A Modern Integrated Approach in the Technology of Wastewater Treatment of Dye-Printed Manufactures of a Textile Enterprise

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Abstract. Based on a modern integrated approach with an economical process for the processing of chemically contaminated industrial wastes and the organization of a closed water supply system, it is proposed to use one of the most promising methods of wastewater treatment - evaporation. In the process of evaporation, a high-quality distillate is obtained, which is returned to the dye-printing industry, and highly concentrated solutions or slurries, which are sent for further processing, disposal or storage. In this article we have studying wastewater containing vat dyes. It was found that the dyes in the water go into undissolved form in acidic medium and the minimum content of such salts as sodium chloride and Glauber's salt. From the various methods of wastewater treatment from vat dyes, a method of electrochemical oxidation has been chosen. It is known that the electrochemical reaction proceeds more intensively in a concentrated solution, which explains the need to introduce the technological process, evaporator and electrolyzer into the main structures. The evaporated distillate is sent to the production, and the resulting concentrate containing the dye is fed into the electrolytic cell for electrochemical processing.

1. Introduction

At the first stage of the research, an experimental search of conditions was performed, allowing re-use of treated effluents and contained contaminant components, and a search was undertaken to reduce the main drawback of the concentration method - high energy intensity. As is known by common methods of cheaper technology are: the search for new technical solutions in the design of evaporators; the use of modern, inexpensive construction apparatus. However, specific options can significantly reduce energy costs: for example, it is advantageous to use waste steam, or secondary steam and own equipment [1-3].

A significant part of the experiment is devoted to the determination of pollutant concentrations in the intended final product; in the process of water purification, they were called concentrates. The studies were carried out on real and model solutions. The composition of the concentrate presented in table 1 was investigated in order to determine the optimal conditions for the electrochemical treatment of the solution for the isolation of vat dyes.
Table 1. Chemical composition of concentrates used for further processing.

| The contaminant | Units | Amount before concentrating dye-printing production | Concentrate |
|-----------------|-------|-----------------------------------------------------|-------------|
| Dye:            |       |                                                     |             |
| dissolved       | g/l   | 0.012-0.018                                         | 0.12-0.18   |
| undissolved     | g/l   | 0.027-0.034                                         | 0.27-0.34   |
| Sulphates       | g/l   | 0.01 – 0.017                                        | 0.1 – 0.17  |
| pH              |       | 8.0 – 8.5                                           | 9.5 – 10.0  |

The anode material was determined, the time and temperature of the treatment, the concentrations of NaOH and NaNSO₃. The indicated composition of the concentrate of dye-printed production is obtained by concentrating the effluents 10-11 times [4].

Model solutions were prepared from the six dyes, with an increased concentration of condensed effluent after the evaporation plant envisaged in the project. In a glass water is poured in view of entering of a matte cube and a solution of caustic soda is added. The solution is heated to the optimum dye reduction temperature, sodium hydrosulfite is added, mixed and then the mother cube is added, washing off the residuals of the uterine cube with the dye solution. To study the influence of various factors on the process of extracting the dye from wastewater, six types of vat dye were taken.

Table 2. The number of reagents and the optimum temperature.

| Dye                       | Powder for dyeing, g | Distilled water, ml | A solution of sodium hydroxide 32.5%, ml | Sodium hydrosulfite, g | Recovery temperature, °C |
|---------------------------|----------------------|---------------------|------------------------------------------|------------------------|--------------------------|
| cubic yellow 3X           | 0,3                  | 200                 | 0,3                                      | 0,1                    | 50                       |
| vat bright orange KX      | 0,55                 | 200                 | 0,3                                      | 0,1                    | 50                       |
| cubed brown K 1           | 1                    | 200                 | 0,3                                      | 0,1                    | 50                       |
| vat bright green 2 G      | 0,3                  | 200                 | 0,6                                      | 0,2                    | 60                       |
| cubic blue O              | 0,33                 | 200                 | 0,6                                      | 0,15                   | 60                       |
| cube scarlet 2 G         | 0,25                 | 200                 | 0,6                                      | 0,2                    | 60                       |

According to the published data, the sodium salt of the leuco compound (≥ C = ONa) formed for dyeing cotton is soluble in water and has an affinity for cellulose fiber, but when oxidized by air oxygen (as provided by dyeing technology), it passes into the corresponding insoluble initial dye (pigment) [5,6].

Analysis of the chemical composition of sewage water of the dye-printed production showed the presence of soluble and insoluble forms, taking into account this factor, model solutions were compiled approximately as a percentage of the actual runoff of the averaged composition over 30 days. Further, these model solutions were oxidized with air oxygen, simulating oxidation during dyeing under production conditions, which allowed to prove: at the existing initial concentrations of the vat dye, when dyeing in CB is not more than 0.018 g / l, the sodium salt of the leuco compound (dissolved form) is present in the initial effluent and the rest in undissolved form of 0.034 g / l.

When choosing the optimal factors for electrochemical processing, studies were carried out with model solutions containing the investigated groups of vat dyes insoluble in acidic media. It is this fact that is taken as the basis for its isolation by electrochemical means from the designated drains. The investigated initial runoff has pH = 8.0-8.5, after concentration of pH = 9.0-9.5. Knowing that only the
water can be oxidized in the anode space with the existing runoff, creating an acidic environment, complex studies have been carried out, which allowed us to recommend not only the required concentrate composition, but also all the conditions for maximum separation of the vat dye [4].

At the maximum values of electrical conductivity and minimum viscosity, electrochemically treating the aqueous medium, reducing the pH of the solution to 5.0-5.4 in the anode space completely transfers the dissolved sodium salt of the leuco compound into undissolved [7].

The most important condition necessary for the successful implementation of the electrochemical process is the choice of the electrode material, which is determined mainly by the nature of the initial and final products of the electrochemical reaction, and also by the chemical stability of this electrode and its inertness with respect to the medium in which electrolysis occurs [8-10].

The main difficulty in this case arises from the fact that most metals are thermodynamically unstable under conditions of anodic polarization (their dissolution or passivation occurs). Special conditions for the operation of the anodes in the electrolysis of dilute NaCl solutions are due to the fact that a significant amount of oxygen is released on them in addition to the discharge of chloride ions.

Given the cost characteristics, for laboratory studies, as an anode material, graphite and stainless steel are selected.

Graphite is a highly electrically conductive, electrochemically active anode material [7]. The combination of these properties with low cost determines its wide application, it is of certain interest for use in technological water treatment systems. However, graphite anodes, due to considerable porosity, absorb large amounts of salt solution, so the effect of electric current is manifested not only on the surface of the anode, but also in the electrode itself, which creates favorable conditions for its destruction. In this case, the "combustion" of graphite by the products of electrolysis occurs, as well as the loosening of its structure by evolved electrolytic gases, resulting in the mechanical scattering of carbon grains. When the voltage varies from 0.6V to 1.6V, the current densities in solutions of dyes change insignificantly. After 1.6V, the current density begins to increase. The potential of stainless steel at current densities from 45 to 80 mA / dm2 is much lower than the potential of the graffiti anode. Due to this, the voltage on the cell with stainless steel anodes at the same current density is 0.2-0.3 V lower than with graphite anodes, which leads to lower energy costs for this reaction. Having determined the anode material, we will search for its optimum area. It is established that the ratio of Sa:Sk = 10:1 is. Thus, the stainless steel material recommended for practical use is an anode. The operating current density is 45-80 mA / dm2 [7].

Then, the time of electrochemical treatment was determined, for which the maximum value of the efficiency of isolation of the vat dye was reached, which was 20-25 minutes.

As, the pH value decreases, which favors the transition of the soluble form of the dye to insoluble. The reaction of the medium is the determining factor in the extraction of the vat dye, since it is the pH of the solution that affects the concentrations of the dissolved and undissolved forms of the vat dye. The higher the pH of the solution, the more the dye is in the form of the sodium salt of the leuco compound; in the dissolved state. Lowering the pH leads to the transition of the dye to the undissolved state [7].

It has been experimentally determined that the maximum efficiency (above 90%) of the transition of the dye into undissolved form is achieved at pH = 5.0-5.5, which corresponds to a treatment time of 20-25 minutes.

Increasing the temperature from room temperature to 60-80 ° C reduces the overvoltage of electrode reactions by 30-40%, and also increases the efficiency of purification, which makes it possible to recommend a reduction in the treatment time when using a solution heating to the appropriate value. For the production site of this study, the optimum temperature is 25 ° C [7].

The concentrate contains a reducer of the vat dye sodium hydrosulfite. The influence of its concentration on the efficiency of water purification was studied in the work [11-19].

In the process of extracting a vat dye from wastewater, the concentration of hydrosulfite affects the electrical conductivity of the solution, which in turn determines the efficiency of purification.
In the process of extracting the vat dye, increasing the concentration of sodium hydrosulfite leads to an increase in the cleaning efficiency, which is caused by an increase in the electrical conductivity of the solution; however, at a concentration of 1.8 g / l, the cleaning efficiency increases insignificantly. The optimum concentration of NaHSO₃ is 2.0 g / l [7].

Based on the conducted studies, the parameters of the electrochemical treatment of the concentrate are recommended, the composition of which is presented in the table 3.

The presented parameters determine the operation of the electrolysis plant, which, when considering the ZCV, is a «tail installation».

Table 3. Parameters of electrochemical treatment of concentrate KPP.

| № according to plan | Name                              | Value  |
|---------------------|-----------------------------------|--------|
| 1                   | Anode material                    | stainless steel |
| 2                   | Processing time, mine             | 20-25  |
| 3                   | pH                                | 8,0-8,5 |
| 4                   | Temperature, °С                   | 25     |
| 5                   | Current density, mA/dm²           | 45-80  |
| 6                   | Concentration NaHSO₃, g/l         | 2,5    |
| 7                   | Sа : Sк                           | 10:1   |

Returning to the above, it should be noted that the organization of a closed system requires the simultaneous study of all elements of the water economy in their interrelationship, and not only individual parts (clean and dirty circulating cycles, local wastewater treatment facilities, etc.). Indeed, the system purifies and uses all production waters of the textile enterprise, tailings process all waste from local cycles, etc. All this must be linked in a single farm. To create a closed system, joint efforts of specialists of different directions are needed: water experts, technologists, economists, hygienists, etc. [20-22].

Figure 1 is a block diagram of the water balance of a closed water supply system based on a low-waste technology that allows not only re-use purified water in production, but also the designated pollutants.

Figure 1. Schematic diagram of the process of wastewater treatment of dye-printing-production.
2. Conclusion
Based on the results of the studies, an electrochemical method for isolating a vat dye from waste water from a dye-printed production was proposed, a modern integrated approach was developed in the technology of wastewater treatment of dye-printing industries, including extraction from sewage and the possibility of further use of vat dyes. Implementation of the developed flowchart allows reusing water up to 90% and completely eliminating the discharge of pollutants of waste water.

3. References
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