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CHEMISTRY, TECHNOLOGY AND EQUIPMENT FOR WASTEWATER TREATMENT
LABORATORY WORKSHOP

*Approved by the Academic Council of The Faculty of Chemical Technology, Igor Sikorsky Kyiv Polytechnic Institute as a tutorial for students,
who study in specialty 161 «Chemical technology and engineering»,
specialization "Chemical technologies of inorganic substances and water purification"*

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Annotation is roughly 650 characters

CONTENT

INTRODUCTION

Water resources are one of the important components of the hydrosphere of the globe and an essential component of the economic and social development of each country. Ukraine belongs to low-income countries for water supplies that are available for use. The greatest impact on the state of natural waters is the waste water of enterprises of various industries, agriculture and communal services. It is from the efficiency and quality of waste water treatment that further affects the state of the aquatic ecosystem and the health of people.

The credit module of the discipline "Technology and equipment for wastewater treatment" is an integral part of the complex program of training specialists and masters in the direction of "Chemical technologies of inorganic substances" specialization "Chemical technology of water conditioning, cleaning and utilization of emissions and waste of inorganic manufactures."

Discipline "Technology and equipment for waste water treatment" promotes knowledge on the physico-chemical bases of waste water treatment of various origins and the choice of the method of water treatment. The laboratory workshop allows you to get acquainted with some widely used methods and methods of waste water treatment on examples of typical water contaminants.

Laboratory work № 1. Removal of dyes from waste water using photo-oxide methods

Purpose: to study the efficiency of using different Fenton reagent catalytic systems for discoloration of waste water containing dyes.

Theoretical information

The presence of dyes in wastewater causes serious difficulties in cleaning them. Much of the dyes used in the industry, virtually unchanged, fall into the biochemical oxidation plants, causing the need for cleanup.

All known methods of physico-chemical treatment of waste water from dyes, surfactants (surfactants), formaldehyde can be divided into three main groups.

The first group of methods provides removal of contaminants by transfer of dyes in the precipitate or float shale by sorption on flakes of hydroxides of metals formed during reagent treatment of waste water (coagulation, reagent pressure flotation, etc.).

The methods of this group are characterized by the following disadvantages: low degree of purification, especially discoloration, the need for utilization of sediment water purification and their dehydration.

The second group includes separatory methods (sorption on activated carbon and macroporous ion exchangers, reverse osmosis, ultrafiltration, etc.). These methods provide a high degree of waste water treatment, but require prior mechanical and chemical treatment to remove insoluble impurities, complex in hardware design, have a high cost of cleaning. Their application can be cost-effective in closed water supply systems of enterprises.

The third group combines destructive methods based on deep oxidation-reduction transformations initiated by various physico-chemical processes, in particular the action of oxidants (O_2, O_3, Cl_2, H_2O_2), ultraviolet and solar radiation.

The advantages of destructive methods include their high efficiency and processability, simplicity of automation and control. In most cases, during their

implementation, no precipitates are formed, additional water pollution is not added to the treated water in the form of chloride, sulfate and other ions.

By photo oxidation it is possible to achieve the destruction of the structure of organic impurities of the chromophore-auxochromic structure, followed by their deep splitting into simpler light oxidizing organic products or mineral compounds. It is therefore advisable, before the biochemical oxidation of waste water containing dyes, to conduct destruction of the organic component under the action of UV radiation.

Photochemical reaction is a chemical transformation, namely, the "bimolecular" interaction of a quanta of light with a molecule, resulting in physical and chemical changes. Excited molecules can enter such reactions that do not run or at least difficult in the non-excited state, since the excess energy facilitates the overcoming of activation barriers, and on the other hand, in the excited state, the molecule often has a completely different distribution of electron density than in the main state, and therefore become "unusual" transformations.

The first law of photochemistry was formulated by Grotthouse (1817) and Draeneer (1843): a photochemical transformation can take place under the action of only light absorbed by matter. For the course of a photochemical reaction, it is required that the light entering the reaction volume is absorbed by a reacting compound or sensitizer (a substance that, when irradiated with light, passes into an excited state and causes a chemical reaction of the main substance). The second law of photochemistry was formulated by Stark (1912) and Einstein (1912): each molecule involved in a chemical reaction that runs under the action of light absorbs one quantum of radiation that causes a reaction.

However, this law is valid only for the initial process, because secondary chain reactions can lead to the fact that the calculated degree of decomposition may be greater than unity. Therefore, the second law should read as follows: absorption of light by a molecule - the single-quantum process and the sum of quantum outputs of primary processes should be equal to one, that is, $\Sigma \varphi i = 1.00$, where φi is the quantum yield of the first primary process, which may be dissociation, isomerization, fluorescence, phosphorescence, irradiation transitions, that is, all possible ways of destroying or

deactivating the excited molecule.

Hydrogen peroxide is used for deep oxidation of products of destruction of dyes in waste water (WW). Its main technological advantages include high solubility in water, stability, the ability to process water in a wide range of temperatures, and simple hardware design. Hydrogen peroxide is an environmentally friendly oxidizer, because its decomposition products are oxygen and water. Especially effective oxidation process occurs in the presence of a catalyst. Thus, in the treatment of HF by hydrogen peroxide with a volume fraction of 15 % and a mass concentration of 0.5 mg / L in the presence of activated charcoal with a mass dose of 200 g / L, the degree of reduction of the chemical oxygen demand (COD) was 80-85 %, and the color - up to 95%. However, during purification of hydrogen by hydrogen peroxide, it is not always possible to achieve the desired degree of purification, since organic compounds such as benzene, toluene, ethanol and others are resistant to H_2O_2, and the rate of oxidation in the processing of diluted WW is rather low. In this regard, oxide methods based on the disproportionation of hydrogen peroxide with the formation of reactive hydroxyl radicals OH · (E_0 = 2,38 V) are widely used; they are electrophilic reagents and can interact with electron donors. These oxidative methods include the photolysis of H_2O_2 and its catalytic decomposition under the action of Fe^{2+} ions (Fenton system).

As a result of the catalytic oxidation of Cu on a catalyst containing Fe^{2+} ions, using the oxygen of air or hydrogen peroxide (0.001M), the concentration of dye active blue and active red decreased by 100 and 10 times, respectively.

By the oxidative action of hydrogen, peroxide is approaching the products of water radiolysis. Most of the radicals react with each other and with hydrogen peroxide, initiating its schedule:

$$HO_2^{\cdot} + OH = H_2O + O_2, \qquad (1.1)$$

$$2\ HO_2^{\cdot} = H_2O + 1,5\ O_2, \qquad (1.2)$$

$$OH^{\cdot} + H_2O_2 = HO_2^{\cdot} + H_2O. \qquad (1.3)$$
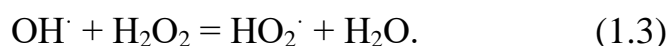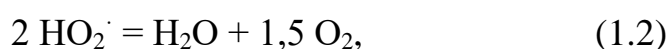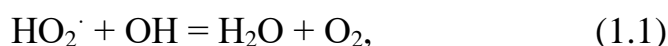
Therefore, when using hydrogen peroxide to oxidize organic substances in aqueous solutions, it is important to identify and maintain optimum conditions for the process. The joint use of hydrogen peroxide with ferric salts (II) significantly

affects the oxidation of organic matter. The mechanism of this process is a set of successive stages and includes the following reactions:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^. + OH^-, \qquad (1.4)$$

$$Fe^{2+} + OH^. = Fe^{3+} + OH^-, \qquad (1.5)$$

$$OH^. + H_2O_2 = HO_2^. + H_2O, \qquad (1.6)$$

$$Fe^{3+} + H_2O_2 = Fe^{2+} + 2H^+ + O_2, \qquad (1.7)$$

$$Fe^{3+} + O_2^- = Fe^{2+} + O_2, \qquad (1.7')$$

$$Fe^{2+} + HO_2^. = Fe^{3+} + HO_2^-. \qquad (1.8)$$
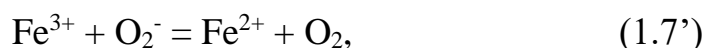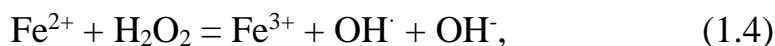
The above steps are realized in a weakly acidic medium (pH> 2) under the condition of $0.5 < [H_2O_2] / [Fe^{2+}] < 200$.

From literary sources, it is known that the oxidation of various types of surfactants is carried out with the joint use of hydrogen peroxide and ferrous (II), (III) or aluminum salts. When the Fe^{2+} catalyst is precipitated into the waste water purified, the quality of water purification is significantly improved. The optimal dose of H_2O_2 in the application of Fe^{2+} as a catalyst is $(1,0 \div 10,0) \cdot 10^{-3}$ g / L. At the dose of Fe^{2+} 0.100 g / L, the effect of cleaning from surfactant is 35 %, and with an additional introduction of 10^{-2} g / L H_2O_2 - 90% [2].

Materials and methods

Apparatus

Glasses (a nominal volume of 100 ml - 6 pcs.; flasks (a nominal volume of 100 ml - 6 pcs.; measurement flasks (a nominal volume of 1000 ml); spatula; pipettes (a nominal volume of 1, 2, 10 ml); sampler; photoelectrocolorimeter KFK - 2; cuvettes; analytical balances.

Reactants and materials

A model solution of contaminated water is prepared with a dye (40 mg / ml) and a volume of 1 L. Aqueous peroxide (35%) and a standard solution of Fe^{2+} (1 g / L).

Calibration graph

The model solution of sewage water is diluted in such a way as to obtain

solutions with concentrations of 2, 4, 5, 10 times less than the original and build a calibration graph using the photoelectrocolorimeter KFK-2, the dependence of the concentration of the dye on the optical density. The calibration graph further determines the residual concentration of the dye after the photooxidation.

The photooxidation is carried out using a modified Fenton reagent, namely:

1). Fenton reagent [Fe^{2+} / H_2O_2];

2). Fenton reagent [Fe^{2+} / H_2O_2] under the influence of UV radiation;

3). Fenton reagent [Fe^{2+} / H_2O_2] under direct sunlight

The process of photooxidation is carried out on an experimental installation (Fig. 1): In a water cooling box 6, a magnetic stirrer 1, a glass with a sample of 2, a UV lamp (250 W), a reflector of UV rays 4 and a starter 5 outside the box are placed on the mist bulb.
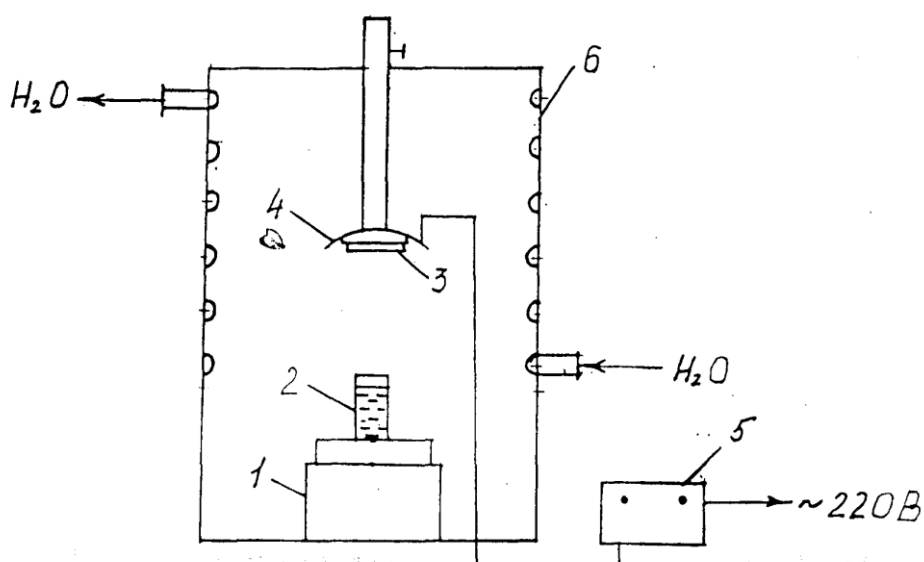
Figure 1. The scheme of laboratory installation

Progress

Experiment 1

Samples of wastewater are collected per 100 cm3 with a dye concentration of 40 mg / L into 3 different glasses (sample number 1, number 2, number 3); concentrated hydrogen peroxide and 1 ml of Fe^{2+} solution at a concentration of 10 mg / L are added (2 ml). After that, the sample number 2 is placed into laboratory installation, the magnetic stirrer is started and the UV lamp is turned on.

Photocoating is carried out for 5 minutes, then the solution is photometrised using the same wavelength and cuvette as for the calibration graph. After a break of 15 min. (cooling time of the lamp), the sample is again subjected to photooxidation for 10 minutes, photometrised and again after a break of 15 min. spend the third photooxidation within 15 minutes. and the final fourth photooxidation for 20 minutes. followed by the determination of the residual content of the dye after the calibration graph after each oxidation step. Based on the results obtained, calculate the degree of oxidation and build a schedule of dependence of the degree of oxidation from time to time; graphically calculate the rate constant of the photooxidation reaction.

The results of laboratory studies are noted in table:

Table 1.1 – Experimental results

Dye	Initial concentration, mg / L	Concentration after oxidation, L			
		after 5 min.	after 10 min.	after 15 min.	after 20 min.

Experiment 2

Sample number 1, after adding hydrogen peroxide and a solution of ferrum, the solution is stirred, placed on the laboratory table under the radiation of an energy saving lamp of different wavelengths (according to the teacher's instructions) and kept for 20 minutes. Then, the solution is filtered (if the solution becomes cloudy or precipitate formed) and photometrised using the same wavelength and ducts as for the calibration graph. After determining the content of the dye add 1 cm3 of Fe2 + solution at a concentration of 10 mg / dm 3 and stand for 20 minutes. on a laboratory table under the lamp, after which they are filtered and photometrically similar to the previously mentioned technique. The remaining dye content is determined every 20 minutes. within the next 120 minutes photooxidation. The degree of discoloration of the model of waste water is calculated.

Experiment 3

Determination of the efficacy of discoloration of sample No. 3 under direct sunlight is carried out in the same way as sample number 1, but under the conditions of solar radiation. The sample is placed on the window sill.

Experiment 4

Investigation of the effect of the ferrum dose on the effluent efficacy of samples No. 1, No. 2, and No. 3 is carried out analogously to the procedure in the experiment 1,2,3, but in the model samples of wastewater, another volume of a Fe^{2+} solution with a concentration of 10 mg / L is introduced, which is determined after carrying out of the previous three experiments on the tasks of the teacher.

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Self-control questions:

</div>

1. To give a description of the methods of purifying SV from dyes.

2. The essence of the methods related to the 1st group.

3. The essence of the methods pertaining to the second group.

4. The essence of the methods belonging to the 3rd group.

5. Characteristics of methods of photoconductive decomposition of dyes by the reagent of Fenton and its modifications.

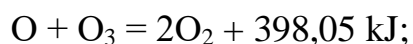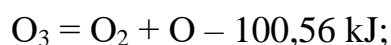# Laboratory work № 2. Removing of dyes by ozonation

Purpose: to master the method of work with ozonizer and to identify patterns of influence of the main factors of the ozonation process on the effectiveness of bleaching waste water, containing dyes.

Theoretical information

In recent years' interest in ozone has grown as a substance that can remove organic pollution from the water. The oxidative effect of ozone on organic matter can be manifested in various forms: direct oxidation by loss of oxygen, as well as by introducing molecular ozone into a substance molecule (ozonation); catalytic action, increasing the oxidative role of oxygen contained in the ozonized air.

As a result of oxidation, harmful substances are also formed that need to be removed, which leads to complication of the technological process and increases the cost of water purification.

Ozone - has strong decontamination properties and is a strong oxidizer. Ozone destroys organic compounds and microorganisms, while decomposing into oxygen.

$$O_3 = O_2 + O - 100{,}56 \text{ kJ};$$

$$O + O_3 = 2O_2 + 398{,}05 \text{ kJ};$$

Total reaction:

$$2O_3 = 3O_2 + 297{,}49 \text{ kJ}.$$
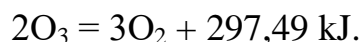
Chemically active gas of blue with a sharp smell, strong oxidizer. At high concentrations it decomposes with an explosion. It is formed from oxygen at an electric discharge (for example, during a thunderstorm). The bulk of ozone is in the upper atmosphere - the ozone layer, at an altitude of 10 to 50 km, with a maximum concentration of 20-25 km (the so-called ozone layer). It is he who protects the Earth from ultraviolet radiation of space. In the second half of the twentieth century. There is a tendency to decrease this layer and even the formation of "ozone holes" - areas with a reduced concentration of ozone in the ozone layer.

This phenomenon is associated with anthropogenic pollution of the atmosphere, including Freon.

It is used in chemical synthesis, for sterilization of water, disinfection and deodorization of air, bleaching of fabrics, paper, mineral oils, etc. Germicide. There is mutagen. The maximum permissible concentration in air is 1 mg / m3.

Ozone has a very high oxidation capacity ($E0 = +2.07$ V, alkaline medium $E0 = 1.24$ V) and, at normal temperatures, destroys many organic compounds. During ozonation simultaneously there is an oxidation of impurities, discoloration, deodorization, disinfection of sewage and oxygen saturation.

The ozone molecule is triatomic and has a triangular structure (Fig. 2.1).
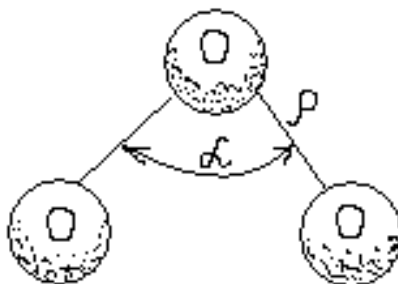
Figure 2.1. Structure of ozone molecule

In a clean and dry air, decomposition occurs more slowly than in wet and contaminated. Numerous studies have found that ozone has a high bactericidal effect. In addition, there is a stronger effect of ozone on spore forms, as well as a faster disinfectant effect of ozone compared to chlorine. However, the treatment of water with ozone has its own characteristics, which often do not allow to realize its benefits as a disinfectant. In this regard, in practice, sometimes with the treatment of water with ozone before supply to the network it is subjected to additional decontamination of chlorine.

The solubility of ozone in water depends on the pH and the amount of impurities in water. In the presence of acids and salts, the solubility of ozone in water increases, in the presence of alkalis - decreases. Ozone dissociate in air and in aqueous solution, turning into oxygen. In an aqueous solution, ozone dissociates

faster. The decomposition of ozone in water increases dramatically in the event of an increase in pH and temperature. The stability of ozone in neutral and acidic environments is associated with the formation of HO_3^+ associates, whose hydrate shell slows down the reaction:

$$O_3 + H_2O = O_2 + O + H_2O.$$
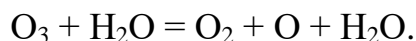
The decomposition of ozone in water is accelerated in the presence of activated charcoal, metals of valency variable (manganese, cobalt, ferrum) of some oxides (P_2O_5), barium peroxide (BaO_2). Materials such as fluorine and chlorinated plastics, glass, some materials, do not pour on the stability of ozone.

The basis of the industrial production of ozone is the reaction of splitting the oxygen molecule into atoms under the action of a quiet or barrier discharge. The high reactivity of ozone is due to the large excess energy of the molecule:

$$O_3 = 3/2\ O_2 + 100\ kJ/mole.$$

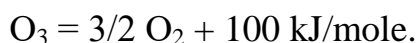Ozone reacts with saturated organic compounds to form free radicals. The limiting process stage is the effect of ozone on the bond C-H:

$$RH + O_3 = R^{\cdot} + HO^{\cdot} + O_2\ (or\ R + HO_3^+).$$
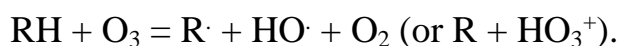
Radicals $R^{\cdot}$, which formed in the atmosphere of oxygen, are mainly converted to peroxide of radicals of moderate activity. Therefore, the chain reaction of oxidation can occur only at a sufficiently high temperature, when the rate of growth chain reaction exceeds the reaction of its cliff. At low ozone oxidation temperature there is a chain reaction with the formation of hydroxyhydroperoxides:

$$R^{\cdot} + O_2 = RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH = ROOH + R\ .$$
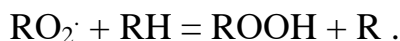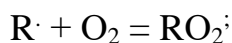
Aldehydes, in turn, are oxidized to peracids, which decompose in dilute aqueous solutions to organic acids and hydrogen peroxide. In parallel, the oxidation reaction of a hydroxyl radical may occur:

$$HO^{\cdot} + O_3 = HO_2^{\cdot} + O_2$$
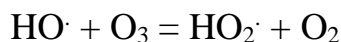
with the next recombination of peroxide-radicals:

$$2HO_2^{\cdot} = H_2O_2 + O_2.$$
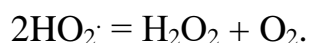
However, in fact, hydrogen peroxide does not accumulate and the consumption of ozone in neutral and acidic media corresponds to the reaction:

$$R\text{-}CH_2OH + 2O_3 = RCOOH + 2O_2 + H_2O.$$

Apparently, at the time of allocation hydrogen peroxide reacts with ozone:

$$H_2O_2 + O_3 = H_2O + 2O_2.$$
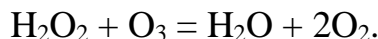
In addition, it is possible that ozone is spent on the decomposition of hydroxyperoxides and peracids. The reaction rate increases under these conditions, which is probably due to the decomposition of hydrogen peroxide, hydroperoxide, peracid and ozone. Simultaneous increase in the number of generated primary radicals initiates the process of oxidation. Consequently, to accelerate the initiation process, the oxidation process with ozone should be carried out in an alkaline medium. For most organic compounds, the intermediate and final oxidation products are alcohols, aldehydes (ketones) and acids.

In practice, ozone is obtained in special devices - ozonizers, in which air is transmitted at a certain speed between two electrodes connected to a power supply (5 - 20 kV).

To obtain a quiet discharge, the electrodes of the ozonizers are separated by a dielectric with the maximum possible surface-to-surface resistance and dielectric constant. A layer of such material serves as a dielectric barrier, which prevents the spark or arc discharge and causes a uniform structure of a quiet discharge. At the same time, it serves as a reactive buffer resistance, limiting the current in the discharge circuit. As an insulator, ordinary or borosilicate glass, enamel, and plastics are used.

Due to the fact that 85 – 95 % of the energy consumed by the ozonizer is consumed by the heat, the electrode system needs to be cooled, because ozone at high temperatures decomposes rapidly. The main value determining the synthesis of ozone is the discharge power, attributed to gas consumption, i.e., the amount of energy that falls on the volume passed through the gas ozonizer.

Materials and methods

Apparatus

Glasses (a nominal volume 250 ml - 2 pcs.); flasks (a nominal volume 100 ml - 6 pcs.); measurement flask (a nominal volume 1000 ml); spatula; conical flasks for titration (350 ml) - 2 pcs.; pipettes with a nominal volume 1, 2, 10 ml; sampler; photoelectrocolorimeter KFK - 2; cuvettes.

Reactants and materials

A model solution of waste water with a dye (concentration $40 - 200$ mg / L) (as a dye, any dye of organic nature, according to the teacher's instruction, is suitable) and a volume of 1 L is prepared. 1n solution of H_2SO_4; 1% starch solution, 0.005 N solution $Na_2S_2O_3$; 10 % KI solution.

Calibration graph

Measured flasks of 100 cm3 are placed; 2.0; 5.0 10; 20; 50,0 ml of the model solution of the drainage is brought to the mark with distilled water and build a calibration graph using the photoelectrocolorimeter KFK-2, the dependence of the concentration of the dye on the optical density. The calibration graph further determines the residual concentration of the dye after the ozonation process.

Progress

Ozonation is conducted in experimental installation (fig. 2.2).

For the process 600 ml of the model solution of sewage water is poured into absorption column 5, in which the ozone-air mixture (OAM) is fed through the porous partition 5.2. Cover 5.3. In the absence of the need to determine the residual ozone, the crane 7 is transferred to position 1. In this case, the gas after column 5 is sent to the absorber 10.

To determine the residual ozone, the crane 7 is transferred to position 2 and carried out in accordance with the procedure for determining O_3 in the OAM.
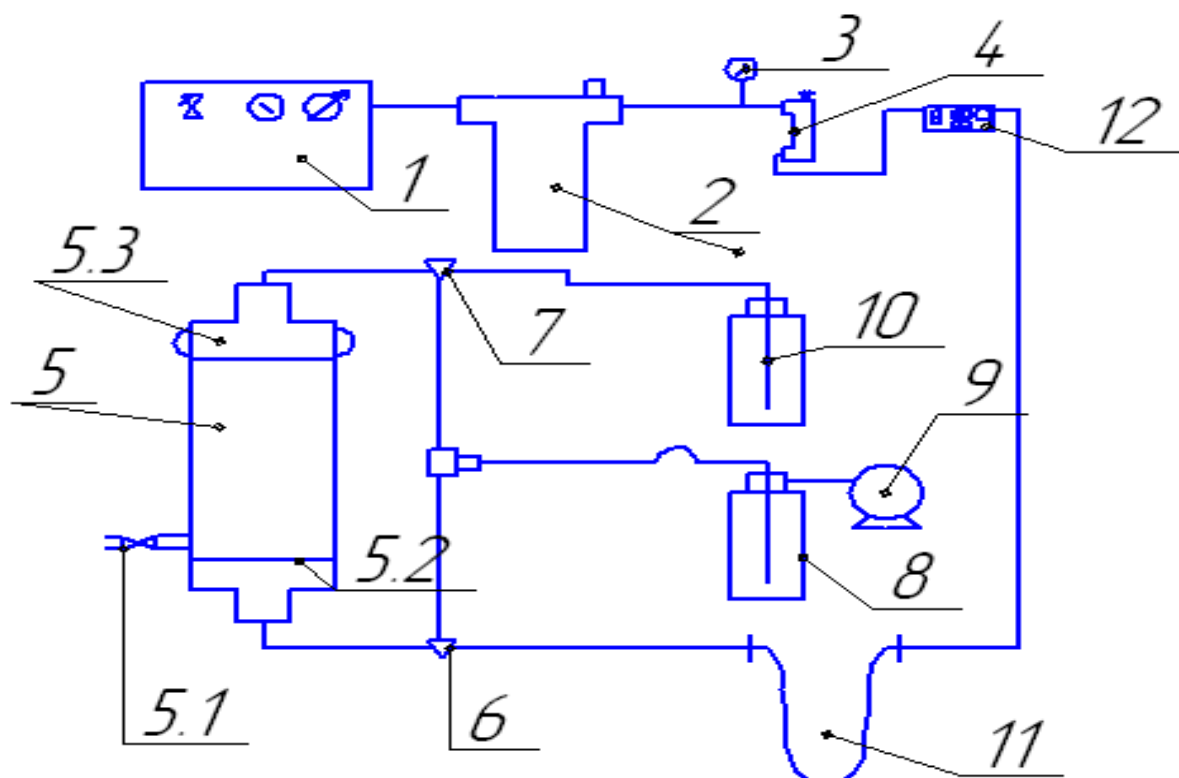
Figure 2.2. Experimental installation of the ozonation process: 1. compressor; 2. a drain filter; 3. pressure gauge; 4. pressure control system; 5. Absorption column: (5.1 sample sampling cube, 5.2 porous partition, 5.3 lid); 6.7 three-way cranes; 8. Drexel for analysis; 9. gas watch; 10. ozone trap; 11. protective loop; 12. ozonizer: 12.1 (ON / OFF, 12.2 mode switches, 12.3 current controller, 12.4 indicator).

To establish kinetics of removing dye every 5 min. Perform determination of optical density, sample for analysis taken through the cock 5.1 for 60 minutes. or to completely bleed the solution.

Before starting, determine the wavelength for this dye and the length of the cuvette, using the stock solution for this purpose.

The degree of discoloration is determined by the formula:

$$Z = (A_{in} - A)/A_{in} \cdot 100\%;$$

where A_{in} – optical density of initial solution.

A – optical density of solution after ozonation.

Determination of the mass fraction of ozone in the ozone-air mixture (OAM)

Determination of ozone in OAM is carried out by the volume-metric method. For analysis, drexel 8 is filled with 2/3 5 ÷ 10 % solution of KI, and the column is distilled water. Turn on compressor 1: using system 4, there is an expense (at which the pressure on the pressure gauge 3 should not exceed 0,15 MPa). The crane 6 should be in position bypassing the column 5. Activate the ozonizer and exert the voltage within the limits of 20 ÷ 35 kV, transmitting 5 ÷ 10 L of OAM, which fixes the time for which this mixture will pass the drake 8. The volume is set by gas clock 9

Transfer the drops solution 8 quantitatively to the titration flask, add 20 ml of 1N H_2SO_4 and 5 to 10 drops of 1% starch solution (the starch must be freshly prepared).

Titrate the resulting mixture, until discoloration, with 0,005N $Na_2S_2O_3$ solution.

The content of O_3 in OAM is determined by the formula:

$$X = (V(Na_2S_2O_3) \cdot K \cdot 0.005 \cdot 24)/V,$$

where: X – O_3 content in OAM, g / L;

$V(Na_2S_2O_3)$ – volume of thiosulfate, spent on titration, ml,

K – correction factor of concentration $Na_2S_2O_3$,

0,005 – concentration $Na_2S_2O_3$,

24 – ozone equivalent,

V – volume of OAM.

The next is finding of volume of OAM.

$$W = V/t,$$

where $V(Na_2S_2O_3)$ – consumption of OAM, L / min,

t – time for which V, L of gas passed.

And then the concentration of ozone is determined:

$$C(O_3) = X \cdot W; \text{ g } O_3 / L.$$

Results

Dye:

Dye concentration, mg / L:

Voltage of an ozonizer, kV:

Wavelength, nm:

Cuvette, cm: Graphs of $C(O_3)_{residual}$ -t, z-t.

The results of the studies are noted in tables 2.1., 2.2.

Table 2.1 – Experimental results

Time, min	A	V, L	V(Na₂S₂O₃), ml	C_residual, g O₃ / L	Z
5					
10					
15					
30					
…					
60					

Table 2.2 – Results of analysis

V, L	τ, min	V(Na₂S₂O₃), ml	X, g O₃ / L	W, L / min	C(O₃), g O₃ / min

Self-control questions

1. How are the physico-chemical properties of the medium influenced the rate of decomposition of ozone?

2. Describe the conditions for improving the process of destruction of ozonation dyes

3. Compare the efficiency of removing dyes from sewage by ozonation and the application of other oxidative methods

4. Is the technological scheme of ozonation energy technology?

Laboratory work № 3. Investigation of the influence of the main parameters on the effectiveness of coagulation and the determination of the optimal dose of coagulant based on waste from alumina production

Purpose: the establishment of regularities of the formation of the contact medium in the process of coagulation clearing the object of research and determining the optimal dose of coagulant based on waste alumina production

Theoretical information

Salts of aluminum and ferrum are the most often used as coagulants for coagulation purification of natural and waste water.

The technology of water purification by coagulants consists of the following basic operations: reagent storage, pre-clarification, water purification, preparation and mixing of coagulant, discoloration and clarification.

In the case of the polydisperse composition of suspended matter, especially in the presence of coarse-dispersed coarse particles (sand, lobes of ore and non-metallic minerals), the waste water is pre-clarified in horizontal tangential and aeration sand-traps with a circular or straight-line motion of water. Smaller mineral or organic curves are also separated by settling or filtration on slow filters filled with sand and gravel, or microfilter. Prefiltering on microfilters can be done in front of slow sand filters, before water treatment with coagulants or before rapid sand filters. As sedimentation structures, sedimentation ponds, horizontal tanks and their combination, as well as various septic tanks of periodic and continuous action (vertical, horizontal, radial, tubular, lamellar, etc.) are used. Hydrocyclones of pressure and non-pressure type are used for separation of coarse substances. The purified water is suspended if the alkaline reserve is insufficient for satisfactory hydrolysis of the coagulants.

Hydrogen and sodium carbonate, calcium carbonate and lime, as well as a

small amount of ammonia and ammonia, are used to water the water and bind the hydroxide of the aggressive oxide of carbon (IV) formed during the hydrolysis of water. In the course of paring the pH values are maintained within (6,5-7,5). It also contributes to reducing the residual content of aluminum and ferrum in purified water and reducing its corrosive properties.

The clarification and discoloration of muddy waters with increased hardness by coagulants is expedient to carry out at high pH, and colored soft waters - for reduced. Especially important is the order of the introduction of reagents. In the case of introduction of shaving reagents in colored water before the addition of coagulants, the process of coagulation and cleaning quality deteriorate. In water there is an increased content of stained substances. It is better to discolour water in the case of introduction of shaving reagents after the introduction of coagulants, because some of the colored matter manages to absorb at the time of formation of hydroxides. Organic substances contained in water in the form of humates of sodium, at low pH values are hydrolyzed to form negatively charged particles. The latter energetically interact with positively charged polynuclear hydroxcomplexes (micelles). Therefore, in the case of treatment with coagulants of highly colored waters, they are subjected after coagulant administration.

One of the most important technological parameters of the process of water purification by coagulation is the dose of coagulant, its optimum value depends on the properties of the disperse system: temperature, the number of suspended and colloid dispersed substances, color, ionic composition of the dispersion medium, pH and other physico-chemical parameters. In the case of an insufficient dose of coagulant, the desired effect of cleansing is not achieved, and in the case of excess - in addition to over-consumption of a high-value reagent, in some cases the effectiveness of coagulation may deteriorate.

With a decrease in the temperature of treated water, the dose of coagulant increases significantly, especially in the case of muddy waters. With decreasing water turbidity, the temperature is lower.

With considerable content of suspended matter, they, coated with a "casing"

of colloidal particles of aluminum hydroxide, coagulate, preventing the formation of long chain bridges from spherical particles. As a result, a smaller dose of coagulant is required. For high-infused waters with an increase in their alkalinity, the dose of coagulant increases, for turbid - decreases.

To coagulate quickly and throughout the volume of purified water, it is necessary to mix the reagents vigorously over a short period of time (1-2 minutes in the case of wet and no more than 3 minutes - dry dosage of reagents) in hydraulic or mechanical mixers. The mixing of the coagulant with water should occur so that a large number of small aggregates originally formed on the surface, on which chemoresubbed charged polynuclear hydroxocomplexes of aluminum having high activity relative to the impurities to be purified. In a one-stage technological scheme, the coagulant is added in the immediate proximity of the filters.

It is desirable to introduce the reagent into a relatively small amount of purified water, and then quickly mix it with the rest (separate coagulation). An increase in the initial concentration of coagulant contributes to the intensification of the coagulation process due to an increase in the partial concentration of coagulant in the treated volume of water (concentrated coagulation). Sometimes we recommend the ratio of volumes of treated and untreated water to 1: 1.5. In the case of concentrated coagulation, the cost of ferrous sulfate is reduced by 20-30 %, as well as the turbidity and color of water are reduced.

Effective is the fractionated (fractional or partial) coagulation of water, in which the coagulant is added to the water to be purified in two or more portions or successively introducing different coagulants.

In this case, the polydisperse aggregates of the coagulant are formed, as well as the period of formation of positively charged polynuclear hydroxocomplexes is increased, as a result of which the coagulation is intensified.

The recommended optimal time interval between the introduction of individual parts of the coagulant is 90 - 120 seconds. In the case of discoloration of water, the first dose of coagulant should be half the total.

Periodic coagulation is based on a combination of methods of concentrated and fractionated. The feeding periods of increased doses of coagulant alternate with periods of complete cessation of coagulation. As a result of such treatment of low-purity water for a two-stage scheme, the cost of coagulant is reduced by 30 – 40 %, the degree of discoloration of water rises. Deeper removal of coloring impurities is due to lower pH values during the feeding of increased doses of coagulant.

Coagulation inactivation is also achieved by recirculation of coagulant (coagulated curvature). The essence of the method is to supply part of the spent siege to the zone of dosage of fresh portions of the coagulant. This helps accelerate the process and form denser flakes. The application of this method is effective for the intensification of coagulation of low-wasting waters, while significantly (up to 30 %) the costs of coagulant are reduced.

The process of formation of flakes successfully occurs with a slow and even mixing of the disperse system, which helps to agglomerate the small flakes into larger ones that easily deposit. It is especially necessary to mix at low temperatures of treated water (below 5 °C). During the mixing, the growth of the particles is accelerated as a result of their collision, the interconnection increases and solid flakes are formed. Mixing positively influences the formation of flakes in the event that the particles have reached a certain size as a result of the Brownian motion (spherical aggregates larger than 0.02 microns and larger).

The mixing of water should not be too intense to prevent the destruction of flakes. In order to ensure optimal mixing conditions in front of the septic tanks, flushing cameras are often equipped with vertical or horizontal movement of water through partitions or whirlpool devices.

The formed coagulant flakes, together with the adsorbed impurities, are separated from the water to be purified during clarification by means of settling, filtering, centrifuging or floating. In the practice of water preparation, the suspended matter is first separated by settling, and then the drains are filtered. Horizontal, vertical or radial tanks are usually used.

Materials and methods

Apparatus

Flasks (nominal volume 100 ml - 6 pcs., 50 ml - 6 pcs.); measurement flask (nominal volume 1000 ml); measurement flask (nominal volume 250 ml – 2 pcs.); spatula; pipettes (nominal volume 1, 2, 10 ml); sampler; photoelectrocolorimeter KFK - 2; cuvettes; analytical balance, litmus paper.

Reactants

A mixture of ammonium molybdate, sulfate acid, stybium chloride and tartaric acid. Up to 300 ml of palladium acetate is stirred with 144 ml of concentrated sulfuric acid, ppm. It is then cooled to 20 ^oC and, when stirred, add a solution of 10 g of sulfamic acid NH2SO8H pda. and 100 ml of distillate solution, 12.5 g of ammonium molybdate $(NH_4)_2Mo_7O_{34} \cdot 4H_2O$ in 200 ml of distillate solution, 0.235 g of sitbium chloride of $SbCl_2$ pda.a. and 0.6 g of tartaric acid odd.a. in 100 ml of distillate. The icons are kept in a glass of orange glass.

Ascorbic acid. 10 % solution. Dissolve 10 g of ascorbic acid in pistacible water and bring the volume of solution to 100 cm3 in a measuring dish. Store the solution in the cold, stable for about 30-40 days.

Potassium phosphate mono substituted - standard solution.

Basic solution: Dissolve 0,7165 g of KH_2PO_4 pda, dried for 2 hours at a temperature of 105 ^oC, in a distillate. Add 2 ml of chloroform and bring the volume of the solution with distillate to 1 dm3 in a volumetric flask. 1 ml of this solution contains 0.389 mg of phosphate.

Working solution 1: Make 10.0 ml of the basic solution to 250 ml of distillate. Use freshly prepared solution. 1 ml of this solution contains 0.0156 mg of phosphate.

Working solution 2: Make 50,0 ml working solution 1 to 250 ml distillate. Use freshly prepared solution. 1 ml of this solution contains 0.00312 mg of phosphate.

Calibration graph

Working solution 2 (50 ml) is placed (0; 1; 2.5; 5; 10; 25 ml) into a volumetric flask of. Add 2 ml of solution of the mixture, 0.5 ml of 10 % solution of ascorbic acid to each flask. The mixture is brought to the mark with a distillate and stirred. The first bulb (without the content of the working solution 2) - "idle experiment". After 20-25 minutes photometrically in a cell 10 mm in wavelength 670 nm and calibration graph "Optical density - concentration of phosphates" is built. An example of the calibration graph is shown in Figure 1.
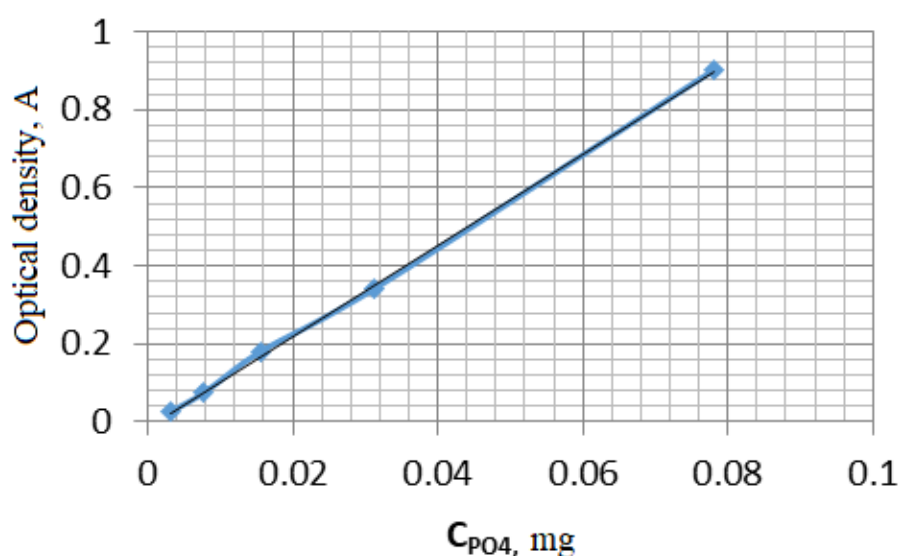
Figure 1. Calibration graph

Progress

Determination of the efficiency of removal of phosphates by coagulation method, selection of the optimal dose of coagulant based on waste from alumina production.

Experiment 1: Coagulation at pH 9 (NaOH substrate reagent).

For study use working solution 1. In 4 cylinders of coagulation pour 100 cm3 of the test solution. Then add a dose of coagulant (a solution of sulfate or iron chloride) to the pipette so that its content in water is 25, 50, 75 and   100 mg / L. Using a solution of sodium hydroxide, the pH of the solution is adjusted to 9-10. After mixing the three-fold turning of the closed cylinder caps, the time of entering

the coagulant in water is noted. After 30 minutes, water from each cylinder is filtered through a "blue ribbon" filter in conical flasks. To analyze the coagulation efficiency, the filtrate is diluted similarly to the preparation of the solution for preparation of the calibration: 5 ml from each cylinder in a 100 ml flask and brought to the label with a distillate. From the obtained solutions, an aliquot of 5 ml is drawn into a 50 ml flask, 2 ml of a mixture solution, 0.5 ml of ascorbic acid is added and distilled to the label. After 20-25 minutes, photometrically, and on the basis of the obtained value, the residual concentration of phosphate in the solution is found.

WARNING! Time to settle solutions before photometry should be the same for all experiments.

Experiment 2: Coagulation with the addition of CaO as a sublutting reagent.

For study use working solution 1. In 4 cylinders of coagulation pour 100 ml of the test solution. Then add a dose of coagulant (a solution of sulfate or iron chloride) to the pipette so that its content in water is 25, 50, 75 and 100 mg / L. On technical scales weigh 0.3-0.5 g CaO. After the introduction of the coagulant and CaO, the solution is mixed with a three-fold turning of the closed cylinder caps. Mark the time when the coagulant is injected into the water. After 30 minutes, water from each cylinder is filtered through a "blue ribbon" filter in conical flasks. To analyze the coagulation efficiency, the filtrate is diluted similarly to the preparation of the solution for preparation of the calibration: 5 cm3 from each cylinder in a 100 ml flask and brought to the label with a distillate. From the obtained solutions, an aliquot of 5 ml is drawn into a 50 ml flask, 2 ml of a mixture solution, 0.5 ml of ascorbic acid is added and distilled to the label. After 20-25 minutes, photometrically, and on the basis of the obtained value, the residual concentration of phosphate is found on the schedule.

Calculations

Removal degree, %:

$$X = \frac{Cv - Ck}{Cv} \cdot 100\% ,$$

where Cv – initial concentration, g / L;

Ck – final concentration, g / L.

Make conclusions about the effectiveness of the dose of coagulant and the conditions for coagulation.

Self-control questions

1. Provide the conditions (mode) of the formation of the contact environment in the suppressed state.

2. How does the characteristic of treated water affect the efficiency of the process?

3. Under what conditions depends on choosing the type of coagulant?

4. Type the types of luminaries and the principle of their operation.

5. Describe the loading of filters used in water treatment technology.

6. Types of filters and the principle of their operation.

Laboratory work №4. Purification of waste water from organic compounds

Purpose: to carry out the purification of waste water from phenol by the method of adsorption. Determine the degree of water purification depending on the method of organizing the sorption process: a) in the stationary (filtering) layer of the sorbent; b) in the device simulating the fluidized contact mode sorbent - purified water. Measure the adsorption isotherm from the aqueous solution on activated carbon. Calculate the adsorption equilibrium constant and reduce the amount of adsorption energy.

Theoretical information

Sorption is one of the most effective methods for purifying industrial water containing impurities of organic origin, and allows to achieve deep water purification to the MPC norms. Adsorption is used to dispose of wastewater from phenols, herbicides, pesticides, aromatic nitro compounds, surfactants (surfactants), dyes, and others. Advantages of the method: the ability to adsorb substances from multicomponent systems, as well as high efficiency, especially when cleaning low-concentration wastewater. From a technical and economic point of view, adsorption is very effective for the removal of valuable products from wastewater for the purpose of using them in a closed loop of the main production.

Very important, especially from a practical point of view, the moment when adsorption purification of industrial waste water is the kinetics of the process, or the rate of adsorption, which determines the choice of the technological scheme, the dimensions of the apparatus, etc. The velocity of the adsorption process depends on the concentration of the adsorbent, the temperature, the nature and structure of the adsorbent, the adsorbent and the adsorbent and is determined by the external and internal diffusion of molecules from the volume of solution to the surface of the grains and in the pores of the adsorbent, the velocity of the adsorption of molecules on the surface and the speed of extruding exchange of molecules, which is adsorbed.

As sorbents, activated carbon, synthetic sorbents and some industrial wastes (ash, slag, chips) are used. Mineral sorbents - clays, silica gels, alumina gels and hydroxides of metals for adsorption of organic substances from wastewater are used little, since the energy of their interaction with water molecules is large - sometimes higher than the adsorption energy. The most versatile of adsorbents is activated carbon.

The process of adsorption wastewater treatment is carried out under different conditions: with intensive mixing of adsorbent with water, by filtering water through a layer of adsorbent or in a fluidized bed at installations of periodic or continuous action. When using filtration type units, sewage water should not contain solid suspended impurities. Installations of a fluidized bed should be used with high content of suspended impurities in sewage.

Physical adsorption is one of the types of manifestation of intermolecular interaction, in which the concentration of gas molecules, vapors, liquids or solution components near the phase separation surface is greater than the average concentration in volume.

The occurrence of physical adsorption, which mainly determines the adsorption on nonpolar surfaces such as carbon adsorbents, is a dispersion (Van der Waals) interaction. This interaction is due to the coordinated motion of electrons in molecules in the immediate vicinity.

Physical adsorption of organic substances - non-electrolytes or weak electrolytes from aqueous solutions most strongly manifests itself when used as an adsorbent of carbon materials. This is due to the fact that the energy of Van der Waals interactions of water molecules with carbon atoms is much less than the energy of interaction of these atoms with organic molecules. As a result of this there is a strong expressed selective adsorption of organic substances on activated carbon, which is used in the technology of water treatment and industrial effluents from organic compounds. A quantitative measure of the adsorption interaction of an organic substance with a carbon adsorbent is the free energy of Helmholtz $-\Delta F_a^0$, which is the difference between the free energies of the adsorption interaction of

water $-\Delta F_v^0$ and the organic matter $-\Delta F_{o.r.}^0$ under standard conditions, since it is known from the course of physical chemistry that the absolute the value F cannot be determined:

$$-\Delta F_a^0 = -\Delta F_{o.p.}^0 - (-\Delta F_B^0). \tag{4.1}$$

At present, $-\Delta F_a^0$ is determined experimentally, by the value of the heat of adsorption or with the isotherm of adsorption, since $-\Delta F_a^0$ is related to the equation of adsorption equation:

$$-\Delta F_a^0 = R \cdot T \cdot \ln K_a; \tag{4.2}$$

At standart temperature 25 °C:

$$-\Delta F_a^0 = 5{,}71 \cdot \lg K_a, \text{ kJ / mole.} \tag{4.3}$$

$-\Delta F_a^0$ for organic non-electrolytes and weak electrolytes from aqueous solutions ranges from 10 to 30 kJ / mole. Substances having $-\Delta F_a^0 < 10$ kJ / mole do not displaced water from the adsorption volume of activated carbon, ie practically not adsorbed from aqueous solutions.

In this paper, $-\Delta F_a^0$ is determined by the adsorption isotherm, which can be represented by a equation of the type of the Langmuir equation suitable for most practical purposes, which is the equation of a convex parabola:

$$K_a = \frac{1000 \cdot a \cdot V_w \cdot 55{,}5}{\left[V_e - a(V_{o.p.} - V_w)\right] C_p},$$

where a - specific adsorption of organic matter, mmole / g of coal;

V_e - limiting adsorption volume of coal, determined experimentally for each grade of coal, cm^3 / g,

$V_{o.r.}$ and V_w - millimolar volume of adsorbate and water, respectively,

$$V = M/\rho, \text{ cm}^3 / \text{mmole};$$

Cp - concentration of organic matter, mmole / ml;

55,5 - number of mole in 1 L of water.

As can be seen, the Ka equation includes only experimentally measurable quantities.

Materials and methods

Apparatus

Measuring cylinder (nominal volume 100 ml); bulbs (nominal volume 100 ml - 5 pcs.; a nominal volume of 250 ml with stoppers - 10 pcs.); funnel - 5 pcs.; pipettes with a nominal volume of 10 and 25 ml; burette for titration; spatula; sampler; analytical weights; a device for shaking flasks; vertical cylindrical glass column.

Reactants and materials

Model of industrial waste water containing phenol; aqueous solution of phenol at a concentration of 5 mmole / L; coal of the brand KAD; bromide-bromate solution - 0.1N; sodium thiosulfate - 0.1 N solution; potassium iodide crystalline; starch – 1 % solution; solution of sulfate acid 1: 3; paper filter.

Progress

Removal of phenol from water by sorption in a fixed (filtering) layer of sorbent Through a vertical cylindrical glass column filled with activated carbon, water contaminated with phenol, at a rate of 2-4 m^3 / $(m^2 \cdot h)$ is passed. According to the teacher's instructions, a certain amount of water is passed through the teacher, after which the phenol content is determined in the samples.

Removal of phenol from water by means of sorption in the apparatus simulating the fluidized contact mode sorbent - purified water.

In the flat-bottomed flasks, weigh the activated charcoal and determine the volume of the sewage, and then place the flasks in the shaking apparatus. According to the teacher's instructions set the contact time of water with sorbent from 10 minutes. up to 1 hour.

Calculation of the degree of water purification

The degree of purification of water from organic compounds (phenol) by

adsorption (X) is calculated by the formula, %:

$$X = (C_p^0 - C_{pi})/ C_p^0 \cdot 100,$$

where C_p^0 - concentration of phenol in the initial effluent, g / L;

C_{pi} - phenol concentration of water samples after sorption, g / L.

Preparation of working solutions of phenol

The working solutions are prepared by dilution of the initial solution of phenol at a concentration of 5 mmole / L in the measuring flasks per 100 cubic centimeters (Table 4.1).

Table 4.1 - Preparation of working solutions

№	Volume of initial solution of phenol V_{ph}, ml	Volume of water, ml	Concentration of phenol C_0, mmole / L
1	20	80	1
2	40	60	2
3	50	50	2,5
4	60	40	3
5	70	30	3,5
6	80	20	4
7	90	10	4,5
8	100	0	5

Measurement of isotherms of adsorption of organic matter on charcoal

KAD by 0.1 g is weighed and entered into dry flat-bottomed flasks of 250 ml. Then, the prepared aqueous solutions of organic matter (phenol) of different concentrations (100 ml) are added to the flask. The flasks are tightly sealed, signed and shaken until an adsorption equilibrium is established (within 2 hours). After that, the coal is filtered and the residual (equilibrium) concentration of organic matter is determined in the filtrate. For the filtering, use a dry bulb.

**Determination of the concentration of phenol in the solution after adsorption**

Determination of the concentration of phenol in water is carried out by the bromide-bromate method based on the bromination of phenol and the determination of excess bromine remaining after the reaction.

When brominated phenol runs the reaction:

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

When bromination of phenol in acidic medium, a solution containing KBr and $KBrO_3$ forms a white precipitate of tribromophenol.

To determine the bromine that has not reacted, crystalline potassium iodide is added to the solution. Bromine displaces potassium iodide from iodine, which is titrated with sodium thiosulfate in an acidic environment in the presence of starch:

$$Br_2 + 2\ KI = I_2 + 2\ KBr,$$

$$I_2 + 2\ Na_2S_2O_3 = 2\ NaI + Na_2S_4O_6.$$
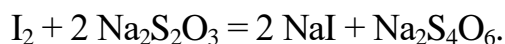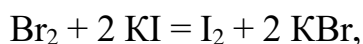
Method for determining phenol

Conical flasks with a capacity of 250 ml are selected for 25 ml of the studied solutions. All the flasks are pipetted with 10 ml of bromide-bromate solution and 5 ml of H_2SO_4 solution (1: 3), close the flasks with stoppers, shake and leave for 5 minutes.

To determine the bromine that has not reacted, add 1 g of potassium iodide to the flasks, close the cork and leave for 3 minutes. Titanium iodine titrate 0.1 N sodium thiosulfate solution in the presence of starch (5-6 drops) to bleach the solution. The starch is added to the solution before the titration is completed, when the titrated solution becomes light yellow.

Before performing the calculations, it is necessary to specify the concentration of bromide-bromate solution. To this end, add 10 cm^3 of bromide-bromate solution and 5 ml of H_2SO_4 solution (1 : 3) into a conical flask of titration, close the flasks with cork, shake and titrate 0.1 N sodium thiosulfate solution in the presence of starch (5-6 drops) to bleach the solution. The starch is added to the solution before the titration is completed, when the titrated solution becomes light yellow.

Knowing the volume of titrant, its concentration and the volume of bromide-bromate solution determine its concentration and use the refined concentration in calculations.

Concentration of phenol is calculated by the formula:

$$C_p = (V_{Br} - V_{ts}) \cdot N_{ts}/(6 \cdot V_v), \text{ mmole / ml} \qquad (4.5)$$

where V_{Br} is the volume of bromide-bromate solution taken for determination (10 ml);

V_{ts} - volume of sodium thiosulfate solution, which was spent on titration, cm3;

N_{ts} -concentration of sodium thiosulfate 0.1 mole / L;

V_v - volume of water sample, 25 ml;

6 is the equivalent of phenol.

Calculation of specific adsorption and filling adsorption volume of coal

In particular, the adsorption of organic matter (a) is calculated by the ratio:

$$a = (C_0 - C_p) \cdot V_{ph} / m, \text{ mmole / g}, \qquad (4.6)$$

where C_0 and C_p - the concentration of organic matter in the solution before and after adsorption, respectively, mmole / ml;

V_{ph} - volume of solution of phenol, adhered to coal smoke, ml;

m - weight of coal, g.

Table 4.2 – Experimental data

C_0, mmole / ml	V_{ts}, ml	C_p, mmole / ml	m, g	a, mmole / g	lgK_a	K_a	Θ
0,001							
0,002							
0,003							
0,004							
0,005							

The filling of the adsorption volume of coal with organic matter is calculated by the formula:

$$\Theta = a \cdot V_{o.r.}/V_w. \qquad (4.7)$$

Experimental data are written in the form of table 4.2 and build on them an isotherm of adsorption, depositing on the axis of the ordinate the value of a, and on the abscissa the value of C_p.

Calculation of the adsorption equilibrium constant and magnitude $-\Delta F_a^0$

To determine the adsorption equilibrium constant, the experimental data are presented in the form of graphical dependence: $\mathbf{lgK_a = f(\Theta)}$. In the logarithmic form, the adsorption isotherm represents a straight line. Extrapolating the straight line to the intersection of it with the ordinate axis, that is, in the region of standard conditions ($\mathbf{\Theta \to 0}$), the ordinate gets a segment numerically equal to the value of $\mathbf{lgKa}$.

The standard reduction of the differential molar free energy of adsorption of organic matter from aqueous solutions on activated charcoal is calculated from the ratio (4.3).

Tasks

1. To carry out purification of sewage from phenol:

a) in a stationary (filtering) layer of sorbent;

b) in a device simulating a fluidized contact mode sorbent - cleared water.

2. Calculate the degree of water purification.

3. Measure the isotherm of adsorption of phenol from aqueous solutions on activated carbon KAD.

Output: $\mathbf{V_{o.r.} = 0{,}089\ ml\ /\ mmole}$; $\mathbf{V_w = 0{,}25\ mg\ /\ g}$; $\mathbf{Uv = 0{,}018\ ml\ /\ mmole}$.

4. To construct an isotherm of adsorption of phenol in the coordinates $\mathbf{a = f(C_p)}$.

5. Calculate the value $\mathbf{-\Delta F_a^0}$ of phenol.

Self-control questions

1. Name the area of application of adsorption sewage treatment.

2. Characteristics and properties of adsorbents.

3. Name the main stages of the adsorption process.

4. On what factors depends sorption rate?

5. The main types of technological schemes of adsorption cleaning.

6. Principle of operation of adsorption cleaning machines.

7. What is the energy characteristic of the interaction of organic matter with a carbon adsorbent?

8. What is the specific adsorption of the substance, the adsorption volume of the adsorbent, the equilibrium concentration in the solution, the filling of the adsorption volume?

9. Give the equation of isotherms of adsorption of organic matter from aqueous solutions to a carbon adsorbent.

10. How is the standard reduction of the free energy of adsorption of organic matter from the aqueous solution from the experimental data?

11. Which of substances will be better adsorbed – alcohol ($-\Delta F_a^0 = 14$ kJ / mole) or p-nitrophenol ($-\Delta F_a^0 = 22$ kJ / mole)?

Laboratory work №5. Purification of waste water from chromium compounds

Purpose: to study existing methods of wastewater treatment of chromium compounds, to conduct a comparative description of reagent and physico-chemical methods of purification, to determine the degree of purification.

Theoretical information

At the plants, waste water containing Cr (III) or Cr (VI) chromium compounds is formed. Sources of pollution are galvanic workshops of machine-building, metal-working, automobile, aviation factories, as well as paint shops of textile enterprises, leather, asbestos-cement, printing, chemical enterprises. As is known, chromium compounds are toxic, in particular, Cr (VI) – MPC = 0.1 mg / dm^3, MPC for Cr (III) – 0,5 mg / dm^3. Therefore, methods for purifying wastewater from Cr (VI) usually involve the transfer of Sr (VI) to Cr (III). There is a large variety of methods for purifying sewage from chromium compounds: reagent (reduction), coagulation, separation, flotation, electrochemical, sorption, ion exchange, catalytic, and photochemical. At present, the most common reagent and ion-exchange methods. Methods of treatment of sewage from hexavalent chromium are based on its reduction to trivalent, followed by precipitation in the form of hydroxide in alkaline medium. As a reducing agent can be used: activated charcoal, ferrous sulfate (II), sodium hydrosulphite, sulfur oxide (IV), organic waste (eg newsprint), pyrite cobs and others. In practice, for the restoration of chromium, the most frequently used solutions are sodium hydrosulfite:

$$4H_2CrO_4 + 6\ NaHSO_3 + 3\ H_2SO_4 = 2\ Cr_2(SO_4)_3 + 3\ Na_2SO_4 + 10\ H_2O.$$
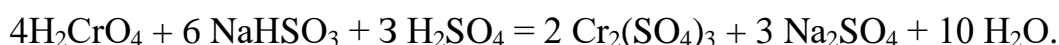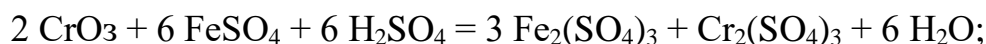
The reaction runs quickly at pH 3 - 4 and excess sulfate acid. To precipitate trivalent chromium, use alkaline reagents Sa (OH)$_2$, NaOH and others (optimal pH value for precipitation 8 – 9.5):

$$Cr^{3+} + 3\ OH^- = Cr(OH)_3.$$
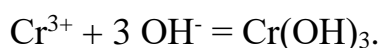
Effective for the deposition of chromium is the use of a ferric sulfate reducer

(II). The process can be carried out both in acidic and alkaline media:

$$2\ CrO_3 + 6\ FeSO_4 + 6\ H_2SO_4 = 3\ Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6\ H_2O;$$

$$2\ CrO_3 + 6\ FeSO_4 + 6\ Ca(OH)_2 + 6\ H_2O = 2\ Cr(OH)_3 + 6\ Fe(OH)_3 + 6\ CaSO_4.$$

The consumption of reagents depends on the pH of the medium and the concentration of chromium. The most favorable conditions for conducting the process are: temperature 20 °C, pH 7 and consumption FeSO4 in 1,15 - 1,3 times more stoichiometrically calculated.

The recovery of sulfur oxide (IV) occurs according to the scheme:

$$SO_2 + H_2O = H_2SO_4;$$

$$2\ CrO_3 + 3\ H_2SO_4 = Cr_2(SO_4)_3.$$

The time required for the complete restoration of Cr (VI) depends on its content in water. For example, at pH 3, to reduce the concentration of Cr (VI) in solution from 50 to 5 mg / L, it takes 1 min, and from 5 to 0.1 mg / L - 35 minutes. In the presence of soda in sewage, chrome is completely removed:

$$2\ Na_2CrO_4 + 3\ SO_2 + Na_2CO_3 + nH_2O = Cr_2O_3 \cdot nH_2O + 3\ Na_2SO_4 + CO_2.$$
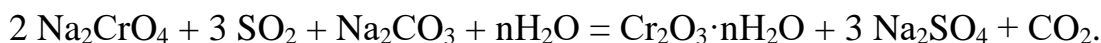
The recovery process is carried out at 90 °C, after separating the precipitate by filtration in sewage, only sodium sulfate remains. The precipitate is fired at high temperature to obtain standard chromium oxide. Zinc hydrosulfite or a mixture of it with lime in various ratios as well as compounds containing phosphorus, natural gas, ammonia, charcoal, hydrogen, etc. can be used as a reducing agent. It is also possible to precipitate Cr (VI) in the form of insoluble compounds without pre-reducing it to Cr (III), for example barium acetate. In this case, Cr (VI) is precipitated in the form of barium chromate. The advantage of this method is the possibility of simultaneous treatment of sewage and SO_4^{2-} ions.

The wastewater treatment by the ion exchange method has recently become more widespread, because this method allows us to dispose of valuable impurities, to clean water to the maximum allowable concentrations and provide the possibility of using purified sewage in production processes or in circulating water supply systems. The purification of sewage from compounds of chromic acid is possible on a strongly basic anion exchange AB-17. Anion exchanger does not

change its properties for a long time at concentrations CrO42- up to 1200 mg / L. Anion exchangers are regenerated with 10-15 % NaOH solutions. However, desorption of chromates proceeds more effectively if the anion exchange is pre-translated into chloride form. During the regeneration of anion exchanger with a solution containing 2 % NaOH and 6 % NaCl, 89-99 % chromates (sorbed) are desorbed. The regenerated solution containing $NaCrO_4$, NaOH and NaCl is suitable for the preparation of passivative solutions. By the H-cationation method, chromate of sodium can be converted to chromic acid. It should be noted that the strongly basic anion exchange agent AB-17 is able to exchange OH^- ions of its active group on anions of water-soluble weak acids only in the absence of strong acids and their salts in water.

Theoretical foundations of the photometric method of chromium determination

Determining the total content of chromium can be relatively easy. It is also easy to determine the content of Cr (VI) in the acids of non-colored sewage and to find the content of Cr (III) by difference. But in neutral or alkaline water separate determination of hexavalent chromium and trivalent complicated by the fact that when acidification of water, if (as is usually the case) contain reducing - ferrous iron salts, sulfites, many organic substances, there is a restoration of hexavalent chromium to trivalent. In waters colored with organic matter, it is not possible to directly determine the color of the hexavalent chromium in those cases where these waters have an acid reaction.

Diphenylcarbazide reacted in acidic medium with dichromate ions to form a purple compound, which contains chromium in reduced form, in the form of Cr (III), and diphenylcarbazide oxidized to diphenylcarbazone. The method is very sensitive: at $\lambda = 540$ nm the molar absorption coefficient $\varepsilon = 4.2 \cdot 10^4$.

Per serving oxidation tests conducted Cr (III) to Cr (VI) persulfate and determine the total content of the sample in both forms of chromium in the other portion of the sample does not hold Cr oxidation and determine only the content of Cr (VI). The difference between the results obtained is the content of Cr (III).

The reaction with biphenylcarbazide is almost specific to chromium. Mo (VI) and Hg (II) diphenylcarbazide form a colored compound, but as the pH at which determine chromium, both of these elements allowed in concentrations up to 200 mg / L. Vanadium prevents, but its presence is tolerable in quantities exceeding the chromium content by 10 times. The ferrum does not interfere with the definition. Mangan, with its high content in the sample and in the absence of a catalyst, silver nitrate may fall in the form of a precipitate in the form of manganese oxide (IV); The precipitate is then separated by filtration through a glass porous plate or through a glass wool.

Materials and methods

Apparatus

Measurement flasks (nominal volume 100 ml - 16 pcs.), a cylinder (400 ml), a flask (250 ml), cylinders (50 and 100 ml), pipettes with a nominal volume of 1, 5, 10 ml, a funnel, a sampler, a vacuum -pump, column with ion exchanger, stirrer, spatula, analytical weights, photoelectrocolorimeter KFK-2.

Reactants and materials

Standard solution Cr with concentration Cr^{6+} = 10 µg / ml; diphenylcarbazide, 0,1% alcohol solution; solution of sulfate acid 1 : 3 and 2 N solution; $FeSO_4$ crystalline; CaO; model of industrial water containing chromium; paper filter.

Progress

Purification of model waste water by redox-oxide method

Purification of chrome-containing wastewater by the reduction-oxidation method is carried out in a laboratory reactor with a stirrer. According to the teacher's instructions, the necessary volume of cleaned water is added to the reactor. When constantly stirring during a given time, a burette is dosed with a calculated amount of reagents ($FeSO_4$, H_2SO_4). The pH of the reaction medium is monitored using indicator paper. Then, in the same reactor, without interrupting mixing, dosage a given amount of lime milk. The pulp is filtered on a laboratory vacuum filter. The filtrate is analyzed for the residual chromium content.

Method of chromium determination

Calibration graph

The calibration graph is constructed for the following chromium concentrations: 10, 20, 30, 40 and 50 µg. To do this, the appropriate amount of standard solution C_p is taken into the pipette and entered into a 100 ml graduated flask. To each sample, 0,5 ml of sulfuric acid, 0,4 ml of diphenylcarbazide solution and 10 to 15 min. determine the optical density in relation to the bulk solutions. The blank solutions are prepared for each sample separately, adding all the reagents except for diphenylcarbazide. Measurements are carried out in cuvettes with a layer thickness of 1-5 cm (may vary depending on the color of the solutions) at $\lambda = 540$ nm. Determine the optical density by means of a gauge graph to determine the Cr content in µg / ml.

Calculation of chromium content and degree of water purification

Chromium content is determined by the following formula:

$$C_{Cr} = \frac{C}{V}, \text{ µg / ml}$$

де C - concentration of chrome by calibration graph, µg;

V - volume of a sample, ml.

The degree of purification of water from chromium is calculated by the formula, %:

$$X = \frac{(C_{Cr}^0 - C_{Cr})}{C_{Cr}^0} \cdot 100,$$

де C_{Cr}^0 - chrome concentration in initial waste water, µg / ml;

C_{Cr} - chrome concentration in purified waste water, µg / ml.

Processing of experimental research

The results of laboratory studies are executed in the form of table 5.1.

Table 5.1 – Experimental results

Samples		Content of Cr, μg	Content of Cr, μg / ml	Removal degree, %
Initial sample				-
After sorption				
Reagent method	1			
	2			
	3			

Tasks

1. Perform the analysis of the initial sample of water on the chromium content by photometric method using the above method.

2. Calculate according to the teacher's instruction the number of reagents: $FeSO_4$, H_2SO_4 and $Ca(OH)_2$.

3. Carry out purification of chromium-containing wastewater by the specified method, determining in the purified water the residual content of chromium and calculate the degree of purification.

4. To carry out purification of chromium-containing wastewater by ion exchange method. To do this, you must skip the teacher's prescribed volume of water through the column with ion exchanger. In the filtrate, determine the residual chromium content by photometric method. Calculate the degree of purification.

Self-control questions

1. Describe the existing methods for cleaning sewage from chromium compounds.

2. Explain the mechanism of neutralization (reduction) method of wastewater treatment of chromium.

3. Write the equation for the ion exchange reaction to remove water from the ions of CrO_4^{2-} on the anion exchange AB-17.

4. Propose technological schemes for the purification of chrome-containing wastewater by reagent and ion-exchange methods.

Laboratory work № 6. Flocculation purification of contaminated water

Purpose: to study of the effect of flocculent on the process of precipitation of colloidal-dispersed impurities in waste water.

Theoretical information

Various flocculants have become widely used to control the stability of disperse systems and, in particular, the significant intensification of water purification processes from colloidal-dispersed substances. Flocculants include inorganic or organic macromolecular compounds that promote the formation of aggregates as a result of the combination of several particles using a macromolecule of adsorbed or chemically bound polymer. The introduction of a small amount of flocculants (thousands or millions of particles from the solid phase mass) substantially changes the stability of the dispersions. They accelerate the formation of flakes, increase the density of the precipitate water purification and the degree of clarification of water. At the same time, the limits of optimal pH values are significantly expanded and the residual content of the ferrum or aluminum (depending on the chosen coagulant) is reduced in the purified water.

Flocculants that are used for water purification can be divided into three groups: inorganic polymers, natural high molecular substances and synthetic organic polymers. Among inorganic flocculants the most active silicic acid (AK) has become active, it is considered as a colloidal system consisting of particles having a clear phase separation surface, that is, as an SiO_2 sol. To macromolecular flocculants of natural origin are starch and its derivatives.

Significantly greater use was made of synthetic macromolecular flocculants (MMF), which are divided into nonionic, anionic and cationic.

Anionic flocculent - polyacrylamide (PAA) is most commonly used in water treatment and water treatment technology. It is a polymer of acrylamide - $CH_2 - CH - CONH_2$.

Adding PAA to coagulated water after the formation of coagulant flakes at the same level of the machine, where there is no mixing and the formation of flakes, even in very small doses (0.5 - 2.0 mg / kg) greatly enhances and increases the weight of the flakes coagulant, which leads to acceleration their deposition and gives an opportunity to raise the speed of lifting water in the illuminators and their productivity. The gap between the introduction of lime and PAA should be not less than 2 - 3 minutes. PAA is available in the form of gel mass (8 – 10 %) and is used as a solution of 0.1 – 0.2 % of its concentration.

Polyacrylamide is usually added during the flood period, but for water with high alkalinity, which requires a large dose of coagulant and contains a large number of suspended particles, it is recommended that it be continuously dosed.

Materials and methods

Apparatus

6 cylinders with a nominal volume of 0,5 L; 2 volumetric flasks of nominal volume of 100 ml; graduated pipettes with a nominal volume of 25,5 and 2 ml – 2 pcs.; measuring cylinder nominal volume 250 ml, font.

Reactants and materials

Solution for coagulant $Al_2(SO_4)_3$, $FeSO_4$, 0.1 % PAA solution, water with suspended solids content 200 mg / L.

Progress

The test water containing suspended matter 200 mg / L is poured into 6 measuring cylinders and added the calculated amount of aluminum sulfate corresponding to the optimal dose of the coagulant.

After entering the calculated amount of coagulant, the cylinders are closed with lids and mixed with their contents (first quickly, within 20-30 seconds, and then slowly for 1-2 minutes.). After that, a solution of PAA in the following quantities is introduced into the cylinders.

Table 6.1 - Optimal dose of coagulant

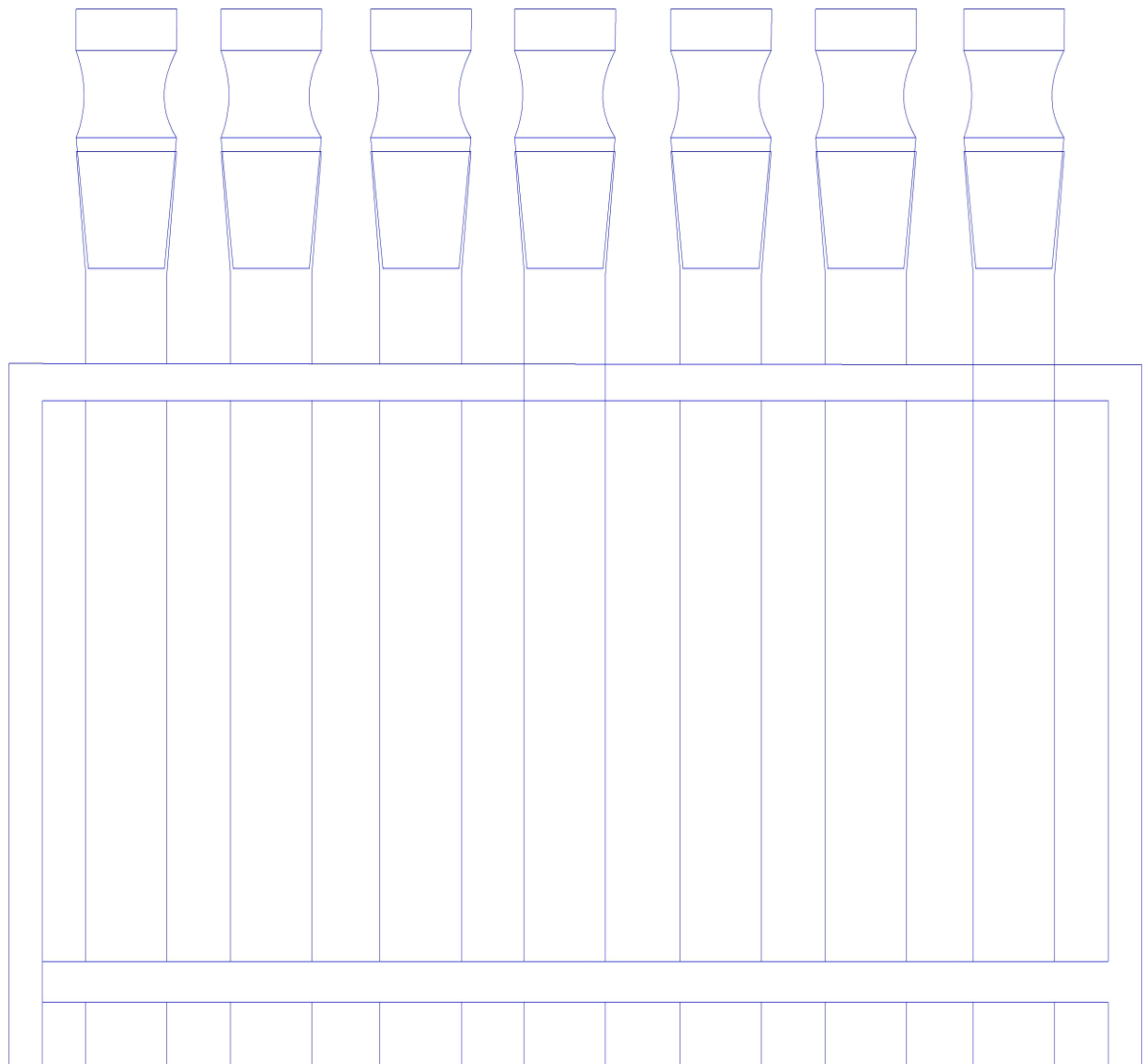| Content of suspended substances, mg / L	Dose of anhydrous coagulant, mg / L
100	35
200	45
300	50
400	55

Figure 6.1. Experimental installation for determining the efficiency of flocculating water treatment

Table 6.2 – Dose of PAA

Cylinder number	1	2	3	4	5	6
Number of injected PAA,%	0	0,2	0,4	0,6	0,8	0,9
The dose of PAA corresponding to its percentage, mg / L	0	4	8	12	16	18
The dose of PAA corresponding to its percentage, mg / 250 mL	0	1	2	3	4	4,5

The samples with the added flocculent are stirred again (first three times to turn the cylinders, after closing them with stoppers, and then slowly stirring for 1-2 minutes) and turning the cylinders on a tripod. When defending the water in the cylinders marked the beginning of the formation of flakes, the beginning of the deposition of flakes and their appearance. After precipitation of the basic amount of flakes, without stirring up the precipitate, from each cylinder a pipette from the upper layer of water is sampled and analyzed for turbidity.

Determination of the turbidity of water samples

The font is a transparent cylinder with divisions. The sample of the illuminated water is gradually placed in the cylinder until the word "font" becomes impossible for reading. The ruler measures the height of the water column.

Table 6.3 – Experimental results

Cylinder number	Dose of $Al_2(SO_4)_3$, mg / ml	Dose of PAA, mg / 250 ml	Beginning of flakes formation, min	Beginning of sedimentation, min	Muddy, mg / ml	
					Initial water	Purified water

Self-control questions

1. What is flocculation?

2. The main types of flocculants.

3. Basic physical and chemical properties of PAA.

4. Limits of application of the method of flocculation water treatment.

5. What determines the dose of the flocculent?

6. Due to which processes there is flocculation?

7. What flocculants are used in Ukraine?

Laboratory work № 7. Acid regeneration of coagulant from sedimentation of sewage treatment

Purpose: to study of the effect of acid dissolution conditions on the efficiency of extracting coagulant from water treatment sediments and establishing a rational regime for the process of acid dissolution.

Theoretical information

In recent years, despite the reduction of industrial activity, the techno genic load on the biosphere still continues to increase, which manifests itself in increasing the amount of waste and volume of wastewater. The level of waste accumulation in Ukraine reaches 30 billion tons, of which 17 billion tons are industrial waste. This also applies to the textile industry, as wastewater from these enterprises is contaminated with surfactants, dyes, non-ferrous metal ions, petroleum products and have a complex colloid chemical composition.

In order to achieve a satisfactory degree of industrial wastewater purification, it is necessary to carry out a set of technological methods: coagulation, filtration, adsorption on activated carbon, ozonation, flotation and oxidation by various reactants.

Coagulation methods are the most common methods for destabilizing a stable colloidal system of sewage from textile production, since, in addition to reducing the coloration of water, chemical and biological oxygen consumption, and the content of surfactants, they allow the removal of stabilized colloidal impurities, which give water a high turbidity. Other methods, such as ozonation, use of hydrogen peroxide, sorption, should be used only as auxiliary methods.

As a result of the treatment of wastewater, containing dyes and surfactants (table 7.1), with coagulants, precipitates are formed.

They have an amorphous structure and a high specific resistivity to filter. In the industry after the sludge treatment with dewatering reagents and its filtration the resulting sludge is taken to special places - dumps that have a negative impact

on the environment. Waste storage sites occupy large areas. Therefore, it is necessary to regenerate the sludge components for their re-use, as this contributes to reducing the amount of sediment and its partial utilization.

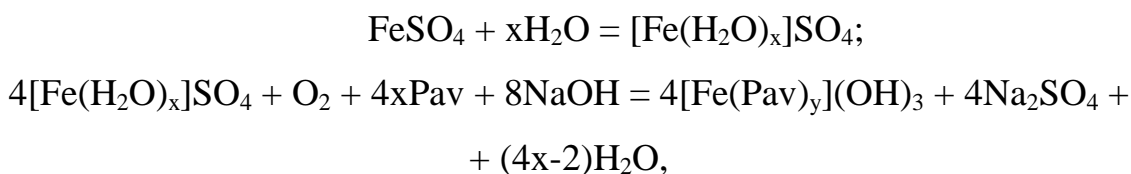*Table 7.1* – Composition of samples of wastewater

Components	Concentration, mg / L
Dyes: Active Direct Disperse Acid	5-10 20-40 10-15 5-10
Surfactants: Anionic Cationic No-ionic	8,0 4,5 1,5
	1

In all cases, after coagulation, a brown precipitate with the characteristics given in eable 7.2, the amount of which is influenced by the dose of the coagulant and the type of surfactant, is formed. The resulting precipitate is to be treated to remove the coagulant for its reuse.

Table 7.2 – Main characteristics of a precipitate

Characteristics of sludge	Dimension
Specific resistance to filtration, cm / g	$0,6012 \cdot 10^9$
Density, g / ml	1,0917
Humidity,%	99,5
Organic content,% wt.	45 – 50
Acidity, pH	7
Total ferrum content,%	37,4

The crude precipitate is a ferroorganic complex formed from the aqua complex in the process of coagulation by the reactions:

$$FeSO_4 + xH_2O = [Fe(H_2O)_x]SO_4;$$

$$4[Fe(H_2O)_x]SO_4 + O_2 + 4xPav + 8NaOH = 4[Fe(Pav)_y](OH)_3 + 4Na_2SO_4 +$$

$$+ (4x-2)H_2O,$$

where Pav – a mixture of textile dyes.

Acid dissolution of the sediment is carried out by the reaction:

$$4[Fe(Pav)_y](OH)_3 + 3H_2SO_4 = 2[Fe(Pav)_m](OH)_3 + Fe_2(SO_4)_3 + 6H_2O +$$

$$+ (4y-2m)Pav.$$
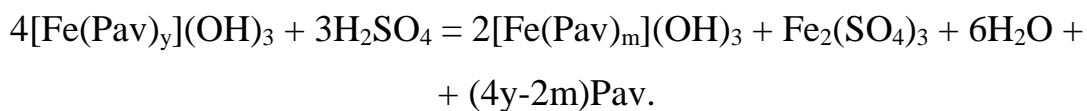
Materials and methods

Apparatus

Experimental installation for acid dissolution; four capacities for coagulation with a volume of 2 L; glasses of porcelain with a nominal volume of 200 ml - 4 pcs.; measured cylinders with a nominal volume of 100 ml - 4 pcs.; pipettes with a capacity of 1, 2, 10 ml; sampler; photoelectrocolorimeter   KFK - 2; cuvettes; analytical weights.

Reactants and materials

Model wastewater 10 L; dye; distilled water, coagulant solution 10 g / L $FeSO_4$; 20 % solution of H_2SO_4.

Conducting wastewater treatment by coagulation method

To purify the model wastewater by coagulation method, a coagulant uses $FeSO_4$, (the dose of coagulant is determined individually, according to the teacher's instructions). The process is carried out in the pH range 9 - 9.5 (adjusted with NaOH solution). Coagulation time 40-60 minutes, after which the decantation method separates the sediment from the solution into a measuring cylinder per 100 cm3. Time to defend the sediment is 20 minutes.

Carrying out the process of acid dissolution of water treatment sediments

Determination of the regularities of the process of acid decomposition of the precipitates of purification of CO of contaminated surfactants and dyes is carried out on an experimental plant (Fig. 7.1), which consists of a thermostat 2, a porcelain reactor 3 and a mixer 1 with an electric drive 5, whose amount of revolutions is regulated by LATV 9.

The precipitate from one cylinder is transferred to the reactor 3 after a coagulation, added the calculated amount of sulfate acid at a given concentration

and 1 ml of H_2O_2 at a concentration of 30 % for oxidation of the dye, which will pass from the precipitate to the solution of the regenerated coagulant. The dissolution process is carried out in turbulent mode (Re ≥ 10000) for 60 minutes, the process temperature is 25 °C.
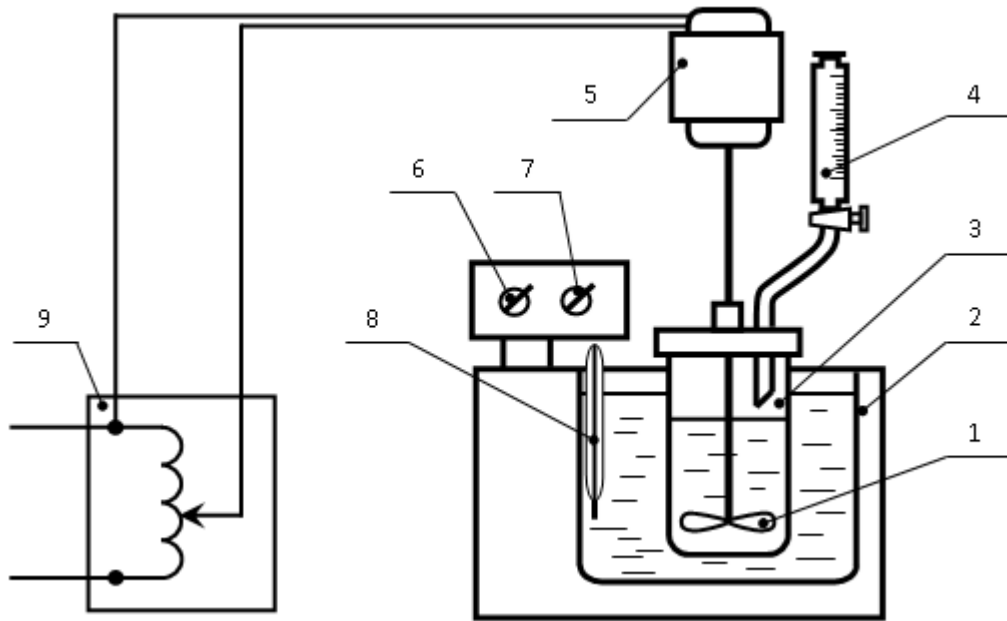
Figure 7.1. Experimental installation for acid dissolution of water purification sludge: 1 - mixer; 2 - thermostat; 3 - reactor; 4 - dispenser; 5 - mixer drive; 6 - temperature controller; 7 - switch mixer; 8 - thermometer; 9 - LAT.

The stoichiometric amount of sulfate acid required to dissolve the precipitate is calculated by the formula:

$$V_{acid} = \frac{3 \cdot m_{Fe}^{pr} \cdot M(H_2SO_4) \cdot 100 \cdot 10^{-3}}{2 \cdot \rho_{acid} \cdot M(Fe) \cdot P}, \qquad (7.1)$$

where M(Fe), M(H₂SO₄) – molar weights of Fe and H₂SO₄ respectively, g / mole;

ρ_{acid} – density of sulphate acid, which is used for acid dissolution of the precipitate, g / ml;

P - acid concentration, % wt.

51

The content of regenerated ferrum in the solution is determined photocorimetrically according to the standard method at a wavelength λ 440 nm and a thickness of 10 mm cuvette.

Determination of the total iron in the presence of sulfosalicylic acid

In the practice of molecular absorption analysis, only complexes that are formed in acidic and alkaline environments are used. The monosulfosalicylate complex is used to determine Fe (III) in the presence of Fe (II), magnesium, manganese, copper, aluminum, rare earth elements. Fe (II) and Fe (III) can be determined in alkaline medium due to light oxidation of Fe (II) to Fe (III) with sulphosalicylic acid.

Apparatus

Flasks of a nominal volume of 100 ml - 7 pcs.; flask nominal volume 250 ml - 3 pcs.; cylinders are rated in nominal volume of 50 and 100 ml; watering cans; spatula; pipettes with a nominal volume of 1, 2, 10 ml; sampler; photoelectrocolorimeter; compressor installation.

Reactants

Standard solution of ferrum (III), 0,1 mg / ml; sulfosalicylic acid 10 % solution; 20 % solution of sulfate acid; 10 % solution of ammonia.

Calibration graph

Alkaline environment. Five volumetric flasks with a capacity of 50,0 ml introduce a standard solution of ferrum containing (mg): 0,05; 0,10; 0,15; 0,20 and 0.30 respectively, 10 ml of water, 5 ml of sulphosalicylic acid solution, 5 ml of ammonia solution. The contents of the flasks are diluted with water to the label. Solutions are photometrised relative to water and build a calibration graph. To determine the fermium in the analyzed solution, an aliquot of this solution is placed in a volumetric flask of 50,0 ml. The solution carries out the same operations in the same sequence as when cooking the solutions used to build the calibration, and then photometrically with respect to water. The content of the ferrum is determined by the calibration graph.

Determination of the influence of the concentration of sulfate acid on the degree of removal of the ferrum from the precipitate

The precipitate is transferred to the reactor after coagulation, add the calculated amount of sulfate acid of different concentrations (variation range is 10…60%). The amount of sulfate acid was calculated by the formula (7.1). The dissolution process is carried out in turbulent mode (Re ≥ 10000) for 60 minutes, the process temperature is 25 ° C.

Determination of the influence of excess sulfate acid on the degree of removal of the ferrum from the precipitate

To the crude precipitate after coagulation add the calculated amount of sulfate acid. The amount of sulfate acid is calculated by the formula (7.1). The excess sulfate acid from stoichiometry b was changed from 1,5 to 4. The dissolution is carried out in turbulent mode (Re ≥ 10000) for 60 minutes, the process temperature is 25 °C.

Determination of the influence of the time of dissolution of the sediment on the degree of removal of the ferrule from the precipitate

The precipitate is formed, transferred to the reactor, add the calculated amount of sulfate acid. The amount of sulfate acid is calculated by the formula (7.1). The dissolution is carried out in turbulent mode (Re ≥ 10000) at a temperature of 25 °C. The time of acid dissolution is 30, 40, 50 and 60 minutes.

Determination of the effect of temperature on the degree of removal of the ferrule from the siege

To the crude precipitate after coagulation add the calculated amount of sulfate acid. The dissolution is carried out in a thermostat in the temperature range from 25 to 50 °C (variation interval of 5 °C). Distillation time 40 minutes.

Tasks

1. To clean the model samples of sewage of textile enterprises by the method of coagulation. In this paper, coagulation is carried out on the J-model samples of

textile productions. The composition of model water samples is given in Table 7.1. As a coagulant is used $FeSO_4 \cdot 7H_2O$ at pH 9 - 9.5 (pH is adjusted by NaOH).

2. Calculate the volume of solution of coagulant of known concentration, which corresponds to the dose given by the instructor dose of coagulant FeSO4 for purification of JI contaminated with dyes.

3. To conduct sulfate-acid dissolution of the sediment obtained as a result of purification of the model samples of sewage by a coagulation method.

4. To investigate the influence of the temperature regime of the process of acid dissolution of SDS purification by coagulation method on the degree of removal of the ferrum, the effect of changes in the concentration of sulfate acid and the duration of the process in order to remove the maximum amount of ferrum from the sediments.

5. Determine the degree of sequestration of the ferrule from the sediment under different technological regimes and to select the rational mode of the acid dissolution process.

Calculations

1. The optimal dose of coagulant in terms of ferrum, mg / L:

$$D^{opt}_{Fe} = D^{opt}(FeSO_4) \cdot M(Fe)/ M(FeSO_4),$$

where D^{opt}_{Fe} - the optimal dose of coagulant in terms of iron, mg / L;

D^{opt}_{FeSO4} - optimal dose of coagulant in terms of anhydrous iron sulfate (II), mg / L;

$M(Fe)$, $M(FeSO_4)$ – molar weights of Fe and $FeSO_4$ respectively, g / mole.

2. The content of the ferrum in the model water sample during coagulation, mg:

$$m_{Fe} = D^{opt}_{Fe} \cdot V_{ww}$$

where D^{opt}_{Fe} - the optimal dose of coagulant in terms of iron, mg / L;

V_{ww} – volume of wastewater, L.

3. The content of the ferrum in the formed precipitate after coagulation, mg:

$$m_{Fe}^{prec} = m_{Fe}.$$

4. Volume of sulfate acid required for acid dissolution, ml:

$$V_{acid} = \frac{3 \cdot m_{Fe}^{prec} \cdot M(H_2SO_4) \cdot 100 \cdot 10^{-3}}{2 \cdot \rho_{acid} \cdot M(Fe) \cdot P},$$

where $M(Fe)$, $M(H_2SO_4)$ – molar weights of Fe and H_2SO_4 respectively, g / mole;

ρ_{acid} – density of sulphate acid, which is used for acid dissolution of precipitate, g / ml (from the reference book);

P – concentration of acid, %.

5. The content of the ferrum in the regenerated solution of coagulant, mg:

$$mp_{Fe} = (C_к /V_a) \cdot V \cdot V_к$$

where $C_к$ – concentration of Fe, determined according to the calibration graph, mg;

V_a – the aliquot amount of regenerated coagulant solution is taken for analysis, ml;

V – dilution;

V – volume of regenerated solution of coagulant, ml.

7. Degree of removal of ferrum from precipitate, %:

$$\alpha = \frac{mp_{Fe}}{m_{Fe}} \cdot 100.$$

Self-control questions

1. Methods of removal of water from the compounds of the ferrum.

2. Calculate the required amount of regenerated coagulant to re-coagulate with the already known dose of coagulant.

3. Introduce approximate mechanism of acid dissolution of sediments with chloride acid.

4. Determine the influence of the sediment characteristics on the process of acid dissolution of the sediment.

Laboratory work № 8. Investigation of the efficiency of sewage removal from synthetic surfactants on a mechanical flotation plant

Purpose: to study the physicochemical method of wastewater (WW) treatment (CB) from synthetic surfactants in a flotation mechanical installation.

Theoretical information

Synthetic surfactants are widely used in railway transport as detergents: washing trucks and passenger cars, tanks; in the mechanized laundry; for washing engines at repair factories and others. The presence of surfactant in wastewater affects the biological purification of WW negatively. In order to successfully clean such WW, it is necessary to dilute them with household appliances. In those cases, where it is impossible to provide the appropriate dilution of production WW households, a preliminary reduction of the concentration of the organic component is necessary. A reliable and economical method for removing surfactants from WW is a flotation method.

Flotation is the process of sticking particles of the floating material to the surface of a section of two phases, usually gas and liquid, due to the excess free energy of the surface boundary layers, as well as surface phenomena of wetting and adsorption.

The process of purifying production WW containing surfactant is due to the combination of molecules or micellar surfactants with air bubbles that rise up in a cleaned liquid. Hydrophobic solid particles, oil and petroleum products also stick to air bubbles. Therefore, flotation units are used for the removal of oils, fats, petroleum products, fine-dispersed suspended solids with a hydraulic size of up to 0,01 mm / sec.

With continuous airflow on the surface of the SB formed a layer of foam, saturated surfactant. When foam is destroyed, an aqueous solution containing up to 2000-3000 mg / L and more surfactants is formed.

The effect of removing surfactant from WW in the impeller flotation plant

depends on many physical and chemical factors: the initial concentration of surfactant, the intensity of air flow, the size of the air bubbles and the uniform distribution of the volume in the installation, the duration of flotation (20-60 minutes). The greater the initial concentration of surfactant, the higher the effect of flotation of surfactants with WW.

Materials and methods

Apparatus

Installation for mechanical flotation, measuring flasks with a hardened lid of 100 and 1000 ml; pipettes with a nominal volume of 25, 10, 5, 1 ml.

Reactants and materials

Bromophenol blue (indicator); chloroform ppm; water distilled; sulfonol; buffer solution with pH 11; a solution of sodium hydrogen sulfate; sodium carbonate solution; cationic surfactant, surfactant of anionic type. $C(AS) = 0.00658$ mole / L, $C(AS) = 0.003591$ mole / L.

Progress

The installation consists of a transparent chamber in which the stator-impeller block is installed. When the impeller is rotated, air is sucked from the atmosphere through the nozzle. The pipe has a valve for controlling the amount of air.

The vigorous mixing of the object of research in flotation impeller installations creates in it a large number of small vertical streams, which allows to receive bubbles of a certain magnitude. A stator is placed above the impeller in the form of a disk with shoulder blades. Flow of water along with air are thrown by an impeller on stationary blades of a stator, there is dispersion of air and formation of bubbles. Foam, which is formed during the flotation process, passes from the compartment of the mixing chamber to the resting chamber through the opening between them. The foam that contains the surfactant is removed by a lobed foam marker.

Analysis

Sulfolol solution is diluted 10 times and poured into a flotation machine. Every 5 minutes of flotation, sampling is performed on 5 cm3 of the solution obtained and dipped into a 100 cm3 flask with a cured stopper, 25 cm3 of chloroform, 25 cm3 of buffer solution, 1 cm3 of the indicator and titrated with a standard KPAR solution that is diluted in advance 10 times. After the introduction of each portion of the KPAR, the flask is closed with a hardened cork and shaken vigorously. Titration is carried out until the full transition of the violet color of the upper layer in blue.

Table 8.1 – Results

Time, min	Volume of cationic surfactant, ml	Concentration of sulfonol after coagulation, mmole / L
5		
10		
15		
20		
25		
30		

Since sulfonol is anionic surfactant, titration is carried out during the work of the cationic surfactant.

The concentration of sulfonol after flotation is calculated by the formula $V_1C_1 = V_2C_2$.

The change in the degree of removal of the organic component and the residual concentration of surfactant in the process of flotation is depicted as graphic dependence.

Self-control questions

1. What is the essence of the flotation process?
2. Types and schemes of flotation water treatment.
3. In what cases reagent is flotation used?
4. Types of flotation machines.
5. To remove what impurities is flotation used?

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