INVESTIGATION OF NATURAL FLOCCULANTS FOR USE IN WASTEWATER PURIFICATION PROCESSES

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Contaminated industrial wastewater significantly reduces the volume of drinking water. A wide range of composition and insufficient treatment of wastewater from enterprises such as the textile, chemical or metalworking industries, which often fall into water bodies, negatively affect the state of aquatic ecosystems, and that is why it is necessary to carefully select the optimal treatment method. Among the types of wastewater treatment, the coagulation-flocculation process has gained considerable popularity, which occurs due to the adhesive and adsorption properties of coagulants and flocculants, which is widely used in the purification technologies of both natural and industrial wastewater from colloidal particles, radionuclides, phosphates, dyes and suspended particles. Coagulants are able to hydrolyze in water with the formation of various coagulation structures with high adsorption and adhesion properties, flocculants, in turn, contribute to the formation of flakes, sedimentation and filtration, stabilize the cleaning process, improve quality and increase the efficiency of equipment.

During the experimental work, the employees of the Department of Chemical Technology and Water Treatment established the advantages of using natural flocculants in the process of wastewater treatment using colored model solutions as an example. A study was made of the influence on the degree of purification of such characteristics as the type of flocculant (for example, chitosan and sodium alginate) and coagulant ($Al_2(SO_4)_3 \cdot 18H_2O$, ALS, PIX-318), the optimal dose of reagents, the type of dye (direct, active, dispersed) , settling time and content of residual ions. During the research, the Jar-test method was used, the essence of which is to simulate the process of floc formation, which is typical for industrial wastewater treatment plants. The study of the composition of model water samples was carried out using the spectrophotometric analysis method.

Keywords: *coagulants, dyes, flocculants, wastewater, wastewater treatment*

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1. Introduction

The result of most technological processes for the synthesis of organic dyes and the processes associated with their use is the formation of a large amount of colored wastewater. Dyes practically do not biochemically oxidize and do not decompose, when released with sewage into open water. Dyes are substances of toxic local action that have a very dangerous effect on living organisms present in water bodies, and through them on the human body. At a dye concentration of more than 0.1 mg/dm^3, the oxygen regime of water, COD, BOD, ammonification and nitrification processes are disturbed. For the treatment of wastewater contaminated with soluble dyes, to the maximum possible concentrations that do not affect the processes of self-purification of

water, which is about 0.001 mg/dm^3, various methods are used, including coagulation-flocculation treatment. Inorganic salts of aluminum and iron preferably are used as coagulants, and high-molecular compounds of artificial and natural origin are used as flocculants. [1,2].

The creation and introduction of effective and environmentally friendly flocculants of natural origin into the purification process of colored aqueous solutions is of current importance. In this regard, the scientists of the Department of Chemical Technologies and Water Treatment of the Cherkasy State Technological University were faced with the task of researching and studying the flocculation characteristics of chitosan and sodium alginate and comparing the effectiveness of their use in the processes of removing soluble dyes from aqueous solutions when used together with inorganic coagulants.

2. Materials and Methods

Conditions of the flocculation process and the determination of optimal doses of flocculant in combination with inorganic coagulants (Jar-test) were studied to establish the optimal mode for the use of flocculants (chitosan and sodium alginate) and coagulants ($Al_2(SO_4)_3 \cdot nH_2O$, ALS, PIX-318). The Jar test method uses glass vessels in which water samples interact with reagents under various mixing conditions, thus simulating the flocculation process. The chromaticity of the studied solutions was determined by a single-beam spectrophotometer Ulab 102. In the course of the work, the example of soluble dyes: direct blue, acid red, and active bright blue, were studied using the interaction of a flocculant (chitosan) with various types of coagulants.

3. Results and Discussion

Dye type impact. Determination of the optimal dose of flocculants (sodium alginate and chitosan) in their complex action with a coagulant was the first stage of the study. Were filled with the same volume of the studied model solution and the optimal dose of coagulant ($Al_2(SO_4)_3 \cdot nH_2O$) was added to each of six glass beakers, predetermined. The optimal dose of coagulant was selected after studies of the degrees of purification from dyes and turbidity, changes in pH and TDS of solutions after adding different doses of coagulant, and settling time. For colored solutions with active, direct and dispersed dyes in the presence of suspended particles of kaolin, the optimal doses are 50, 40 and 40 mg/dm^3, respectively.

After intensive stirring at a speed of 140 rpm for three minutes, a 1% flocculant solution was added to the beakers - from 1 to 20 cm^3, which corresponds to a content of 10 to 200 mg/dm^3, while the first beaker remained the control (only with coagulant). Next, the stirring speed was reduced to 50 rpm, and flakes formed within 10 minutes.

Graphical dependences are shown on Fig. 1 and Fig. 2 presented the results of the experimental determination of the optimal dose of flocculants. It has been established that using chitosan, is achieved a higher purification efficiency of colored solutions than with using sodium alginate. It can be explained by the fact that chitosan, due to the presence in its structure of a large number of hydro-oxidizing and ammonium functional groups, contributes to the formation of more durable and compact agglomerates, which accelerates their precipitation.

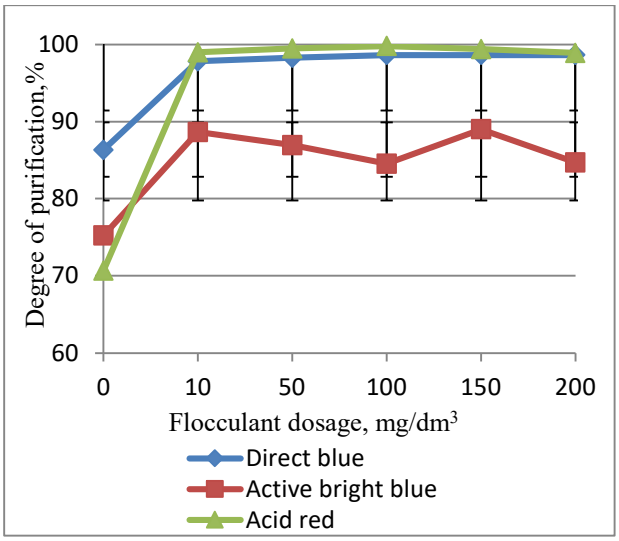

Fig. 1. *Dependence of the degree of purification of colored model solutions from dyes in the presence of suspended kaolin particles and the dose of the flocculant - chitosan (the optimal dose of coagulant for each dye determined at the previous stage of research)*

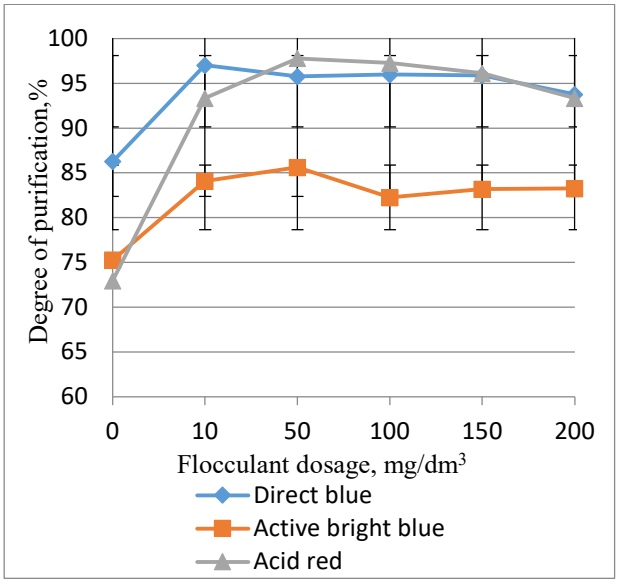

Fig. 2. *Dependence of the degree of purification of colored model solutions from dyes in the presence of suspended kaolin particles on the dose of the flocculant - sodium alginate (determined at the previous stage of research by the optimal dose of coagulant for each dye)*

The relative effectiveness of two flocculants for different types of dyes was determined by the average value of the differences in degrees of purification from flocculant doses.

The impact of different types of coagulant. The next stage of the study was to compare the action of the flocculant (chitosan, as more effective) together with different types of coagulants based on aluminum ($Al_2(SO_4)_3 \cdot nH_2O$ and ALS) and iron-based (ferric chloride sulfate - PIX-318), taken in the amount of predetermined optimal doses, amounting to 40, 20, and 40 mg/dm^3, respectively (Fig. 3-4). For this, all six glass beakers were filled with the same volume of the model solution (direct blue dye) and the same optimal dose of coagulant was added. After intensive mixing, doses of a 1% solution of chitosan flocculant were introduced into the beakers in the range from 0.2 to 3.4 cm^3, which corresponds to a chitosan content of 2 to 34 mg/dm^3, while the first beaker remained the control.

The results presented in Fig. 4 indicate that the optimal dose of chitosan flocculant, determined 60 minutes after the start of the process and when used together with various coagulants, contains 20 mg/dm^3 - with PIX-318 and $Al_2(SO_4)_3 \cdot nH_2O$ and 34 mg/dm^3 with ALS.

Also, as a result of the experiment, it was found that an increase in the dose of chitosan flocculant contributes to the formation of larger flakes, and this, in turn, accelerates the sedimentation process, in contrast to the aggregates formed from PIX-318, which form stable compounds, and the degree of purification, in this case, can reach almost 100%.

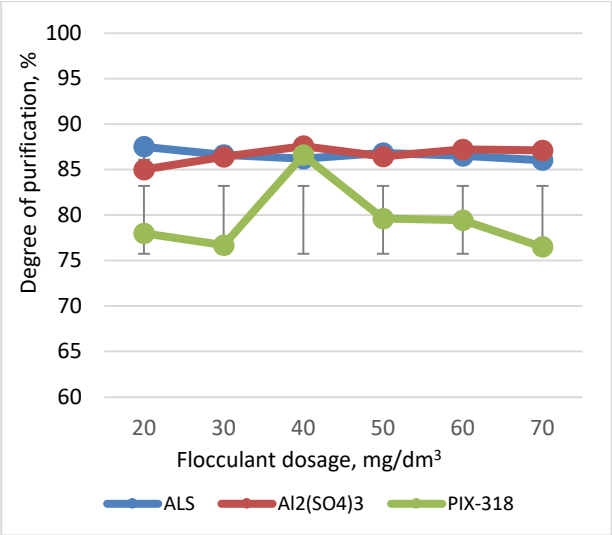

Fig. 3. *Dependence of the degree of purification of colored wastewater with a dye content of 20 mg/dm³ on the dose of different types of coagulants (duration of the sedimentation process is 60 minutes)*

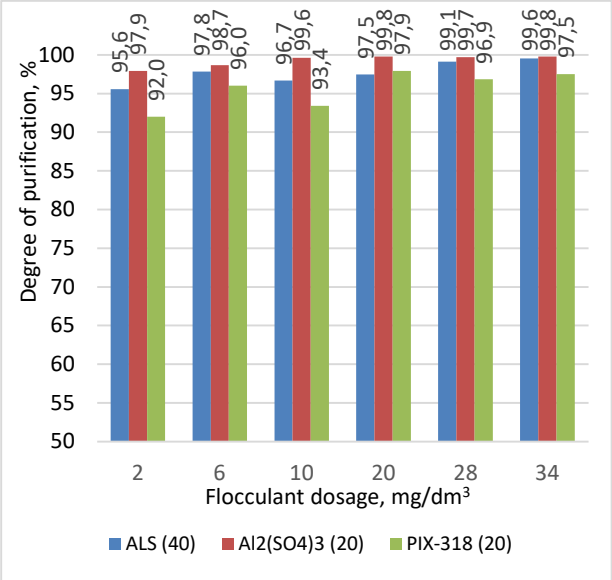

Fig. 4. *Dependence of the degree of purification of colored wastewater with a dye content of 20 mg/dm³ on the dose of flocculant-chitosan when acting in combination with different types of coagulants (duration of the sedimentation process is 60 minutes)*

Impact on residual ion content. In the study of the optimal dose of coagulant, it was also found that as a result of using PIX-318 purified water contains several residual Fe^{3+} ions, the presence of which increases the color of the solutions (Table 1).

At the same time, the addition of a small amount of chitosan flocculant from 6 mg/dm³ makes it possible to halve the iron content and even completely extract it (Table 2).

In our opinion, this is due to the chelating properties of chitosan, which it exhibits to heavy metal ions [3,4].

Table 1. *The content of residual Fe^{3+} ions in pure water after coagulation with coagulant PIX-318*

Dose of PIX-318, mg/dm³	**Concentration Fe^{3+}-ions, mg/dm³**
10	0
20	0,014
30	0,014
40	0,144
50	0,38
60	0,524

Table 2. *The content of residual Fe^{3+} ions during the complex action of the flocculant-chitosan with the coagulant PIX-318 (40 mg/dm³)*

Dose of flocculant, mg/dm³	**Concentration Fe^{3+}-ions, mg/dm³**
2	0,66
6	0,03
10	0
20	0
28	0
34	0

4. Conclusions

When conducting research on the study of the properties of flocculants, using the example of chitosan and sodium alginate, the prospects for their use in coagulation-flocculation processes for treating colored effluents were established. When conducting a comparative analysis of the action of flocculants, it was established that the natural biopolymer chitosan is more effective for use in a complex with the coagulant $Al_2(SO_4)_3 \cdot 18H_2O$ than sodium alginate (by 2.1% for direct, 3.1% for active and by 6.0% for acid dyes), and the resulting sediment is denser and characterized by greater aggregate stability.

During the study of the process of purification of solutions with different types of coagulants (PIX-318, ALS and $Al_2(SO_4)_3 \cdot nH_2O$), it was recorded that when using an iron-containing coagulant, the residual content of iron (III) ions is present in the purified water samples, and it was proved that the addition of a certain dose chitosan flocculant allows to completely remove iron ions from purified water.

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ДОСЛІДЖЕННЯ ПРИРОДНИХ ФЛОКУЛЯНТІВ ДЛЯ ВИКОРИСТАННЯ У ПРОЦЕСАХ ОЧИЩЕННЯ ЗАБАРВЛЕНИХ СТІЧНИХ ВОД

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Забруднені стічні воли промислових підприємств значно скорочують об'єми питної води. Широкий діапазон складу і недостатнє очищення стічних вод таких підприємств як текстильної, хімічної або металургійної галузей, часто потрапляють у водойми та негативно впливають на стан водних екосистем, і саме тому викликає необхідність ретельного вибору оптимального методу очистки. Серед видів очищення стічних вод набув значної популярності коагуляційно-флокуляційний процес, який відбувається за рахунок адгезійних та адсорбційних властивостей коагулянтів та флокулянтів, що широко застосовується в технологіях очищення як природних, так і промислових стічних вод від колоїдних частинок, радіонуклідів, фосфатів, барвників та зважених частинок. Коагулянти здатні гідролізуватися у воді з утворенням різних коагуляційних структур, що володіють високими адсорбційними та адгезійними властивостями, флокулянти, у свою чергу, сприяють утворенню пластівців, відстоюванню та фільтруванню, стабілізують процес очищення, підвищують якість та збільшують ефективність роботи обладнання.

Під час виконання експериментальної роботи співробітниками кафедри хімічних технологій та водоочищення були встановлені переваги використання природних флокулянтів у процесі очищення стічних вод на прикладі пофарбованих модельних розчинів. Проведено дослідження впливу на ступінь очищення таких характеристик як тип флокулянту (на прикладі хітозану та альгінат натрію) та коагулянту ($Al_2(SO_4)_3 \cdot 18H_2O$, ALS, PIX-318), оптимальна доза реагентів, тип барвника (прямий, активний, дисперсний), час осадження та вміст залишкових іонів. При проведенні досліджень використовувався метод Джар-тесту, сутність якого полягає в імітації процесу утворення пластівців, характерному для промислових установок очищення стічної води. Дослідження складу модельних зразків води проводилося з використанням спектрофотометричного методу аналізу.

Ключові слова: *барвники, коагулянти, очищення стічних вод, стічні води, флокулянти*