Sorption post-treatment of accumulator waste

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Annotation. The main goal when creating typical waste water of JSC "Tyumen Battery Plant" is to bring the composition as close as possible to real waste water. The aim of the work is to study the process of sorption post-treatment when working with different types and concentrations of coagulants and flocculants, to select the most effective coagulants and flocculants and their doses, which give maximum effect of sorption post-treatment from colloidal-dispersed impurities and lead ions. For work the following coagulants were selected: FeSO₄·7H₂O; FeCl₃ and Al₂(SO₄)₃ in various relations (1:1), (2:1), (1:2); Flocculants: Flopam FO 4125 SH, Flopam FO 4440 SH, Flopam FO 4115 SSH; Praestol 2531 TR, Praestol 650 TR, Na₂O·mSiO₂·nH₂O sodium metasilicate (Liquid glass). In process of operation method of dynamic sorption on sorbent of КФГМ-7 is used for additional purification of waste water from lead ions. Based on the data obtained, recommendations can be made to intensify the subsequent treatment of waste water from battery production using the following reagents: FeCl₃ (83mg/l) + Al₂(SO₄)₃ (42mg/l) and Liquid glass (1mg/l); FeSO₄·7H₂O (150 mg/L) и Flopam FO 4115 SSH (1mg/L); FeSO₄·7H₂O (150 mg/L) and liquid glass (1 ml).

1. Introduction
One of the most important factors in the national security of any country is the provision of drinking water to the population. Drinking water is a necessary element of life support of the population, because its quality, quantity and uninterrupted supply depend on the state of health of people, the level of their sanitary and epidemiological well-being, the degree of improvement of the housing stock and urban environment, the stability of the work of the communal and domestic sphere. Wastewater treatment is of particular importance to any enterprise. The development and implementation of programmes aimed at protecting the environment and preserving the flora and fauna of water bodies are taking place in each region. Today, there are several methods of cleaning contaminated waters, among which the coagulation method of water purification, which is classified as chemical and does not pose a threat to nature, has become particularly popular. Coagulation and flocculation processes are the main process for removing coarse impurities in suspended state and colloidal organic contaminants present in dissolved form in water. Various microbiological contaminants are removed from the 90 - 99% during coagulation treatment of water. The efficiency of their removal depends on the depth of water purification by turbidity, chromaticity and permanganate oxidability. An important feature of coagulation is also that, depending on the process conditions, the efficiency of further...
clarification and purification of water at the first stage and filtration facilities and, ultimately, the quality of drinking water are determined [1-3].

The most dangerous pollutant of waste water of JSC "Tyumen Battery Plant" - lead (Pb^{2+}), its concentration in factory waste water is large and reaches 600 mg/l, if permissible Lead concentration in wastewater allowed to be discharged into the centralized water disposal system - 0.25 mg/l. Treatment of water from lead and its compounds is a primary task of wastewater treatment [4,5].

The aim of the study is to investigate the process of sorption post-treatment when working with different types and concentrations of coagulants and flocculants, to select the most effective coagulants and flocculants and their doses, which give the maximum effect of sorption post-treatment from colloidal-dispersed impurities and lead ions.

Physical adsorption is used as a method of post-treatment of wastewater, after its pre-clarification (coagulation and flocculation). The water adsorption purification step is one of the final ones, and is intended to remove the residual lead (Pb^{2+}) and heavy metal ions to the minimum values set by the MPC, also referred to as the post-purification step. The waste water post-treatment process was performed by dynamic sorption. Dynamic sorption occurs when the separated mixture is directed through the sorbent layer. It is important that during dynamic sorption static processes of distribution of substances between different phases (sorbent-solution) are repeated repeatedly and automatically. Column efficiency corresponds to tens, hundreds, and thousands of individual static acts of sorption. This method was used by analogy with JSC "Tyumen Battery Plant." KFGM-7 was used as the sorbent. This adsorbent was not chosen by accident, it is used at the production of JSC "Tyumen Battery Plant." KFGM-7 - ceramic, filtering, granulated material, externally - granules of different color (white, grey, yellow, light pink) with size 1.5-2.5 mm. Sorption column characteristic: assuming that the optimal rate for sorbent filtration is KFGM-7 up to 4 m/h, the rate of dripping was set to 3 m/h. The height of the loading layer was selected by a trial method and the minimum recommended height was set at 70 cm [6].

For work the following coagulants were selected: FeSO_4·7H_2O; FeCl_3 mixed and Al_2(SO_4)_3 in different ratios (1:1), (2:1), (1:2); Flocculants: Flopam FO 4125 SH, Flopam FO 4440 SH, Flopam FO 4115 SSH; Praestol 2531 TR, Praestol 650 TR, Na_2O·mSiO_2·nH_2O - sodium metasilicate (liquid glass) [7-10].

Praestol flocculant is produced according to a unique technology, including the step of biological synthesis of polymers since the late 1980s, during which time they have gained popularity in many areas of industry. Now Praestol flocculants are produced by Solenis, whose representative office is located in Moscow and called Solenis Eurasia. At present, there are many grades of this flocculant, from each other they differ, past molecular weight, in composition, which may be based on a high molecular weight electrolyte of cationic, anionic or nonionic activity based on acrylamide and cationic or anionic comonomer. The commercial shape can also be different, liquid, gel-like, powder. Due to the action of Praestol, microchlops combine into macrochlops whose deposition rate is several hundred times higher than conventional particles. Thus, complex exposure to Praestol flocculant contributes to intensification of precipitation of solid particles [11,12].

Floculant Flopam - Products of SNF Floerger (France), which today is considered one of the leading enterprises in the world in the field of coagulants and flocculants for water purification. The anionic and non-ionic flocculant Flopam PWG series (Potable Water Grade) is a class of drinking water, produced as a powder with different charge density and molecular weights. Nonionic flocculant Flopam is an acrylamide homopolymer that is produced by polymerizing acrylamide monomers. The Flopam anionic flocculant is prepared by the copolymers of acrylamide and sodium acrylate monomers. The cationic flocculant of Flopam is obtained by copolymers of the monomers of acrylamide and methyl chloride.

Flopam polymers are used in conjunction with coagulants to increase the size of the flakes formed and to remove them further. Flopam flocculants have high molecular weight, have low cation - up to 15% or anion - from 0 to 50% [13].
Flocculant (liquid glass) is synthesized by condensation of low molecular weight silicic acids. The mechanism of action of the flocculant is interaction with positively charged colloidal particles of the coagulant and colloidal particles to form macrochlopies. The efficiency of this flocculant is maximum at pH = 5.5. Recommended dose of flocculant AK 2-3 mg/l [14].

2. Methods and materials
Selection of doses of coagulants and flocculants: optimal doses of coagulants were selected on the basis of literary data. Dose range of different coagulants is chosen from 100 to 300 mg/l [15-17].

Determination of lead concentration in initial model waters was carried out according to GOST 18293-72 "Drinking water. Methods of determining the content of lead, zinc, silver, "colorimetric (plumbonic) method [18].

The lead calibration graph was plotted using a standard lead ion solution composition. This graph was used to convert the optical density to lead concentration, the graph was plotted according to GSO 7252-96.

Construction of a calibration graph for turbidity - according to a standard model. GOST R 57164-2016 "Drinking water. Methods for determining odor, taste and turbidity ";[19,20].

3. Results
It is apparent from the analysis of the obtained data (Figure 1) that after the coagulation process followed by flocculation, the most effective is the mixed coagulant FeCl₃ (1.66ml) + Al₂ (SO₄)₃ (0.83ml) in the ratio [2:1] with the flocculant Liquid glass (Na₂SiO₃).

The smallest efficiency sulfate of iron FeSO₄ x 7H₂O (3 ml) with flokulyanty Praestol 2531TR (1 ml) which is a cationic flokulyant and also the mixed FeCl₃ coagulant (1.66 ml) + Al₂ (SO₄)₃ (0.83 ml) in the ratio [2:1] with flokulyanty Praestol 650TR (1 ml) showed coagulant.

After the sorption post-treatment, as the analysis (Figure 2) showed the best result: coagulant FeSO₄ x 7H₂O (3 ml) with flocculant Liquid glass (Na₂SiO₃) (1 ml).

Slightly less effective were mixed coagulant FeCl₃ (1.25ml) + Al₂ (SO₄)₃ (1.25ml) [1:1] with flocculant Praestol 650TR (1ml); coagulant FeSO₄ x 7H₂O (3 ml) with flocculant Flopam FO 4125SH (0.75 ml).

The mixed coagulant FeCl₃ (1.66 ml) + Al SO₄ (0.83 ml) [2:1] with the flocculant Praestol 650TR (1 ml) was not effective; coagulant FeSO₄ x 7H₂O (3 ml) with flocculant Flopam FO 2531SH (1 ml); coagulant FeSO₄ x 7H₂O (3 ml) with Praestol 2531TR flocculant (1 ml).

The only one did not change its data after the post-treatment process: mixed coagulant FeCl₃ (1,66ml) + Al₂ (SO₄)₃ (0.83ml) with flocculant Liquid glass (Na₂SiO₃) (1ml).
Table 1. Model effluent turbidity values after coagulation processes followed by flocculation at different coagulants and flocculants and their doses.

| No | Names of coagulant and flocculant | Turbidity, EMF |
|----|-----------------------------------|---------------|
| 1  | FeCl₃ (1,66ml) + Al₂(SO₄)₃ (0,83ml) [2:1] + Liquid glass (Na₂SiO₃) (1ml). | 1             |
| 2  | FeSO₄ x 7H₂O (3 ml) + Flopam FO 4125 SH (0,75ml) | 5             |
| 3  | FeSO₄ x 7H₂O (3 ml) + Na₂SiO₃ (1ml) | 5             |
| 4  | FeCl₃ (1,25ml) + Al₂(SO₄)₃ (1,25ml) [1:1] + Flopam FO 4444SH (1ml) | 6             |
| 5  | FeCl₃ (1,25ml) + Al₂(SO₄)₃ (1,25ml) [1:1] + Praestol 650TR (1ml) | 6             |
| 6  | FeSO₄ x 7H₂O (3ml) + Flopam FO 2531 SH (1ml) | 6             |
| 7  | FeCl₃ (1,66ml) + Al₂(SO₄)₃ (0,83ml) [2:1] + Praestol 650TR (1ml) | 10            |
| 8  | FeSO₄ x 7H₂O (3ml) + Praestol 2531TR (1ml) | 10            |

The optical density was converted to EMF turbidity units according to GOST 18293-72 (ratio 1 EMF/litre = 0.58 mg/l). The turbidity of the original model wastewater exceeded 40 EMF. Turbidity of all waste water samples after sorption post-treatment is less than 1 EMF (Table 1).

After carrying out the stage of dynamic sorption on the КФГМ-7 waste water sorbent, the following data of concentrations of Pb²⁺ cations after coagulation and after sorption post-treatment were obtained (Figure 3).
Figure 3. Concentrations of Pb\(^{2+}\) cations after coagulation and after sorption purification.

All samples except coagulant FeSO\(_4\) x 7H\(_2\)O (3 ml) with Praestol 2531TR flocculant (1 ml) showed the best sorption purification result. Coagulant FeSO\(_4\) x 7H\(_2\)O (3 ml) with flocculant Flopam 2531SH (1 ml).

4. Conclusion
Based on the obtained data, it is possible to make recommendations for intensification of waste water treatment at JSC "Tyumen Battery Plant" by coagulation method followed by sorption post-purification. The following reagents are proposed: mixed coagulant FeCl\(_3\) (83 mg/l) + Al\(_2\) (SO\(_4\))\(_3\) (42 mg/l) [2:1] with flocculant Liquid glass (1 mg/l); Coagulant FeSO\(_4\) · 7H\(_2\)O (150 mg/l) with flocculent Flopam FO 4115 SSH (1 mg/l); Coagulant FeSO\(_4\) · 7H\(_2\)O (150 mg/l) with flocculent Liquid glass (1 mg/l). The concentration of lead after sorption post-treatment was 0.001 mg/l, which is significantly lower than the maximum permissible, turbidity - less than or equal to 1 EFM. Obtained results can be used in technology of treatment of waste water of accumulator production.

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