Development of technology for organic dyes removal from wastewaters

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Abstract. High efficiency of using a sorbent-coagulant, prepared on the basis of montmorillonite clay, for cleaning highly concentrated colored solutions is shown. In this case, clay plays the role of a surface that provokes the first stages of coagulation-sorption interaction, and promotes the formation of dense aggregated structures. For deep wastewater treatment, a galvanochemical method is proposed. It was experimentally proved that in this case a conjugated mechanism is realized that combines oxidative degradation of dyes and coagulation removal of reaction products. The technological scheme for local wastewater treatment of dyeing fur is proposed. Its high efficiency was confirmed by semi-industrial tests, while COD decreased by 98% and amounted to 15 mgO₂/L.

1. Introduction
One of the global problems of mankind is the pollution of natural waters. Despite the measures taken, the flow of inadequately treated industrial wastewater into natural reservoirs continues. Among them, special attention is given to wastewater containing synthetic dyes. Although the content of dyes in surface natural waters is insignificant and they are classified as micro-pollutants, they are found in almost all objects of natural ecosystems [1].

About a million tons of dyes are produced annually in the world [2,3] and their assortment is quite wide, more than 100 thousand items. The main consumers of synthetic dyes are textile, leather and fur, paper production industries and printing.

Wastewater from the dyeing plants of the textile and leather and fur industries is among the leaders in terms of the volume of micro-pollutants entering to aquatic ecosystems. Dyeing plants are quite water-intensive. Process solutions contain dyes in gram concentrations and approximately 8–20% of unused dyes and auxiliary chemicals are discharged into wastewater [4,5]. Thus wastewater is formed daily, containing tons of dyes, characterized by a high level of BOD and COD, the discharge of which without treatment into the environment creates an environmental threat in the form of a violation of photosynthesis and death of aquatic plants [6-9]. In addition, most of these dyes and their decay products are carcinogenic and mutagenic, which has a harmful effect on all living things on Earth. [10-12]. Even the presence of a small amount of these compounds (less than 1 mg /L) in water can have adverse effects. In most countries there are strict rules prohibiting the discharge of wastewater containing dyes without proper treatment, which necessitates the search for modern and effective treatment technologies.
Several approaches are possible to reduce the release of dyeing effluents into the environment: introduction of changes to the dyeing technology, for example, in the leather and fur production, the introduction of spreading dyeing technology; the introduction of a recycling water supply system, which allows to reduce the volume of discharged coloured wastewater, and the development of integrated wastewater treatment methods.

Methods for removing dyes from wastewater are very diverse [13-16]. The choice depends on the concentration of dyes in the effluent and the required level of treatment. The most widely used reagent methods to remove the bulk of the dyes from concentrated solutions. But at the same time, a significant amount of precipitation is formed, and often purified water does not meet the requirements for process water and is not suitable for discharge. Therefore, these methods can be considered as pre-treatment. For deeper treatment, the most promising are Advanced Oxidation Processes (AOPs), which can be used to degrade toxic and persistent chemicals. [17-19]. The essence of AOPs is the liquid-phase oxidation of impurities by reactive oxygen species (ROS). As precursors of ROS, hydrogen peroxide, persulfates, molecular oxygen, and ozone can be used. AOPs are more environmentally friendly because when using them, it is fundamentally possible to completely mineralize hard-oxidizing pollutants to simple inorganic compounds (CO₂, H₂O₂, etc.). The most energy-efficient and economical are AOPs combining physical effects (radiation, ultrasound, hydrodynamic cavitation, microwave, etc.) and catalytic oxidation systems.

The aim of this work was to create theoretical and experimental approaches to the development of combined technology for local treatment of wastewater from dyes using the example of effluents from the fur industry.

2. Materials and Methods

The objects of research were aqueous solutions of dyes and effluents from oxidative dyeing of sheepskin black. Experiments to determine the effectiveness of coagulation purification were carried out in a glass reactor. As coagulants, we used a 10% solution of “chemically pure” grade FeCl₃ × 6H₂O. After adding the coagulant, the solution was stirred vigorously for 1-3 minutes, basified to pH 8 and settled.

The study of galvanochemical treatment (GCO) processes was carried out in a reactor loaded with a mixture of iron chips and coke with aeration. The mass ratio of coke: iron chips was 2:4, the size of the loading components was 2 mm. Photochemical oxidation experiments were carried out in an original setup containing a DB-30 low-pressure mercury lamp as a source of UV radiation, described in detail earlier [20]. Hydrogen peroxide was dosed as 0.1% solution. The purified water after the experiment was neutralized to pH 8 and settled.

To prepare the sorbent-coagulant, 200 ml of 0.1 M iron chloride solution was added to 20 g of clay and treated with ultrasound at a frequency of 22 kHz for 3 minutes. To obtain sorbent-coagulant, clay from the Mukhor-Taly deposit (the content of montmorillonite ~ 70 %) was used, which has a chemical composition (mass%): SiO₂ – 69; Fe₂O₃ – 2.6; Al₂O₃ – 16.7; TiO₂ – 0.3; CaO – 1.5; MgO – 1.3; K₂O – 2.8; Na₂O – 2.2; SO₃ – 0.2; H₂O₂ – 5.7.

Dye concentrations in the initial and purified solutions were determined spectrophotometrically using an Agilent 8453E UV-visible system. COD was determined by the standard dichromate method, the concentration of total iron generated during GCO was determined by the photometric method with sulfosalicylic acid.

The temperature was maintained constant at 20 °C±0.2. The pH and the conductivity of solution were measured using Universal Pocket Meter MultiLine P4.

The decolorization efficiency (%) of an dye was determined as follows:

\[
Decolorization = (1 - \frac{C_t}{C_0}) \times 100
\]

where \( C_0 \) and \( C_t \) are the initial and final concentration of a dye, respectively.

\[2\]
The specific dye removal ability, expressed as $q \, (g/g)$, which is the amount of dye removed after treatment at the optimal coagulant dosage per gram of iron, was calculated using the following expression:

$$q = \frac{\text{Decolorization} \times C_0}{(100 \times D_{Fe})}$$

(2)

where Decolorization is the percentage color removal after treatment at the optimal coagulant dosage, %; $C_0$ is the initial dye concentration, mg/L; $D_{Fe}$ is the optimal coagulant dosage, mg/L.

3. Results and Discussion

When processing raw materials at the enterprises of the fur industry, a significant amount of wastewater is produced, the nature of which is determined by the specifics of the technological processes carried out in a particular production. In solving problems of improving the quality of fur products, updating and expanding their assortment, dyeing occupies an important place. The range of dyes used is quite wide. Dyes have a diverse structure, giving them various physicochemical properties. High light resistance, resistance to chemical and temperature influences of modern dyes, their toxicity, high water consumption of fur dyeing processes, as well as the fact that dyeing out of the working solution does not exceed 60%, necessitates the development of technologies for local treatment of wastewater from dyeing plants to reduce technological loads of fur enterprises on ecosystems, especially in places where there are no biological wastewater treatment facilities.

An effective reagent based on natural montmorillonite modified with iron compounds using ultrasound (Fe-MM) was developed and tested for the treatment of highly contaminated wastewater. Ultrasonic treatment leads to the formation of ultrafine sorbents with a developed specific surface (up to 400 $m^2/g$) and with a high sorption capacity to anionic dyes (up to 120 mmol/100 g). In addition, the coagulation activity of iron in the composition of modified montmorillonite is significantly higher than in FeCl$_3$ (Figure 1). It has been established that, when Fe-MM is used, a combination of coagulation and sorption mechanisms occurs. Clay plays the role of a surface that provokes the first stages of coagulation-sorption interaction, and promotes the formation of dense aggregated structures.

![Figure 1. Decolorization efficiency of the Direct Black (a) and Acid Brown (b) dye solutions. 1 - Fe-MM; 2 – Fe(III). $C_{in}=750$ mg/L.](image)

At the second stage, it is proposed to use the galvanocoagulation (GCO) method for deep decontamination, which is based on the use the effect of numerous microgalvanic pairs that occur when the aerated solution is in contact with an active load - iron-coke. Based on the different standard potentials of coke and iron, the half-cell reactions occurring at microscopic corroding surfaces can be represented as

\[
\text{Fe}^{0} + 2\text{e}^- \rightarrow \text{Fe}^{2+} \\
\text{C}^{0} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{C}^{2+} + \text{H}_2
\]
while on the iron surface, anode corrosion and transition to solution take place in the form of Fe$^{2+}$ ions as active coagulant precursors \textit{in situ}.

\begin{align*}
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \quad \text{(at pHs 2–6)} \tag{3} \\
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \quad \text{(at pHs 6–10)} \tag{4}
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\begin{align*}
Fe^0 & \rightarrow Fe^{2+} + 2e^- \tag{5} \\
Fe^{2+} + 2OH^- & \rightarrow Fe(OH)_2 \tag{6} \\
4Fe(OH)_2 + O_2 & \rightarrow 4FeOOH + 2H_2O \tag{7} \\
4Fe(OH)_2 + O_2 + 2H_2O & \rightarrow 4Fe(OH)_3 \tag{8}
\end{align*}

The experiments conducted with various azo dyes unambiguously confirm the higher efficiency of the galvanocoagulation method compared to traditional coagulation (Figure 2). It can be explained by differences in chemical and electrochemical coagulation. Freshly generated iron hydroxides (II, III) are unstable and decompose simultaneously with the formation of iron oxides. And then in aqueous medium the forms of magnetite or goethite are formed. Iron hydroxide (III) and goethite are good sorbents and sorption processes in galvanocoagulation, mainly, occur on these compounds. Besides, at GCO a change of properties of removed compounds may occur because of increasing reactive ability at their partial anodic oxidation \cite{21,22}.

However, not all dyes are successfully removed during galvanic coagulation treatment. In this case, it is necessary to apply AOPs. It has been established that methods based on Fenton-like oxidizing systems, if necessary photoinitiated, have the greatest efficiency for the post-treatment of wastewater containing micropollutants, including dyes (Figure 3).

As a source of iron ions, its salts, metallic iron, as well as the cast iron-coke galvanopair considered earlier, can be used. If an oxidizing agent (H$_2$O$_2$, K$_2$S$_2$O$_8$, etc.) is added to the purified water before galvanocoagulation, the conditions for the existence of the Fenton system (GCO) are realized in the system and oxidative destruction of pollutants occurs. Moreover, as with the use of metallic iron, the catalyst is generated \textit{in situ}, which gives a number of advantages (reduction in the cost of the process due to the use of metallic iron instead of its salts, processes at lower concentrations of the catalyst, higher degradation rate and efficiency of the process, etc.). Additional photoactivation allows full mineralization of dyes and other auxiliary substances in the dye bath (surfactants, equalizers, etc.).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Comparison efficiencies of various dyes removal obtained for chemical coagulation and galvanocoagulation treatment. Initial dye concentrations were 20 mg/L.}
\end{figure}
Conventional mercury lamps, excilamps and natural sunlight can be used as a source of UV radiation. On model solutions of phenols and dyes, the basic laws and mechanisms of oxidation of organic compounds are established. Experimental data indicate that a mixed mechanism is realized in iron-peroxide systems, combining the oxidative degradation of targeted compounds and the coagulation removal of reaction products. The intensifying ability of UV radiation is proved.

Figure 3. Decolorization of Methyl Orange solutions in various oxidative systems. $C_i=10$ mg/L, $C(H_2O_2)=5.5$ mg/L, $C(Fe)=5$ mg/L.

The obtained experimental and theoretical data made it possible to develop a conceptual scheme of dyeing wastewater treatment for fur industry, which includes, at the first stage, sorption-coagulation treatment to extract the bulk of pollutants, at the second stage, galvanic coagulation treatment and/or, if necessary, oxidative destruction by Fenton-like systems. The results of semi-industrial tests treatment of effluents from dyeing of furs in black color with oxidative dyes are presented in the table.

It should be noted one more important feature of the use of Fe-montmorillonite for treatment of oxidative dyeing effluents. In addition to dyes, this wastewater contains chrome (up to 150 mg/L), which is washed out of the semi-finished product, since the dyeing process is preceded by chromate “mordanting”. After treatment by modified sorbent-coagulant, the chromium concentration is reduced by 80%. It is likely that chromium is bound by dye molecules and is sorbed on the clay surface in the form of organometallic complexes, and also forms complex compounds with iron on the surface of the modified clay.

Tests carried out on real wastewater after dyeing of sheepskin black using oxidative dyes confirm high efficiency of the obtained sorbent-coagulant (table 1).

Table 1. Results of technological tests for the treatment of averaged wastewater after oxidative dyeing of fur in black. $C(Fe-MM)=20$ ml/L, $C(H_2O_2)=28$ mg/L.

|                        | Initial | After treatment |                        |                        |                      |
|------------------------|---------|-----------------|------------------------|------------------------|----------------------|
|                        | pH      | $I$ stage       | II stage (GCO)         |                        |
|                        |         | (Fe-MM)         | Without oxidant        | With addition oxidant  |
| pH                     | 7.4     | 3.5             | 6.1                    | 5.7                    |
| COD, mg O$_2$ /L       | 855     | 70              | 40                     | 15                     |
| Dyes, mg/L             | 285     | 19              | 11                     | 3                      |
| Chromium total, mg/L   | 17      | 3.4             | 0.5                    | 0.2                    |
Sewage sludge formed during wastewater treatment with Fe-montmorillonite was disposed of by composting with the participation of earthworms. Based on a comparative analysis of the group and fractional composition of the organic matter of composts, it was found that dyes due to their aromatic nature during vermicomposting are included in the composition of the bound, least mobile, humic acids. The introduction of utilized sewage sludge does not cause a deterioration in the quality of the organic matter of the obtained vermicomposts.

4. Conclusion
The high efficiency of the use of Fe-montmorillonite, activated by ultrasound, for the treatment of highly contaminated wastewater containing organic dyes is shown. A comparative analysis of the methods of galvanocoagulation and traditional coagulation using iron (III) salts for wastewater treatment from azo dyes is carried out. It was found that the degree of decontamination in terms of the dose of iron generated during galvanic coagulation is higher than with reagent coagulation. This is due to differences in the mechanisms of chemical and electrochemical coagulation. If it is necessary to achieve a higher efficiency, it is proposed to use Fenton-like oxidizing systems. The technological scheme of local wastewater treatment for dyeing fur sheepskin with direct and acid dyes was developed and proposed for implementation.

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