Treatment of wastewater from textile factories using modified bentonite

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Abstract. The modern textile industry uses large quantities of water and produces significant volumes of wastewater at various stages of production. This especially applies to the dyeing stages and fabrics processing. In the wastewater of the OJSC “S.M. Kirov Spinning and Thread Combine” significant excesses were revealed in almost all studied indicators, except for calcium and nitrites. The excess of Cu2+ copper ions reaches 800 times. Laboratory studies of the effectiveness of sorption materials with respect to Cu2+ ions were carried out using model solutions of CuSO4·5H2O. Research has made it possible to establish bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized, as the most effective adsorbent. A comparative analysis of models of adsorption of Cu2+ ions on hydrophobized bentonite showed compliance of the adsorption process by to the Freundlich model (R2 = 0.978). A technological scheme of a local water purification station for a textile enterprise has been proposed, including a two-component adsorption filter loaded with bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized.

1 Introduction

The textile industry of the Russian Federation is currently developed at a fairly high level. In almost every region of the country, textile enterprises exist and operate successfully, producing threads, yarn, natural and synthetic fabrics for various needs of the national economy. The leaders of the textile industry in the Russian Federation are the Ivanovo, Moscow, Leningrad, Kaluga, Smolensk, and Kostroma regions. Many enterprises produce both natural and synthetic threads, yarn and fabrics.

The modern textile industry uses large quantities of water and produces significant volumes of wastewater at various stages of production. This especially applies to the stages of dyeing and processing of fabrics.

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Wastewater from industrial dyeing shops often contains reactive dyes and other toxic substances. Typically, textile wastewater contains complex components, large amounts of aerosols, high concentrations of chromium, dyes, chemical oxygen demand (COD) and biochemical oxygen demand (BOD), and it also contains significant concentrations of heavy metal ions [1]. The toxic effect of dyes and other organic compounds, acidic and alkaline pollutants entering the wastewater of industrial textile production enterprises is dangerous for various ecosystems.

One of the leaders in the production of yarn and threads for various purposes in Russia is the OJSC "S.M. Kirov Spinning and Thread Combine" (OJSC "S.M. Kirov STC", St. Petersburg).

OJSC "S.M. Kirov STC" has existed for almost 200 years. This combine appeared on the banks of the Neva River in 1833 under the name of the Baron Ludwig Stieglitz paper spinning mill. Currently, the combine is the largest full-cycle enterprise for the production of sewing, knitting, and embroidery threads not only in Russia, but also in Europe. The combine accounts for 60% of the domestic production of threads and yarn. Currently, the enterprise is considered unique in the breadth of its product range. The combine produces the best threads in Russia for embroidery floss on a cotton basis in more than 50 colors and shades.

Research of the composition of wastewater from the enterprise OJSC S.M. Kirov CTK" was carried out at the Testing Laboratory Center (TLC) "EcoOS" in the Yuri Gagarin State Technical University of Saratov in 2020-2022. Employees of the research and production enterprise "LISSCON" (RPE "LISSCON"LLC) took part in the study. Research was carried out to develop recommendations for improving the wastewater treatment technology of the combine [2].

During the environmental survey of the enterprise, it was found out that one of the main suppliers of pollutants into the wastewater of the enterprise is the bleaching and dyeing shop. In the bleaching and dyeing shop of the enterprise, technological operations for the preparation and dyeing of synthetic and natural sewing, knitting and embroidery threads are carried out [2]. Processing of threads in production is performed in two types - in bobbins and skeins on devices of appropriate designs.

The main technological operations when dyeing threads with active dyes include: mercerization, boiling, bleaching, locking, dyeing, acidification, soaping and softening. Each of the listed stages of the technological process of thread processing is accompanied by a washing operation. The concentration of the working solution of caustic soda is 260 g/dm^3. The “Cemessol SM-M” reagent to working solutions as a wetting agent is added. Antifoam agent “Defoamer BA” to extinguish foam is used.

The technological process of coloring or bleaching is divided into a number of technological operations. On average, 5 technological operations are carried out per batch of threads. After each operation is completed, a volume of waste solution or wash water is discharged from the apparatus, equal to the free volume of the apparatus of the corresponding brand in which the threads were processed [2].

When dyeing threads with dispersed and direct dyes, the average liquid solid module is 10:1. The maximum number of technological operations per batch is 9 pieces. The average amount of wastewater per day is 27.0 m^3/day.

More detailed experimental studies to further improve the technology for treating wastewater from textile enterprises were proposed to be carried out on the basis of the “EcoOS” TLC in the Yuri Gagarin State Technical University of Saratov.

2 Materials and methods

The main objects of research were wastewater from the enterprise OJSC "S.M. Kirov STK", as well as model solutions of copper ions Cu^{2+} of different concentrations. The content of copper ions in samples of enterprise wastewater and in model solutions was determined according to PND F 14.1:2:4.48-96 [3]. In this case, the main standard solution was prepared by dissolving 24.20 g of copper sulfate 5-aqueous ($CuSO_4 \cdot 5H_2O$), weighed with an error of 0.02 g, in 1000 cm^3 of distilled water. To prepare model aqueous solutions, copper sulphate (II), 5-aqueous (chemically pure) produced by the Buysky Chemical Plant was used.

Another object of research was sorption materials based on modified bentonite: 1) bentonite modified with carbon nanotubes (CNTs), granulated and fired at a temperature of 550 °C;2) bentonite, granulated, fired at a temperature of 550 °C and hydrophobized by impregnation produced by RPE "Rogneda" LLC (St. Kupavna) using a special technology. The determination of the sorption characteristics of modified and hydrophobized bentonites was carried out in "EcoOS" TLC Yuri Gagarin State Technical University of Saratov on a model solution of Cu^{2+} under static conditions.

The original bentonite was imported from the Sarigyukh deposit (Armenia).This bentonite contains more than 80% montmorillonite clay, which justifies the feasibility of its use for the production of sorption materials [4]. The production of bentonite granules, including modification of CNTs, pelletizing and firing, was carried out on the basis of the RPE "LISSCON" LLC enterprise (Saratov). Hydrophobization of finished bentonite granules was carried out on the basis of "EcoOS" TLC at Yuri Gagarin State Technical University of Saratov.

To study the composition of wastewater from OJSC "S.M. Kirov STC" at the enterprise, samples of industrial wastewater were taken after each of the previously listed technological operations. Averaged water samples were prepared from the selected solutions. The studies were carried out in "EcoOS" TLC using the photometry method, implemented using a PE-6100UF spectrophotometer (manufactured by Shanghai Mapada Instruments Co., Ltd, China), followed by statistical processing of the results [5].

3 Results and discussion

The results of chemical analysis of the composition of wastewater from the enterprise OJSC "S.M. Kirov STC" showed the presence of heavy metal ions, organic compounds, dyes, as well as the presence of an alkaline environment of increased hardness in water samples.

The values of water sample indicators are given in Table 1.

Table 1. Composition of wastewater from the enterprise OJSC "S.M. Kirov STC"

Indicators, units of measurement	Quantitative composition of wastewater			Standard RF (GN 2.1.5.1315-03; SanPiN 2.1.5.980-00)
	Sample1	Sample 2	Sample 3	
pH	**13.6±1.1**	**12.1±1.4**	**10.5±0.9**	7.0
Turbidity, mg/dm^3	**253.0±12.7**	**241.0±12.9**	**239.2±13.9**	<0.6
Color	**831.0±9.4**	**833.1±17.4**	**824.2±18.1**	9.0
General water hardness, mg/dm^3	**11.0±1.5**	**14.0±1.1**	**13.8±1.6**	7.0
Calcium, mg/dm^3	29.0±3.6	**34.1±3.8**	**38.3±2.2**	30.0
Magnesium, mg/dm^3	**206.8±11.8**	**214.9±12,7**	**200.8±10.1**	50.0

Indicators, units of measurement	Quantitative composition of wastewater			Standard RF (GN 2.1.5.1315-03; SanPiN 2.1.5.980-00)
	Sample1	Sample 2	Sample 3	
COD, mgO_2/dm^3	**1543.0±51.2**	**1382.0±45.3**	**1346.6±34.2**	30.0
Sodium, mg/dm^3	**3511.1±8.9**	**3647.6±71.3**	**3561.0±52.1**	200.0
Cadmium, mg/dm^3	**0.22±0.01**	**0.090±0.005**	**0.11±0.008**	0.005
Total iron, mg/dm^3	**9.6±0.5**	**9.2±0.8**	**11.9±0.4**	0.1
Copper, mg/dm^3	**0.61±0.04**	**0.89±0.03**	**0.88±0.05**	0.001
Manganese, mg/dm^3	**1.61±0.09**	**1.54±0.32**	**1.32±0.42**	0.1
Nickel, mg/dm^3	**0.92±0.07**	**0.78±0.08**	**1.11±0.07**	0.02
Ammonium, mg/dm^3	**7.46±0.06**	**7.3±0.05**	**6.4±0.09**	1.5
Nitrates, mg/dm^3	**153.2±4.8**	**151.6±6.1**	**141.0±12.3**	45.0
Nitrites, mg/dm^3	2.8±0.9	3.1±0.8	3.0±0.9	3.3
Sulfates, mg/dm^3	**2542.0±33.9**	**2541.0±22.7**	**2556.0±17.8**	500.0
Phosphates, mg/dm^3	**142.0±11.7**	**151.1±14.1**	**150.6±21.3**	3.5
Chlorides, mg/dm^3	**28521.0±98.2**	**28534.0±67.3**	**28541.0±55.3**	350
Dry residue, mg/dm^3	**9940.0±14.9**	**9750.0±15.6**	**9780.0±21.6**	1000

Analyzes of wastewater samples show exceeding standards (up to 100 times) for all indicators, except for nitrites. Slight excesses are observed in water hardness (1.6÷1.9 times). The analyzes results confirm the need for high-quality multi-stage treatment of wastewater from an enterprise before discharging it into a city sewer or natural reservoir.

The greatest excesses in wastewater samples were noted for Cu^{2+} ions. These excesses reached 610÷800 times. Therefore, it was decided to analyze the sorption capacity of the proposed adsorbents using model solutions of $CuSO_4{\cdot}5H_2O$ containing a large amount of Cu^{2+} ions.

As a result of a laboratory experiment, the values of equilibrium concentrations of Cu^{2+} ions and the corresponding adsorption values on both variants of sorption materials were established (Fig. 1).

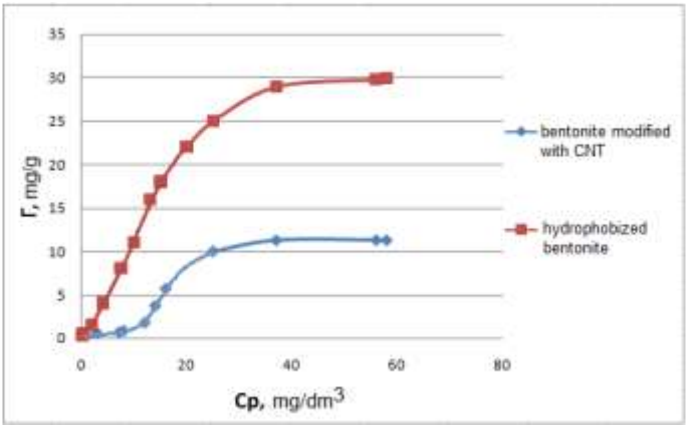

Fig. 1. Adsorption isotherms of Cu^{2+} ions depending on the equilibrium concentrations C_p on bentonite of various modifications.

Analysis of the obtained adsorption isotherms showed a clear advantage of using sorption material, which is bentonite, granulated, calcined at a temperature of 550 ºC and hydrophobized, when extracting Cu^{2+} ions from a model solution.
Next, the sorption characteristics of this modification of bentonite with respect to Cu^{2+} ions were established by calculation (Table 2).

Table 2. Characteristics of the process of adsorption of Cu^{2+} ions by bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized.

Adsorbed ion	Sorption material type	*SEC*, mg/g	K_d, dm³/mg	*S*, %
Cu^{2+}	Bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized	29,92±1,84	0,516±0,013	92,10±4,21

Studies of the mechanism of interaction of Cu^{2+} ions with the sorbent under study were carried out in accordance with the sorption models: Langmuir, Freundlich and Bronauer-Emmett-Theiler (BET isotherms) [6-7]. The adsorption isotherm of Cu^{2+} ions on hydrophobized bentonite in Langmuir linearized form is shown in Fig. 2.

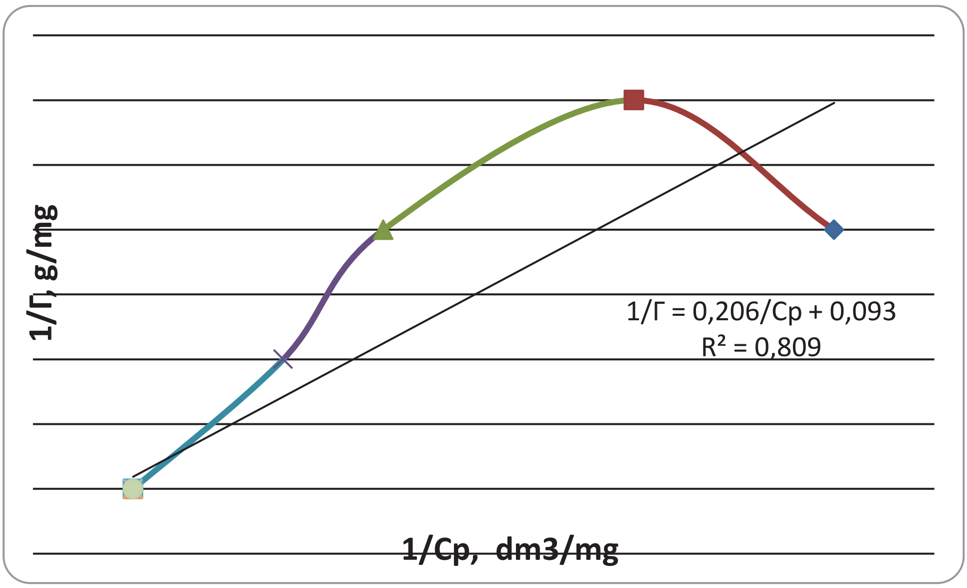

Fig. 2. Adsorption isotherm of Cu^{2+} ions in Langmuir linearized form.

The reliability of the approximation of the obtained dependence $1/\Gamma=f(1/C_p)$ was $R^2=0.81$.
The adsorption isotherm of Cu^{2+} ions on hydrophobized bentonite in Freundlich linearized form is shown in Fig. 3. In this case, the reliability value of the approximation of the obtained dependence $\lg\Gamma=f(\lg C_p)$ was $R^2=0.978$. When approximating the adsorption process with the BET model, the reliability value of the resulting expression was $R^2=0.12$, which is significantly less than the two previous cases. Therefore, we did not accept the model of the adsorption process BET linearized for further consideration.

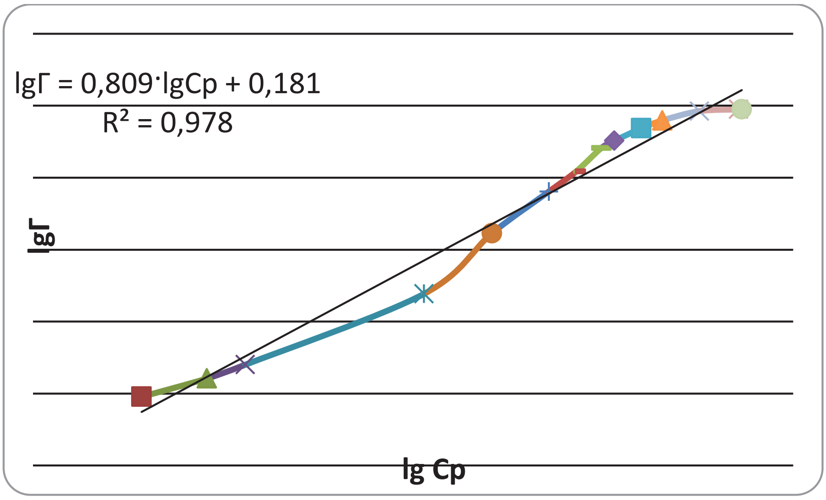

Figure 3. Adsorption isotherm of Cu^{2+} ions in Freundlich linearized form.

The calculated parameters of the adsorption models of Cu^{2+} ions on bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized, within the framework of the Langmuir and Freundlich models are given in Table 3.

Table 3. Data on the adsorption of Cu^{2+} ions by hydrophobized bentonite.

Langmuir isotherm				
Adsorbent	The equation	K_L, dm³/mg	Γ_∞, mg/g	R^2
Bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized	$1/\Gamma = 0{,}206/C_p + 0{,}093$	0,451	10,753	0,809
Freundlich isotherm				
Adsorbent	The equation	K_F, (mg/g)·(dm³/mg)$^{1/n}$	n	R^2
Bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized	$\lg\Gamma = 0{,}809\cdot\lg C_p + 0{,}181$	1,517	1,236	0,978

A comparative analysis of the adsorption models described by Langmuir and Freundlich showed the preference for the correspondence of the adsorption process of Cu^{2+} ions to the Freundlich model [8].

Thus, the experiments showed that to purify wastewater from a textile enterprise with an excess amount of Cu^{2+} ions, it is advisable to use adsorption filters mainly with a filter load of bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized.

A technological diagram of a local water treatment plant for a textile enterprise with a two-component adsorption filter was proposed [9], shown in Fig. 4.

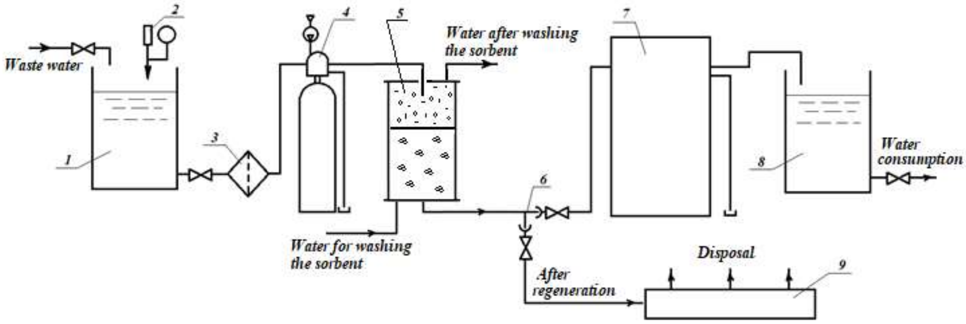

Fig. 4. Scheme of a local treatment plant for a textile enterprise: 1 – settling tank; 2 – water measuring device; 3 – coarse water filter; 4 – aerator; 5 – two-component adsorption filter containing a load from hydrophobized bentonite; 6 – adapter; 7 – nanofiltration unit; 8 – container for clean water; 9 – sludge receiver.

The technological process of wastewater treatment includes the following stages:

– the flow of wastewater into a receiving tank, its neutralization by chemical interaction with substances (direct mixing of acidic wastewater with alkaline wastewater, adding a reagent in the concentrations required for neutralization). When feeding liquid reagents into the receiving tank, water accounting means are used. Next, the water settles in a receiving container;

– rough purification of pre-neutralized and settled wastewater from mechanical impurities using coarse filters;

– aeration of pre-treated wastewater using an oxygen compressor;

– softening and adsorption purification by passing the purified water through an adsorption filter loaded with hydrophobized bentonite;

– additional purification of water on a nanofiltration unit by passing it through membrane filters, including electrically neutral and charged polymer membranes;

– the flow of purified water into a storage tank to ensure a reserve of clean water and water accounting when discharged into an natural body of water or for further circulation in a circulating water supply system;

– periodic regeneration of sorption materials placed in the adsorption filter;

– recycling of used sorption material (including lowering the hazard class) with the subsequent possibility of using it in construction.

The technological scheme of the wastewater treatment plant was developed by us by analogy with the scheme of treatment facilities developed by our partners - Scientific and Production Enterprise "LISSCON".

4 Conclusion

The conducted research allowed to come to the following conclusions.

1. In the wastewater of the OJSC "S.M. Kirov STC" enterprise there are significant excesses (up to 100 times) in almost all studied indicators, except for calcium and nitrites. The most significant were the excesses of Cu^{2+} ions (up to 800 times).

2. When extracting Cu^{2+} ions from a model solution using the adsorption method, the greatest efficiency of using a sorption material was established, which is bentonite, granulated, calcined at a temperature of 550 °C and hydrophobized.

3. A comparative analysis of the models of adsorption of Cu^{2+} ions by hydrophobized bentonite, described within the framework of the Langmuir and Freundlich models, showed that this process is more consistent with the Freundlich model ($R^2 = 0.978$).

4. To purify wastewater from a textile enterprise with an excess amount of Cu^{2+} ions, it is advisable to use adsorption filters with a filter loading in which at least one of the layers consists of granulated bentonite, calcined at a temperature of 550 °C and hydrophobized.

5. A technological scheme of a local water purification station for a textile enterprise has been proposed, including a two-component adsorption filter loaded with the proposed sorption material.

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