Надано характеристику стічних вод коксохімічного виробництва. Показано актуальність розробки нової технології очистки фенольних стічних вод. Встановлено, що при використанні бентоніту з добавкою флокулянту для очистки фенольних стічних вод від кам'яновугільної смоли її концентрація в очищеній воді зменшується до 10 мг/дм^3. Доведено, що ефективність біологічного очищення стічних вод від фенолів із застосуванням комбінованого аеротенка-відстійника становить 99,9 %

Ключові слова: бентоніт, кам'яновугільна смола, флокуляція, біологічне очищення, феноли, активний мул, аеротенк-відстійник

Дана характеристика сточных вод коксохимического производства. Показана актуальность разработки новой технологии очистки фенольных сточных вод. Установлено, что при использовании бентонита с добавкой флокулянта для очистки фенольных сточных вод от каменноугольной смолы ее концентрация в очищенной воде уменьшается до 10 мг/дм^3. Доказано, что эффективность биологической очистки сточных вод от фенолов с использованием комбинированного аэротенка-отстойника составляет 99,9 %

Ключевые слова: бентонит, каменноугольная смола, флокуляция, биологическая очистка, фенолы, активный ил, аэротенк-отстойник

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DEVELOPING OF EFFECTIVE TREATMENT TECHNOLOGY OF THE PHENOLIC WASTEWATER

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1. Introduction

Industrial wastewater, including that of coke and chemical plants, is among the most toxic sources of anthropogenic pollution. The main pollutants in this category of water – phenol, cyanide, thiocyanate, ammonia, tar, are harmful to the environment and the health of employees and residents of the surrounding areas. Coke production gives rise to a significant amount of wastewater (from 0.4 to 0.6 m^3/t of coke) subject to physicochemical, mechanical and biological treatment [1]. Treated wastewater of coke and chemical plants is used mainly for coke quenching, so a large amount of various pollutants remaining in the water evaporate in contact with glowing coke and enters the atmosphere. In addition, some harmful substances (hydrogen sulfide, hydrogen cyanide, and sulfur dioxide) are additionally formed in the interaction of glowing coke with water. Therefore, even with a small concentration of pollutants in the wastewater, their content in the vapor from the coke quenching towers exceeds the maximum allowable concentration according to existing regulations. The complete industrial wastewater purification from dissolved organic matter is one of the most important and at the same time difficult problems.

2. Literature review and problem definition

Using clay materials as adsorbents in industrial wastewater treatment is becoming more common every year [2]. Among other materials for this purpose, preference is given to natural clay mineral – bentonite, general formula $Al_2[Si_4O_{10}](OH)_2 \cdot nH_2O$. There are two most common varieties of bentonite – highly hygroscopic sodium and low hygroscopic calcium [3]. The essence of water treatment with bentonite is the adsorption of contaminants by the developed surface of the latter, which can further be activated by treatment with special substances. However, this leads to a significant increase in the cost of treatment [4]. Known from foreign sources examples of using bentonite for water purification from various organic substances (such as oil, petroleum products, lubricants, etc.) indicate its ultra-high treatment ability, combined with environmental safety. In each case, the bentonite sediment, saturated with tar is formed, which, depending on its content settles or floats from a liquid [5]. In various treatment technologies of tar- or oil-containing wastewater, bentonite is used both as a coagulant and an adsorbent. Flocculants are added very often to intensify removal of contaminants from wastewater. Minor amounts of these macromolecular substances (0.1 to 5 mg/dm^3) can speed up the treatment process by several times [6]. The use of bentonite in Ukraine is restricted by the areas far from water treatment (construction, medicine, etc.), unlike countries with the developed petrochemical industry (Middle East, USA) [7]. Data on the use of bentonite clays in wastewater treatment processes, including phenol, are unavailable in Ukrainian scientific periodicals. This necessitates research to establish the fundamental possibility of using bentonite for industrial application at coke and chemical plants of Ukraine.

The biological treatment process with the use of activated sludge is one of the major stages of industrial wastewater treatment, which is the basis for almost any flow diagram [8].

Biological wastewater treatment of coke and chemical plants is the conversion of dissolved organic matter (phenol, thiocyanate, cyanide and hydrogen sulfide) into mineral compounds due to the activity of the phenol-thiocyanogen-decomposing microorganisms [9]. The microorganisms take from organic matter all necessary for reproduction, increasing the active biomass. In the treatment process, the activated sludge microorganisms decompose organic and inorganic compounds in special facilities – aeration tanks – in conditions of aeration of wastewater and sludge that is in suspension due to aeration.

Biological oxidation of phenol and thiocyanate is a complex process that takes place in several stages. It can be represented by the following chemical reactions:

$$C_6H_5OH+O_2 \rightarrow CO_2+H_2O, \quad (1)$$

$$CNS^{--}+2O_2+H_2O \rightarrow SO_4^{-2}+NH_4^{+}+CO_2. \quad (2)$$

The use of biological method provides the most complete wastewater purification from soluble organic contaminants up to 95–98 % [10].

The biochemical oxidation intensity is determined by the functioning conditions of activated sludge and essentially depends on the process parameters, the design features of units and corresponding treatment flow diagrams. Various methods are used for the biological treatment intensification, which are limited mainly to the use of technical oxygen or enriched air; application of specific microflora of activated sludge; introduction of ozone and hydrogen peroxide to the sludge mixture; application of ultrasound to increase the dehydrogenase activity of biocenosis; biological treatment using reagents; increasing doses of activated sludge [11].

One of the promising areas of biological treatment intensification is the use of combined facilities, which in various combinations serve as an aeration tank and a secondary clarifier [12].

The combined facilities of foreign companies "Infilco" (USA), "Pamerson" (England), "Degremont" (France) are the most popular and widespread in the world [13].

The known facility is the aerator-clarifier unit, developed by the K. D. Pamfilov Academy of Municipal Economy (Russia), the testing of which in industrial conditions revealed a number of significant weaknesses of the activated sludge return system. The most significant drawback of that aerator-clarifier unit is that the design did not provide normal circulation of activated sludge between the settling and aeration zones. This led to the sludge accumulation in the settling zone, digestion, and removal with clarified wastewater [14].

At present, developing various modifications of combined facilities that would intensify the treatment process, reduce the area occupied by facilities and reduce capital costs is promising [15].

The phenolic wastewater treatment technology involves two stages: mechanical purification from tars and oils, and biological – from phenol, thiocyanate, cyanide, etc. It is necessary to observe strictly the MAC (maximum allowable concentration) of tars of no more than 25 mg/dm^3 after mechanical treatment to maintain the microorganisms of activated sludge that decompose molecules of the mentioned compounds, in a viable state. Even a slight excess of the MAC leads to the mass death of bacteria. As a result, the desired treatment of hazardous substances (especially phenol) is not provided, insufficiently treated water is fed to the coke quenching, thus polluting the atmosphere.

The tar content after mechanical treatment often exceeds the MAC at PJSC "EVRAZ DKHZ" (Dniprodzerzhynsk, Ukraine) because of the inefficient treatment technology of phenolic water. As proof, we present the results of laboratory monitoring of average monthly tar content before and after mechanical treatment at PJSC "EVRAZ DKHZ" for the period of July-February 2015–2016, shown in Fig. 1, 2, respectively.

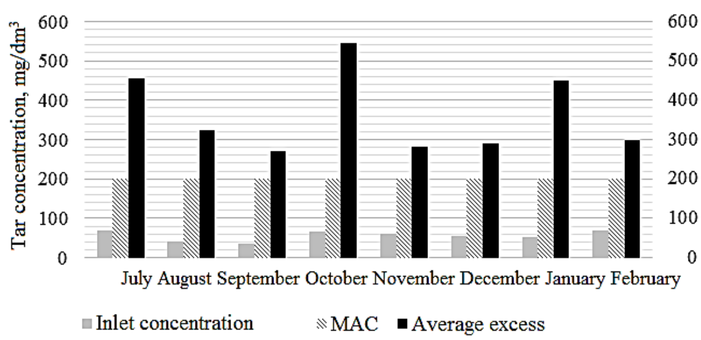

Fig. 1. The results of laboratory monitoring of coal tar content in phenolic wastewater before mechanical treatment for the period of July-February 2015–2016

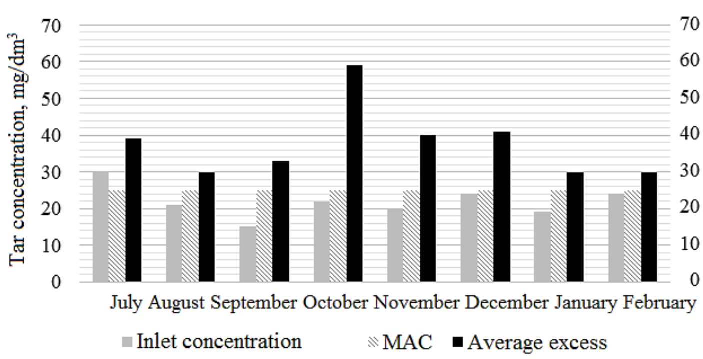

Fig. 2. The results of laboratory monitoring of coal tar content in phenolic wastewater after mechanical treatment for the period of July-February 2015–2016

Despite the fact that the average monthly inlet tar concentration does not exceed the MAC, one should take into account that each month there are about 2–10 cases of the MAC excess by 2–3 orders of magnitude. This fact leads to synchronous outlet tar MAC excess (after mechanical treatment), the negative consequences of which have already been mentioned. It is also known that the outdated equipment almost does not provide the desired treatment, even when the tar content is about 200 mg/dm^3. In this context, we consider relevant a search for a way of leveling the tar MAC excess effects, which can be implemented in the existing treatment technology.

Fig. 3, 4 show the content of pollutants, namely phenol and thiocyanate at the inlet of the plant of biochemical treatment (BCT) of phenolic wastewater and in the balance tank.

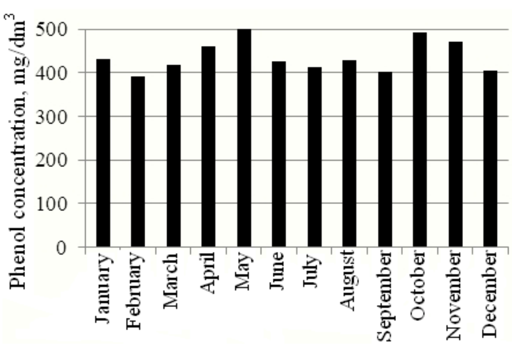

Fig. 3. The results of laboratory monitoring of phenol and thiocyanate content in phenolic wastewater at the BCT plant inlet for 2015

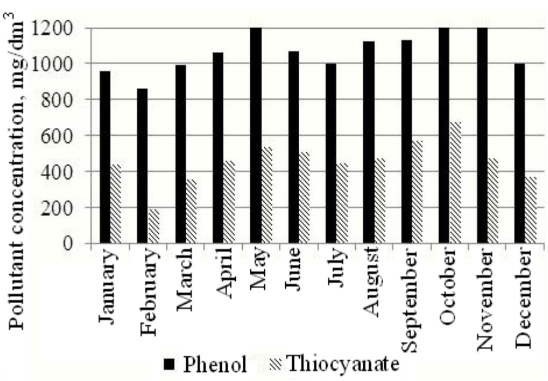

Fig. 4. The results of laboratory monitoring of phenol content in the BCT balance tank for the period of January-December 2015

From these data, we can conclude that the original phenol content varies widely during the year. This suggests that the biological treatment process at present is unstable. There is a need to develop new methods to improve the wastewater treatment.

3. Research goal and objectives

The goal is to develop a new effective technology of phenolic wastewater treatment, which comprises mechanical and biological treatment.

Realization of this goal involves solving the following tasks:

– determining the residual tar dependence on temperature, type of bentonite and initial concentration;

– examining the efficiency of the combined unit for biological treatment of phenolic wastewater;

– determining the optimum time of wastewater treatment process in the combined aerator-clarifier unit;

– developing a new technology for phenolic wastewater treatment by including wastewater treatment with bentonite and flocculant before the biological treatment and replacing the conventional aeration tank with a combined energy-efficient unit.

4. Materials and methods of research of phenolic wastewater treatment technology

Model samples of phenolic water with precisely known tar concentrations (125, 245, 265 mg/dm^3) were placed in a 400 cm^3 reactor. Wastewater temperature was raised to 50 °C by heating in a drying cabinet for compliance with process conditions the closest to industrial. The heater built in the magnetic stirrer was used to achieve the temperature of 12 and 20 °C. The ambient temperature was 12 °C. The scheme of laboratory setup is shown in Fig. 5.

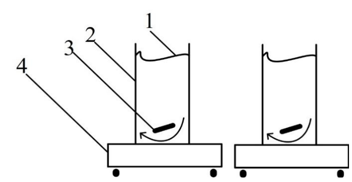

Fig. 5. The scheme of laboratory flotation setup: 1 – phenolic wastewater; 2 – reactor glass; 3 – magnet; 4 – magnetic stirrer with built-in heater

400 cm^3 of phenolic wastewater of the same temperature and with the same tar were placed in each of the two reactors. Then the mixer was turned on (mixing intensity of 1000 rev/min). The exactly known quantity of calcium bentonite – 88 mg/dm^3 and in a minute 8 mg/dm^3 of cationic flocculant were added to the first reactor. Similar operations were performed with the second reactor, sodium bentonite and flocculant were added. Then the time was measured needed for maximum water clarification, that is the most complete removal of all dissolved and colloidal impurities by making them a sediment, which, depending on water temperature settled to the reactor bottom or floated to the water surface (Fig. 6). A 100 cm^3 sample was taken from the upper liquid layers of each reactor with a graduated pipette in 20 minutes after the addition of bentonite to water for determining the residual tar concentration. The course of the experiment was precisely reproduced for all investigated temperatures (12, 20 and 50 °C). The latter temperature regime complies with the industrial treatment conditions.

a *b*

Fig. 6. The model samples of phenolic wastewater: *a* – before treatment using bentonite with the flocculant addition; *b* – after treatment using bentonite with the flocculant addition

Experimental study on phenol and thiocyanate removal from wastewater by biological treatment was performed on a laboratory model of the 10 dm^3 combined aerator-clarifier unit (Fig. 7). Phenolic wastewater from the BCT balance tank and activated sludge from the secondary clarifier were taken at a ratio of 1:1. The process was carried out for 24 hours at 28 °C.

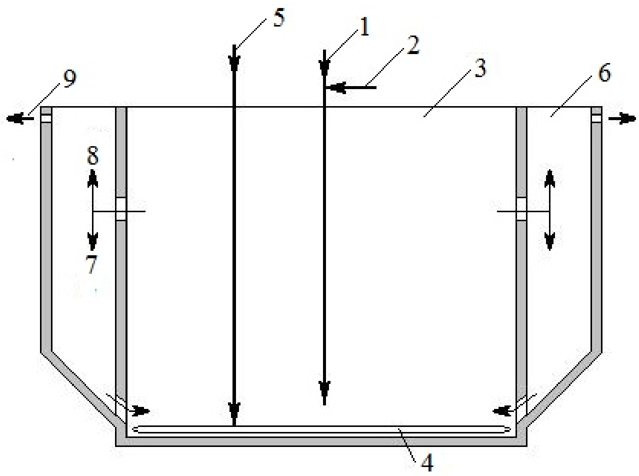

Fig. 7. The laboratory model of the combined aerator-clarifier unit of radial type: 1 — incoming wastewater; 2 — activated sludge; 3 — aeration zone; 4 — porous diffuser; 5 — air supply pipe; 6 — settling zone; 7 — circulating activated sludge; 8 — treated wastewater; 9 — treated wastewater for discharge

The laboratory model works as follows: incoming wastewater 1 and activated sludge 2 are fed to the aeration zone 3. Air is supplied through porous diffusers 4 to the pipe 5, the pipes are laid on the aerator-clarifier unit bottom in the aeration zone 3, thus giving rise to biological oxidation of wastewater impurities. Uniformity of the aeration system along the aeration zone allows improving the oxygen regime and keeping a constant load on the activated sludge, as well as eliminates the possibility of sludge stagnation zones. Using the air flow coming from porous diffusers 4, the water-sludge mixture through the upper overflow boxes enters the settling zone 6 where the separation of the water-sludge mixture takes place. Activated sludge settles to the settling zone bottom to the lower overflow boxes and returns to the aeration zone using the air flow coming from porous diffusers 4. Treated wastewater 9 is removed by gravity.

5. The results of research of phenolic wastewater treatment technology

Experimental data obtained from the experiments are presented in Table 1.

The results of the pilot study of biological treatment of phenolic wastewater in the laboratory model of the combined aerator-clarifier unit are shown in Table 2.

The pilot study revealed that phenol concentration decreased significantly after 6 hours, from 484 mg/dm^3 to 0.33 mg/dm^3 (with the standard value of up to 1 mg/dm^3). Thus, the biological treatment duration was reduced by 4 times, because the standard value for phenol at the operating BCT plant is achieved only within 24 hours.

Table 1

The results of the pilot study of efficiency of phenolic wastewater purification from tar using bentonite

Initial tar concentration, mg/dm^3	Tar concentration after treatment with bentonite, mg/dm^3		Time required for complete clarification, min
	sodium	calcium	
50 °C			
265	40	38	4
200	30	27	3
125	13	10	2
20 °C			
265	50	44	5,5
200	36	33	3,5
125	18	16	2,5
12 °C			
265	70	60	15
200	40	35	10
125	28	28	5

Table 2

The results of the pilot study of biological treatment in the combined unit

Parameters	Source water	Time of experiment, h			Standard value
		6	12	24	
pH	8.1	7.6	7.6	7.7	7.0–8.0
Phenol mg/dm^3	484.0	0.35	0.35	0.33	up to 1.0
Thiocyanate, mg/dm^3	326.0	93.6	43.8	5.1	up to 5.0
Volatile ammonia, mg/dm^3	131.0	81.0	74.0	69.0	not standardized
Orthophosphate, mg/dm^3	7.0	3.6	3.2	3.0	not standardized

6. Discussion of results of research of phenolic wastewater treatment technology

Based on Table 1, it was found that the use of both types of bentonite allows achieving the tar MAC required for stable operation of biological treatment plants. This applies particularly to those experiments, conducted at phenolic wastewater temperature of 50 °C, i. e. similar to industrial.

The experiment revealed that clarification was faster in the reactors with sodium bentonite than those with calcium bentonite. However, calcium bentonite discolors water somewhat better than sodium. Swelling of sodium bentonite when added to the water is much stronger than that of calcium one. Flakes of sodium bentonite are larger than those of calcium one, and therefore have a greater specific surface area. It was also found that the degree of oil removal with sodium bentonite is slightly higher than that of calcium one in all experiments (Table 1).

The physicochemical nature of the above phenomenon was limited to the combined adsorption of contaminants by the bentonite surface and subsequent coagulation of the units formed. The hydrolysis of the flocculant led to the intense association of bentonite particles with adsorbed oils by polymer bridges, which allowed achieving rapid (2–15 min) water clarification visible to the naked eye. It is known that both types of bentonite have a highly developed specific surface area that can effectively adsorb dissolved and colloidal phenolic water pollutants, intensively clarifying and discoloring the latter. Mud formed in the treatment at 50 °C mostly floated to the liquid surface, and settled to the reactor bottom at lower temperatures. This mud can be removed from the water surface by a scraper device in industrial conditions since the substance formed exhibits high adhesion properties. The experiments revealed that the volume of the mud formed is directly proportional to the content of phenolic water pollutants, that is, the dirtier the water, the more the precipitate. This precipitate may be used as a binder for cement and asphalt.

The studies prove the feasibility of using bentonite for phenolic water purification from coal tar. Considering the above bentonite advantages, as well as low cost, the introduction of this substance in the treatment process of phenolic wastewater of coke and chemical plants can be considered economically viable and reasonable.

It is desirable to conduct research aimed at establishing the fundamental possibility of using other types and grades of flocculants (anionic, non-ionic) to intensify the process of wastewater treatment with bentonite, as well as dose optimization.

During the pilot study of biological wastewater treatment, the hung layer of activated sludge was observed in the settling zone, which results in a higher clarification of the water-sludge mixture. At the same time, there is the additional purification due to wastewater passage through a layer of suspended activated sludge, microorganisms of which actively absorb organic contaminants. Thus, wastewater treatment to standard values in the combined unit is achieved in a short period of time. The "stagnation zones" where the activated sludge can be accumulated, digested and float, were not formed in the settling zone of the aerator-clarifier unit. In the lower part of the facility, there are overflow boxes through which activated sludge is circulated between the zones with the help of aerator. The latter in addition to its direct purpose acts as a pumping device that eliminates the need for airlift installations and provides significant economic benefit. In the process of treatment, activated sludge is in a state of continuous circulation between the aeration and settling zones and therefore the recirculation value is significantly higher than that in the conventional facility, thus creating more favorable conditions for microorganisms of activated sludge.

Based on the above, the effectiveness of the combined aerator-clarifier unit in the treatment technology of industrial water of coke and chemical plants is proved.

7. Conclusions

It was found that the coal tar treatment intensity increases with increasing wastewater temperature; sodium bentonite purifies phenolic wastewater more effectively than calcium, so it is recommended for industrial application; the time required for complete wastewater clarification increases with increasing initial coal tar concentration, providing the desired MAC.

It was experimentally proved that efficiency of biological treatment of phenol is 99.9 % due to the use of the combined aerator-clarifier unit.

It was determined that phenolic wastewater treatment to MAC standards for all indices in the combined unit is achieved in 6 hours. Using this unit at coke and chemical plants will lead to a significant reduction in energy consumption for the treatment process.

A new flow diagram of phenolic wastewater treatment (Fig. 8), proposed for implementation at coke and chemical plants in Ukraine and abroad was developed.

The flow diagram operates as follows. Phenolic wastewater (PWW) enters the pressure tank 1 for pressure damping and composition averaging. A dispenser of bentonite, which regulates its quantity according to the treatment needs is mounted in the PWW feed line from the pressure tank to the flotator 2. Air is also fed to the flotator to ensure the fluid mixing and pre-oxidation of organic contaminants. The flotation concentrate formed in the flotation process floats to the liquid surface where it is collected by the scraper device 3 and passed for further processing. The flocculant is also dosed to the flotator for the coagulation activation. Both agents are recommended to be administered as powders (dry dosage). It does not matter the mixing of the liquid and the reagent is conducted mechanically or pneumatically. It is only necessary to provide the most intense mixing of bentonite with wastewater Wastewater purified from tar is fed to the combined aerator-clarifier unit 4 for deep treatment of phenol and thiocyanate. Treated water after the combined aerator-clarifier unit is fed for the coke quenching.

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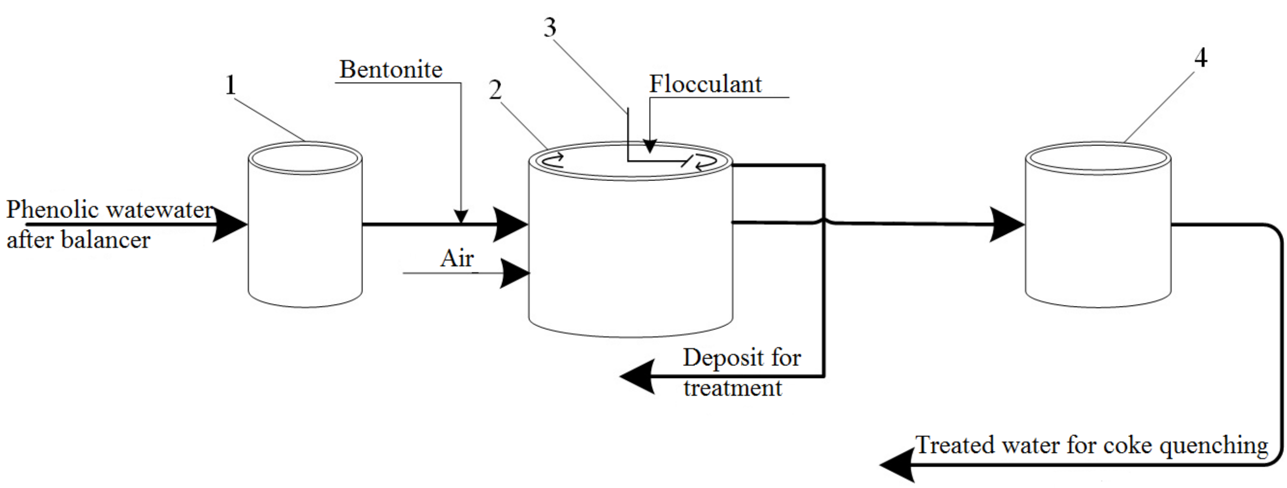

Fig. 8. The flow diagram of phenolic wastewater treatment:
1 – pressure tank; 2 – flotators; 3 – scraper; 4 – aerator-clarifier unit

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