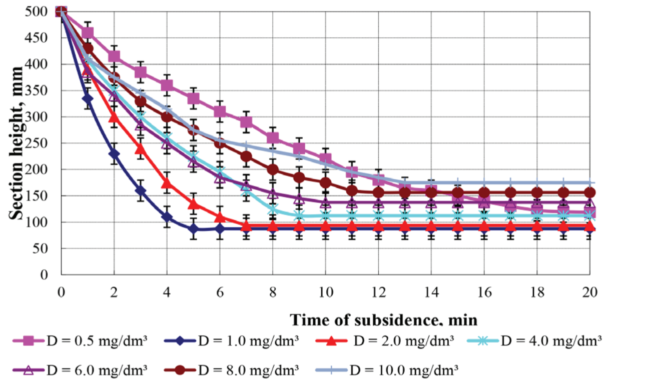

Fig. 2 *Kinetics of the sedimentation of the model water using different coagulants and a 0.1% cationic flocculant solution of Extraflock*

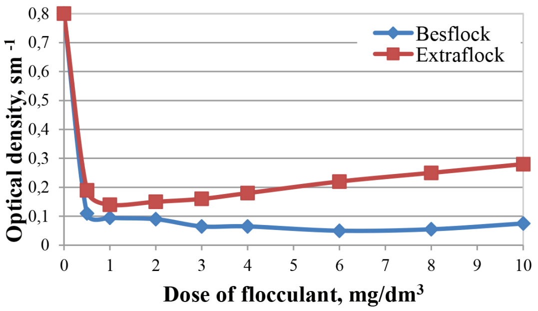

Fig. 3 *Effect of the process of the sedimentation of the suspension with the addition of the Extraflock and Besfloc cationic flocculants (D = 0.5-10.0 mg/dm³)*

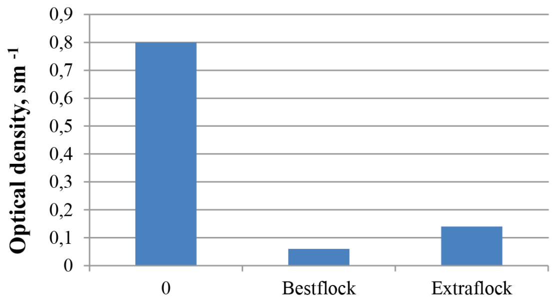

Fig. 4 *The effect of different types of flocculants on the efficiency of clarifying model water (optical density)*

results on the introduction of the flocculant solutions for the clarifying of the model water are listed in Tab. 2 and Figs. 1-4.

As a result of the research conducted on the model water of the Kharkiv Coke Plant with the introduction of various doses of flocculants, the high efficiency of the removal of suspended substances in the model water of the Kharkiv Coke Plant was established. It was revealed that an effective reagent is a Bescloc cationic flocculant at a dose of 6 mg/dm³ and Extraflock at a dose of 1 mg/dm³.

3.2 Influence of coagulants and flocculants on the clarification of the circulating water

In the study of the existing state of the wastewater treatment at the Kharkiv Coke Plant, it was revealed that a composite coagulant (0.1% solution of $FeSO_4$: $AlCl_3$ in a ratio of 3.4:1, respectively), followed by water precipitation in sewage regulator is used for the local wastewater treatment of individual plants. It was established that the addition of such a composite coagulant to the water leads to a decrease in the pH and alkalinity of the water and requires adjusting the pH to 7-8.5 units; it therefore causes more inefficient water purification.

In the research on and selection of modern coagulants and/or flocculants, experiments were conducted. The preparation of the test solutions of the coagulants (aluminum sulfate $Al_2(SO_4)_3$, aluminum hydroxychloride Pro-AQUA-18) and the Extraflock and Besfloc flocculants were carried out in laboratory conditions.

The use of aluminum sulfate is ineffective at a dose of 130 mg/dm³ (Fig. 5). The formation of flakes, i.e., more than 20 hours is timed. The use of aluminum sulfate for water treatment was inefficient and reduced the pH of the water. Since the use of certain coagulants, especially in large doses, leads to acidification of wastewater, it is necessary to additionally adjust the pH with alkaline reagents.

In general, the research results indicate a high degree of efficacy using the Pro-AQUA-18 coagulant and the Extraflock and Besfloc flocculants when used independently and in conjunction with aluminum sulphate (Figs. 5-7) (Nesterenko et al., 2012, 2013).

The use of cationic flocculants in the water treatment at the Kharkiv Coke Plant showed a high degree of efficiency in the removal of the suspended solids compared with anionic and ionic flocculants at a dose of 2-6 mg/dm³. This is due to the fact that high-molecular flocculants lead to the enlargement of flakes and an increase in the rate of release of the coagulated pollution (Draginskiy and Alekseeva, 2005; Get`mantsev et al., 2008).

The greatest effect is achieved when using these flocculants on their own for sewage treatment by settling, because, as was found in the experiments, they provide for the formation of the largest

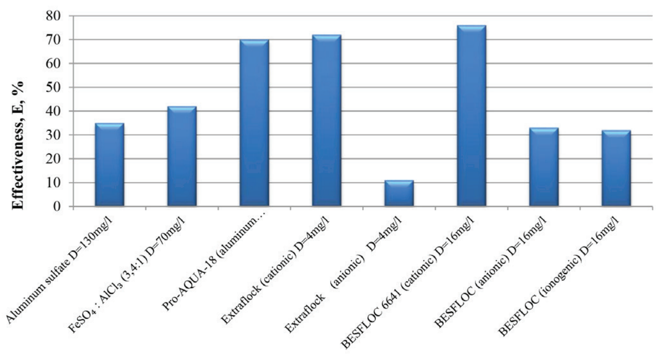

Fig. 5 *Effect of coagulants and flocculants on the purification of circulating water*

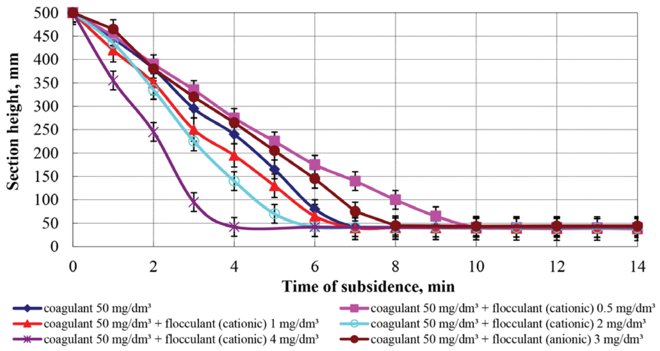

Fig. 6 *Kinetics of the process of sedimentation of the suspension with the addition of the coagulant – aluminum hydroxychloride Pro-AQUA-18 (D = 50 mg/dm³) and the Extraflock cationic flocculants (D = 0.5-4.0 mg/dm³)*

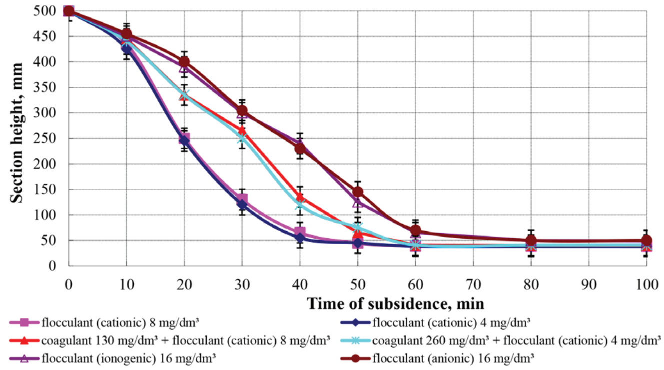

Fig. 7 *Kinetics of the process of sedimentation of the suspension with the addition of the coagulant – aluminum sulfate (D = 130-260 mg/dm³) and the Besfloc cationic flocculants (D = 4-8 mg/dm³)*

flakes. This method of improving the technology of the flocculation of wastewater treatment by using only organic flocculants instead of mineral coagulants allows you to:

- completely eliminate secondary pollution of purified water by products of the hydrolysis of aluminum and iron salts
- reduce the corrosive activity of the water;
- return the purified water for repeated use;
- reduce the reagent consumption by tenfold;
- improve the efficiency and stability of the water treatment;
- increase the productivity and reliability of the treatment plant.

When dissolved in water, cationic organic flocculants dissociate into positively charged macro-ions and low molecular weight ions; i.e., they acquire a positive charge, which results in their high degree of efficiency in phenolic wastewater.

It was experimentally shown that the use of organic flocculants (at a dose of 2-6 mg/dm³) to clarify the water studied does not lead to the secondary pollution of the water and does not increase its corrosive activity (Nesterenko et al., 2013). In the case of a high content of suspended substances in water, it is recommended to conduct water purification with Pro-AQUA-18 coagulant at a dose of 50 mg/dm³ or a flocculant (Extraflock or Besfloc) at a dose of 2-4 mg/dm³.

Thus, we have shown the use of the proposed reagents to clarify the circulating water without increasing its corrosive activity.

3.3 Industrial testing of the application of the coagulants/flocculants studied

As a result of the analysis of the quality of the wastewater treated at the biochemical plant, it was established that the values of the indicators (suspended solids, phenols and rodanids) do not meet the requirements for using water in the enterprise's water supply cycle, as shown in Tab. 3.

Tab. 3 *Results of the analysis of the quality of the wastewater of the Kharkiv Coke Plant*

Name of indicators	Indicators Value, mg/dm³		
	before	after	for use in water-cooling system
	the biochemical installation		
pH, unit	8.3	8.3	6.5-8.5
Suspended substances, mg/dm³	300-500 (600)	60	40
Phenols, мг/дм³	263	17	1-2
BOD, mg/dm³ of oxygen	1800	150	150
Soluble ether, mg/l	9	6	20
Sulphides, mg/l	1	1	1
Phosphates, mg/dm³	3	3	5
Synthetic surfactants, mg/dm³	0.1	0.1	-
Iron, mg/dm³	5	3	4
Rodanids, mg/dm³	955	47.2	5
Ammonium nitrogen, mg/dm³	780	50	150
Petroleum products, mg/dm³	30	3	50
Cyanides, mg/dm³	30	5.0	28
Salt content, mg/dm³	1200	1200	2000

Note: water quality results provided by the laboratories of the Kharkiv Coke Plant and UkrVODGEO.

Tab. 4 *Industrial tests of the circulating water in the water-circulation system at the Kharkiv Coke Plant with the use of the Besfloc flocculant at a dose of 4 mg/dm³*

Parameters	**Date**				
	August	September	October	November	December
pH, unit	7.3	7.3	7.0	7.7	7.5
Rodanids, mg/dm³	6.8	6.4	5.7	5.5	4.8
Suspended substances, mg/dm³	90	93	54	82	60
Iron, mg/dm³	4.5	6.3	9.7	12	20
Chlorides, mg/dm³	585	532	425	745	755
Phenols, mg/dm³	0.5	0.4	0.5	0.6	0.55
Dry residue, mg/dm³	3530	3364	2756	3640	3665

The assessment of the quality of the circulating water with the dosage of flocculants was carried out on the water-cooling systems of the Kharkiv Coke Plant; the results of the research are given in Tab. 4.

As follows from Tab. 4, the efficiency of the water treatment at a dosage of 0.1% flocculant solution achieves a reduction in the content of the suspended substances from 500-600 mg/dm³ to 50-100 mg/dm³. Such a high degree of efficiency of the flocculant application is explained by the proposed reagent supply technology, since the circulating water supply system is fed into the effective composition of the supplying water, which is settled in a separate container.

The process of the physico-chemical purification of phenolic waters by using effective reagents should be intensified, i.e., Besfloc or Extraflock flocculants at a recommended dose of 4 mg/dm³. In the technological scheme for the purification of the phenolic water, it is recommended to dispense the flocculant solution with the help of the Automatic Polymer Solution Preparation Units "SMART Mix" SPR 2100 BV, produced by the EKOTON Industrial Group (Ekoton, 2018) with a capacity of 100 l/h, which is made of construction material, i.e., polypropylene. The equipment is a two-chamber installation for the cyclic preparation of a polymer solution from a dry starting product and continuous dosing of the finished solution.

The recommended quality of the water purification for use in a water-circulation system is achieved by means of the deep purification of the water after the equipment of the secondary clarifier. To do this, it is necessary to install an additional filtration unit using a layer of quartz sand as the filtering load. The use of the proposed solution ensures uninterrupted operation of the heat exchange equipment due to a decrease in the amount of suspended solids up to 20 mg/dm³ and allows for the reuse of the water in the circulating water supply system (see Tab. 5).

Tab. 5 *Designed quality of wastewater treatment on filters*

Parameters	Value of indicators	
	before filter	after filter
pH,unit	7-8.5	6.5-8.5
Suspended substances, mg/dm³	60	20
Phenols, mg/dm³	0,4	0,4
Rodanids, mg/dm³	5	5
Resins and oils, mg/dm³	25	2
Cyanides, mg/dm³	0,7	0,7

After the implementation of the above requirements, the quality of the treated wastewater will meet the requirements for the use of water for technical purposes of the water-circulation system at the plant. The treated wastewater can be used for the technical purposes of the plant.

The proposed technical solution using conditioned phenol runoff and/or with fresh water or instead of fresh water allows for reducing the amount of reagents necessary for stabilization treatment, as well as significantly reducing the discharge of sewage into the city sewer network and fresh water from the artesian wells.

4 CONCLUSIONS

As a result of the analysis performed, it was established that the purification of phenolic wastewater from coke plants is inefficient and is caused by insufficient purification in biochemical plants. This is due to the insufficient purification at previous stages, particularly at the physical and chemical stages of water purification from suspended solids, resins, oils, etc. The analysis of the phenolic wastewater treatment methods and experience of coke plants showed a need to intensify the water purification process when using effective flocculants and coagulants and the need for the purification of water by filtration.

The research results show the feasibility of using Pro-AQUA-18 coagulants at a dose of 50 mg/dm³, Extraflock flocculants at a dose of 2-6 mg/dm³, and Besfloc at a dose of 2-4 mg/dm³, separately and together with sulfuric acid aluminum for water purification. It was revealed that the use of cationic flocculants in water treatment showed a high degree of efficiency in the phenolic wastewater and a high removal of suspended solids compared to the anionic and ionic flocculants (E = 80-90%).

The analysis of the results of the experiments showed that the reagent treatment of water by applying organic flocculants (at a dose of 2-4 mg/dm³) to clarify the water under study does not lead to secondary water pollution and reduces the amount of suspended substances in the circulating water (50-100 mg/dm³), which allows intensification of the process of water purification at coke plants.

The use of the proposed solution ensures uninterrupted operation of heat exchange equipment due to a decrease in the amount of suspended solids to 20 mg/dm³ and allows for the repeated use of water in water-cooling systems.

The test results showed that the intensification of the water purification process is achieved by improving the biological purification units (using effective reagents) and deep purification of water after the secondary clarifiers (using a filtration unit using a layer of silica sand as the filtering load).

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