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DEVELOPMENT OF RESOURCE-SAVING TECHNOLOGY OF DYEING COTTON FABRICS BY REACTIVE DYES WITH REUSE OF TREATED WASTEWATER FROM DYEING AND FINISHING PRODUCTION AND CREATION OF A BASIC TECHNOLOGICAL SCHEME

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Abstract

Consumption of water resources of the textile industry and the generation of large amounts of wastewater negative impact on the environmental ecosystem. The development of resource-saving technologies with the reuse of wastewater treated by adsorption method as a secondary resource in fabric dyeing technology is relevant. The work presents the results of the wastewater reuse treated with a natural zeolite sorbent during the cotton fabric Coarse calico (art. 3399) coloring with reactive dyes: Reactive Blue CB-RF, Reactive Red S-matrix, and Reactive Yellow S-3R. It was practically determined that using purified wastewater in the dyeing cotton fabric technology ensures the fabric coloring intensity 96–99 % compared to the standard (100 %). The obtained color's stability is at the 4–5 points according to the «Gray standards scale». A series of experiments resulted in the possibility of using the doubly purified wastewater for dyeing cotton fabric with Reactive Blue CB-RF and Reactive Red S-matrix dyes to get a hue within 96 %. The color difference of all examined fabric samples (DE < 2) (when comparing between reference and dyed samples). Thus, the principle diagram of dyeing cotton fabric with reactive dyes and the repeated use of wastewater purified by the adsorption method has been developed. Dyeing according to this scheme has been tested in the production conditions of the Private Joint Stock Company Cherkasy Silk Plant (PJSC CSP) (Cherkasy, Ukraine). The expense of water treatment is calculated by comparing the costs of the water softening process and cleaning wastewater with a zeolite sorbent for its reuse. Cost savings of 10%. The spectrophotometric method was used in the work. The dyeing stability was determined according to Ukraine's current state and international ISO standards. The Python programming language, engineering, and scientific data visualization libraries Matplotlib and Seaborn were used to visualize the experimental data.

Keywords: dyeing and finishing industry; wastewater; adsorption; zeolite; reactive dyes; Coarse calico; dyeing; scheme.

РОЗРОБКА РЕСУРСОЗБЕРІГАЛЬНОЇ ТЕХНОЛОГІЇ ФАРБУВАННЯ БАВОВНЯНИХ ТКАНИН РЕАКТИВНИМИ БАРВНИКАМИ З ПОВТОРНИМ ВИКОРИСТАННЯМ ОЧИЩЕНОЇ СТІЧНОЇ ВОДИ ФАРБУВАЛЬНО-ОПОРЯДЖУВАЛЬНОГО ВИРОБНИЦТВА ТА СТВОРЕННЯ ПРИНЦИПОВОЇ ТЕХНОЛОГІЧНОЇ СХЕМИ

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Анотація

Споживання водних ресурсів текстильною промисловістю та утворення великої кількості стічних вод має негативний вплив на екосистему. Актуальним є розробка ресурсозберігальних технологій з повторним використанням очищених адсорбційним методом стічних вод, як вторинного ресурсу, в технології фарбування тканини. Очищення стічних вод фарбувально-опоряджувального виробництва адсорбційним методом є одним із способів їх повторного використання, як вторинного ресурсу, в технології фарбування тканини. У роботі представлені результати повторного використання стічної води, очищеної природним сорбентом цеолітом, в технологічному процесі фарбування бавовняної тканини Бязь (арт. 3399) реактивними барвниками: Реактивного синього CB-RF, Реактивного червоного S-matrix та Реактивного жовтого S-3R. Практично визначено, що використання очищеної стічної води в технології фарбування бавовняної тканини, забезпечує інтенсивність її забарвлення 96–99 % у порівнянні з еталоном (100 %), стійкість одержаного забарвлення 4-5 балів за «Шкалою сірих еталонів». Серією експериментів досліджено, що двократне очищення однієї і тієї ж стічної води дозволяє використовувати її для фарбування бавовняної тканини барвниками Реактивним синім CB-RF та Реактивним червоним S-matrix з рівнем інтенсивності одержаного забарвлення в межах 96 %. Кольорова відмінність всіх досліджених зразків DE < 2 між еталонними та пофарбованими зразками. Розроблено принципову схему технології фарбування бавовняної тканини реактивними барвниками з повторним використанням стічної води, очищеної адсорбційним методом. Фарбування за такою схемою апробовано у виробничих умовах ПрАТ «Черкаський шовковий

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комбінат» (м. Черкаси, Україна). Розрахована собівартість обробки води шляхом порівняння вартості витрат на пом'якшення технологічної води та очищення стічної води сорбентом цеолітом з метою її повторного використання. Економія витрат 10 %. У роботі застосовувалися спектрофотометричний метод; визначення стійкості фарбування здійснювалося згідно до діючих державних стандартів України та міжнародних стандартів ISO; для візуалізації експериментальних даних використовувалися мова програмування Python, бібліотеки візуалізації інженерних і наукових даних Mathplotlib і Seaborn.
Ключові слова: фарбувально-опоряджувальне виробництво; стічна вода; адсорбція; цеоліт; реактивні барвники; бязь; фарбування; схема.

Introduction

The textile industry, closely related to the national economy, consumes many water and energy resources [1]. Moreover, it has the most significant environmental impact on the surrounding ecosystem, producing 60 billion kilograms of fabric annually and using up to 9 trillion gallons of water [2]. The production of clothes has almost doubled recently. Since textiles satisfy a significant part of human needs, experts estimate the total clothing supply will reach 160 million metric tons in 2050. This will significantly increase the textile industry’s negative impact on the environment. Water and energy consumption, as well as pollutants discharged with wastewater, will grow [3]. According to the World Bank, 20 % of water pollution worldwide is caused by textile processing, which is associated with considerable wastewater. These effluents contain many suspended solids, phosphates, dyes, salts, and organic substances. The increase in water scarcity and environmental regulations has led to the textile industry’s need for sustainable wastewater treatment methods, which will help reduce emissions and operating costs for textile materials processing [2].

The dyeing process consumes more water than other textile processes. Consequently, it generates a larger volume of wastewater that can be an effective resource for reuse treatment. However, water used in textile processing, especially in the dyeing stage, must meet stricter quality requirements than those used for discharge into the environment [4; 5]. Thus, the effective wastewater purifying processes must be developed to make the reuse of treated wastewater economically viable. On the other hand, the study of new wastewater purifying technologies should be aimed at removing color and organic substances and recovering salts and other components [6; 7].

Therefore, it is urgent to create new resource-saving technologies for wastewater cleansing from the dyeing and finishing industry and the possibility of their reuse during the coloring of textile materials.

A recent research and publications analysis have shown that few comprehensive publications cover textile wastewater treatment and its closed-loop reuse in other technological processes [8–11]. The work [12] describes new alternative wastewater regeneration due to catalytic ozonation with new catalysts. «Two novel ozonation catalysts, mesoporous carbon aerogel and its supported cobalt oxide nanoparticles, were successfully prepared and used in catalytic degradation of residual dyes in waste effluents with ozone». The effluents after catalytic ozonation were reused for successive dyeing in the same process. It was confirmed that the waste effluents were effectively regenerated and could be additionally reused twice without compromising the quality of the fabric.

The work [13] presents the intensifying effect of purified wastewater when dyed with sulfur coloring agents. The correct selection of coagulant and flocculant and the determination of the flotation device’s optimal operation parameters helped to achieve a high degree of wastewater treatment. It was established that using purified water in a ratio of 1 : 1 with technical water contributes to optimizing the working dyeing solution pH due to aluminum ions and surface-active substances in the purified wastewater. The optimal regime and design parameters were found experimentally. They significantly affected the flotation treatment of textile enterprises’ wastewater.

The work [14] shows the possibility of wastewater electrooxidation from dyeing production using a boron-doped diamond anode, which ensures the quality of purified wastewater required for reuse. The results of two dyeing cycles of wool (100 %) twill fabric with Nylosan acid dyes with the reuse of treated wastewater showed that effective sequential reuse can be achieved using water of moderate quality. Electrooxidation reduced the ecotoxicity of sewage up to 18.6 times, allowing the reuse of treated wastewater without significant accumulation of ecotoxicity.

Scientists from India [15] suggest finding an alternative source of fresh water to support the textile industry by reusing effectively treated

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domestic wastewater. Such an effluent was effectively treated using sequential microbial local reactors, disinfection, and sand filtration. Water purified in this way was used for textile dyes production and fabric coloring. It was compared with the quality of dyes obtained using fresh water. The tensile strength value of both dyed fabric samples remained unchanged (8.53 kg/cm^2). The value of the obtained dyes' fastness colored with purified water was higher than that of the fabric dyed with fresh water.

Great attention was paid to the wastewater collected from the discharge of one of the textile factories in Croatia specializing in cotton clothing production [16]. Scientists recommend purifying wastewater using a membrane hybrid method, the first stage of which is pre-treatment of wastewater with sand (filtration) and coagulation, to reuse purified water during the cotton-knitted fabric dyeing. The second stage consisted of wastewater purification using UF flat sheet membranes with 5, 10, 20, and 50 kDa pore sizes corresponding to 1.1 nm, 1.42 nm, 1.78 nm, and 2.4 nm, respectively [17]. The UF 5 kDa (1.1 nm) membrane was determined to provide the best permeate quality regarding chemical oxygen demand and turbidity. The color change of purified water was 54.5%, 83.9 %, 94.2 %, and 45.7–83.3 % higher, respectively. The last stage was wastewater treatment with nanofiltration and reverse osmosis. The efficiency of controlled pollutant removal in effluent ranged from 59.2 % to 98.1 %. However, the conclusion about the possibility of purified wastewater reuse in the fabric dyeing process was based on the thorough sewage analysis (without testing the dyeing of cotton knitted fabric).

Scientists from Poland [3] are investigating the purification of model textile wastewater using a two-stage membrane filtration process that includes nanofiltration and reverse osmosis. After cleaning, sewage was reused in cellulose fibers coloring with reactive dyes. Studies have confirmed that textiles dyed using reverse osmosis filtrates did not differ in dyeing quality from those colored in pure deionized water.

The analysis of scientific articles shows the need to solve the problem of resource-saving water as the fabric dyeing process's main component (environment). It's essential to create a reversible (cyclical) use of wastewater in the dyeing textile materials technology, provided by cleaning wastewater from dyeing and finishing production. This will lead to a decrease in the cost of textile products and a reduction in the ecological burden on the environment and water resources. This is the basis for conducting laboratory and industrial research.

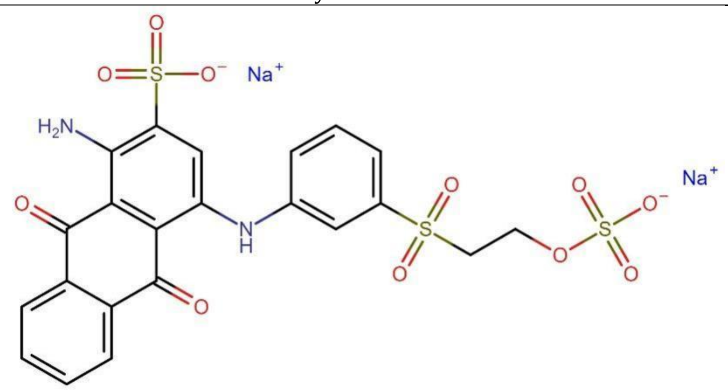
The work aims to experimentally investigate the possibility of reusing wastewater from the dyeing and finishing industry, purified by adsorption, in the dyeing cotton fabric technology with reactive dyes; to develop a resource-saving technology for dyeing textile materials with the reuse of treated wastewater from the dyeing and finishing production; to create a basic technological scheme.

Materials and methods

Reactive dyes are one of the most used in the textile industry for dyeing cellulose fiber. They have many advantages: good solubility in water, ease of application on fibrous material, variety of application methods, availability of different hues, color shades brightness, good or excellent resistance to washing, light fastness, resistance to the destructive effects of sunlight, and moderate price [18; 19]. Reactive dyes of three primary colors were used in the work (Table 1).

Table 1

Textile reactive dyes

The name of the dye	Dye formula
Reactive Blue CB-RF (Reactive Blue 19 [20]) disodium;1-amino-9,10-dioxo-4-[3-(2-sulfonatooxyethylsulfonyl) anilino] anthracene-2-sulfonate	

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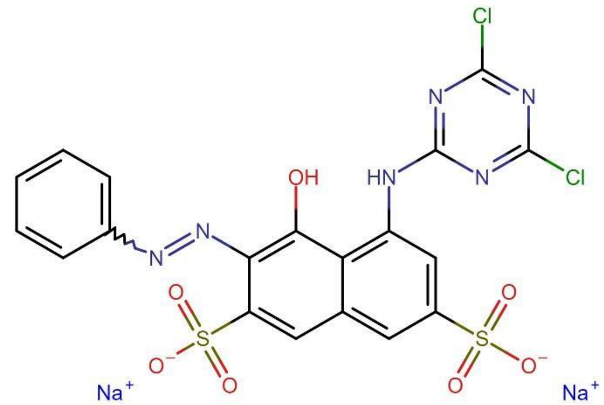
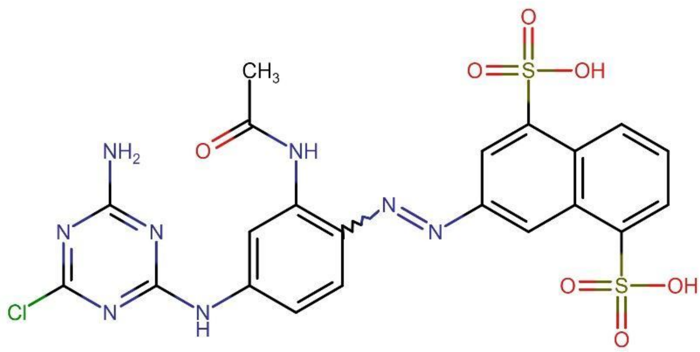
Continuation of the table 1

Reactive Red S-matrix (Reactive Red 2 [21]) disodium;5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-phenyldiazenylnaphthalene-2,7-disulfonate	
Reactive Yellow S-3R (Reactive Yellow 3 [22]). 3-[[2-acetamido-4-[(4-amino-6-chloro-1,3,5-triazin-2-yl)amino]phenyl]diazenyl]naphthalene-1,5-disulfonic acid	

Sodium chloride (table salt, NaCl GOST 4233-77) (100 g/dm^3) is well-soluble in water and a non-toxic crystalline substance. Salt is used to improve the affinity of the dye with cellulose, increase the absorption of the dye by the fiber, reduce the rate of hydrolysis of dyes in an aqueous solution, and neutralize the electronegative charge of the fiber surface when immersed in the solution [18].

Sodium carbonate (crystalline soda, Na_2CO_3 GOST 32802-2014), (100 g/dm^3) is poorly soluble in cold water white powder. Its solubility increases significantly when heated. Its density is 2.5 g/cm^3. It is used as an alkaline reagent to initiate and accelerate the dye-fiber reaction. The amount of soda depends on the solution's pH required for a certain type of reactive dye group and the dyeing method [26].

Coarse calico is a dense cotton fabric with a plain weave. It is made of 100% cotton, has high density and low cost [27]. The chemical composition of cotton is following: α-cellulose (94.5–96 %), waxy substances (0.5–0.6 %), pectin substances (1–1.2 %), protein substances (1.2 %), mineral substances (1–2 %), and other substances (0.3–1.3 %). Cotton fiber is sufficiently robust and is characterized by slight elastic and large plastic elongation. It's hygroscopic (7–8 %) and it swells and increases in cross-section by 15–30 % in an aqueous environment, leading to a strength boost of 5–10 %. The fibers have low thermal conductivity and can withstand short-term heating up to a temperature of 180–200 °C. They are well-stained with many dyes [28, pp. 40–43]. We used the fabric Coarse calico (art. 3461) produced by the Private Joint Stock Company Cherkasy Silk Plant (PJSC CSP) (Cherkasy, Ukraine).

A photocolorimetric method and a spectrophotometer UV-5800 PC (China) were used to study the analysis of dye solutions and wastewater. The color characteristics of the examined tissue samples were determined via an automatic computer system of objective color measurement Datacolor Spectrum 400 (Datacolor, USA) using the CIELAB color space system.

The quality and stability of the obtained colors were determined by comparing them with the standard used by the samples of PJSC CSP and by determining the stability of coloring by the current state standards of Ukraine and international ISO standards (DSTU 3998-2000 [29], DSTU ISO 105-X12:2016 (to dry crocking) [30], DSTU ISO 105-A02:2005 (Gray standards scale) [31], DSTU EN ISO 105-C10:2020 (washing with soap) [32], DSTU ISO 11641:2012 (color fastness to perspiration) [33]. Colorfastness to dry crocking is measured on the Staining Tester (Computex, Hungary) in accordance with DSTU ISO 105-X12:2016 [30]. The head of the device, which is covered with a white cotton fabric, makes 10 forward and backward movements on a 10 cm sample of the tested fabric under a load of 9H. At least three samples are taken for the test. The arithmetic mean of all measurements is perceived as the result.

Mathematical analysis and modern computer technology (MS Excel table processor) were used in the experimental data processing. The Python programming language, engineering, and scientific data visualization libraries Matplotlib and Seaborn helped visualize the innovative information. Python scripts for generating graphic images were created in JSON program file format in the Microsoft Visual Studio Code integrated development system in Jupyter Notebook.

Results and discussion

Average diluted (1 : 100) wastewater from the dyeing and finishing production of PJSC CSP was subjected to adsorption purification. This process was carried out with natural zeolite (sokyrnit) from the Sokyrnytskyi deposit of the Zakarpattia Oblast (Ukraine) with a fraction size of 2.5–5.0 mm (Fig. 1).

a в

Fig. 1. Natural sorbent of the Sokyrnytskyi deposit with a fraction of 2.5–5.0 mm: A – native zeolite, B – spent zeolite

It was experimentally determined that zeolite required preliminary preparation before use: washing, thermal activation (at a temperature of 450 °C for 4.5 hours) and acid modification (using a 10 % solution of sulfuric acid). Adsorption purification is carried out by one of the most widespread and effective methods of adsorption - long-term contact of liquid and solid phases in a state of rest. It's about loading a stationary zeolite layer into the volume of wastewater being purified, followed by coagulation and flocculation. In order to reuse the treated wastewater in fabric dyeing technology, its physicochemical analysis was carried out and compared with the properties of the process softened water of PJSC CSP (softening is carried out using Cationite KU-2-8 GOST 20298-74 P.12, Volume 2). The results of the study are shown in Table 2 [34].

Table 2

Comparative analysis of the studied water systems

Indicator	Average diluted wastewater (quarterly average)	Wastewater treated by coagulation and flocculation	Softened process water of PJSC CSK
Colour	red-brown	colourless	colourless
Turbidity, mg/dm^3	0.81	0.16	0.1
Smell, points at 20 °C	3	0	0
Sediment and floating impurities	flakes	missing	missing
Total alkalinity, mmol/dm^3	8.3	7.7	7.5
pH	8.1	7.27	7.36
Chemical oxygen demand dichromate (COD), mgO$_2$/dm^3	223.83	2.84	2.79
Sulphates (SO_4^{2-}), mg/dm^3	152.8	3.7	3.57
Chlorides (Cl^-), mg/dm^3	137	0.17	0.12
Orthophosphates (PO_4^{3-}), mg/dm^3	0.84	not detected	not detected
Ammonium nitrogen, mg/dm^{3}g	6.95	0.1	0.09
Total iron, mg/dm^3	0.43	0.03	0.026
Total hardness*, mmol/dm^3	-	0.15	0.1

* The permissible total hardness content for process water during fabric dyeing is in the range of 0–25 ppm (0–

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0.25 mmol/dm³) [35]. The dye is not fixed on the fabric at a hardness of more than 0.25 mmol/dm³, which leads to the need for repeated processing and dyeing, and subsequently to the disposal of the scroll of defective fabric.

Since the colour of dyes is a consequence of their interaction with light, the quantitative assessment of the colour of wastewater and treated water was carried out by the spectrophotometric method using a UV-5800 PC spectrophotometer (China).

The degree of purification of the studied water systems was mathematically calculated according to the results of the optical spectra using the formula:

$$\omega = \left(1 - \frac{D_1}{D_2}\right) \cdot 100\ \% \qquad (1)$$

where ω is the degree of purification, %;
D_1 is the optical density of purified water;
D_2 is the optical density of diluted average wastewater [36].

The result of the physicochemical analysis confirms the compliance of the treated wastewater to the process softened water, and the degree of wastewater treatment is 91 % [34]. This indicates the possibility of its use in the technology of dyeing textile materials and requires further research.

In order to recycle or possibility of reuse the spent zeolite, its phytotoxicity was determined by laboratory phytotesting. Phytotoxicity was determined by a series of experiments, which consisted of germination of winter barley seeds of the variety "Ninth Val" of Ukrainian selection, using different initial conditions and on different research substrates [37]. So, the aqueous extracts of native and spent zeolites prepared according to DSTU 7534:2014 were studied. Three samples were tested as substrates: 1 – distilled water (control), 2 – water extract of native zeolite, and 3 – water extract of spent zeolite. Plants have been growing at a temperature of 18 °C for 12 days. Each version of the experiment was carried out in triplicate. The following parameters were recorded during the study: seed germination time, the total number of seeds that emerged, the height of stems, and the length of the root system. Changes in the state of plants at various stages of their development were observed throughout the experiment. The germinating capacity of winter barley grains for control is 90 %, for water extraction from native zeolite – 95 %, and for spent zeolite – 85 %. Photos of germinated seeds are presented in Fig. 2.

a b c

Fig. 2. Photos of germinated winter barley seeds on different substrates: a - distilled water (control), b - aqueous extract from native zeolite; c - aqueous extract from spent zeolite

The phytotoxic effect is determined as a percentage by any bioparameter: by the length of the root or stem system, the number of suppressed plants, the number of seeds that have sprouted, the weight of plants, etc. The height of the barley stalks that germinated during the entire experiment was chosen as the bioparameter for calculation in the conducted experiment. The phytotoxicity index is calculated according to the formula [20]:

$$P = \frac{(B_c - B_i)}{B_c} \cdot 100\ \% \qquad (2)$$

where P – phytotoxicity value, %;
B_c – the average value of the stem height bioparameter for the control sample, cm;
B_i – the average value of the stem height bioparameter for the investigated sample, cm.

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The studied samples show phytotoxicity in a case when P > 20 % [39]. In this study, it was determined and mathematically calculated that the phytotoxicity of spent zeolite does not exceed 20 %, which, according to existing criteria, indicates the absence or low level of its toxicity [37]. Thus, we can predict its use as a secondary material resource: as part of the road clothing or the car surface to ensure the stable operation of the road construction. It can be utilized to produce building materials (cement, concrete solutions, foam, and aerated concrete). Spent zeolite can even be a bioadditive for plant growth and development, but it is possible only in the case of more detailed agrochemical and biological research. The possibility of reusing spent zeolite solves the problem of its disposal as a solid by-product of adsorption wastewater treatment, which will significantly reduce the ecological burden on the environment. The reuse of spent zeolite will mitigate the economic costs of its disposal.

The possibility of using purified wastewater in fabric dyeing technology was investigated experimentally when coloring Coarse calico (art. 3461) fabric with reactive agents. Dyeing was carried out on the laboratory dyeing machine AHIBA NUANCE CH-6015 (Datacolor, USA) in the conditions of the real dyeing and finishing production of PJSC CSP according to the company's recipe (Table 3).

Table 3

The dyeing solution recipe according to which the Coarse calico was dyed (art. 3461) (solution per volume of 0.08 dm^3 for a laboratory machine)

Dye solution reagents	The amount of reagent according to the PJSC CSP	The amount of reagent using purified wastewater
Solution (12%) of pre-boiled reactive dye, cm^3	12	12
Crystal soda Na_2CO_3, g	2	2
Table salt (NaCl), g	3	3
Process water (softened)*, cm^3	63	-
Wastewater purified by the adsorption method, cm^3	-	63

*softening is carried out at PJSC CSP.

According to the technological regime of the enterprise, 2 g of cotton fabric is immersed in the coloring solution. Dyeing is carried out periodically at 60°C for 60 minutes. The samples are washed after coloring several times with cold tap water and hot (t = 80–90 °C) water, soaped with a detergent (liquid soap with a concentration of 1–2 g/dm^3) for 10–15 minutes. Then, they are washed with hot and cold tap water and dried in an oven at 100 °C for 5–7 minutes. The resulting dyed tissue samples (Fig. 3) are examined for color intensity and stability.

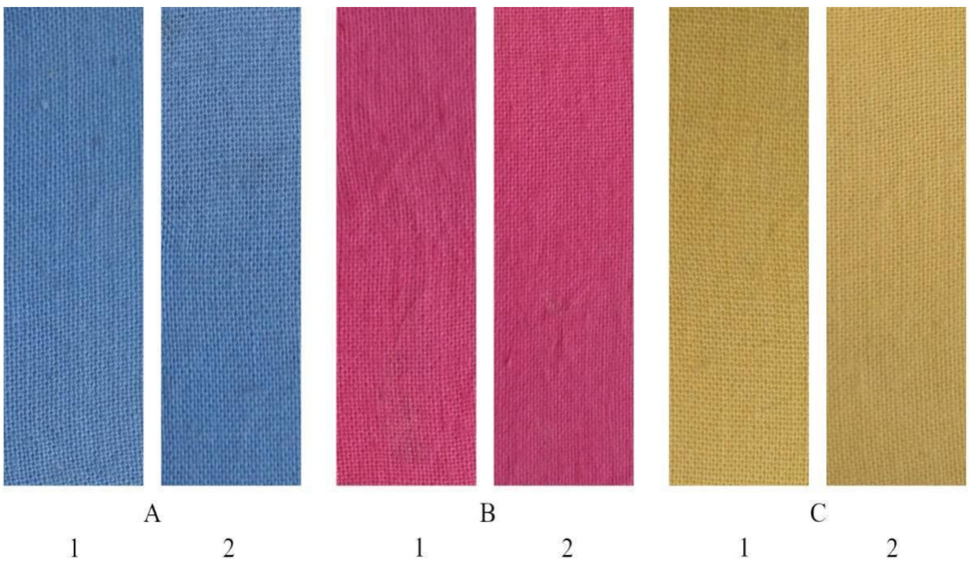

Fig. 3. Samples colored with reactive dyes Coarse calico (art. 3461): A – Blue CB-RF dye, B – Red S-matrix dye, C – Yellow S-3R dye; 1 – with the use of softened process water, 2 – with the use of adsorption purified water

The quality and stability of the obtained colors were determined by comparing them with the reference ones used by the samples of PJSC CSP (Table 4).

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Table 4

Color characteristics of the dyed with reactive dyes Coarse calico (art. 3461) fabric using adsorption purified water

Dye	Lightness dL	Hue (red-green) dA	Hue (yellow-blue) dB	Color difference dE*	Color intensity, % according to the standard (100%)
Reactive Blue CB-RF	–0.17 darker	–0.02 greener	–0.37 bluer	**0.45**	**98.3**
Reactive Red S-matrix	+0.10 lighter	+0.14 redder	–0.24 bluer	**0.29**	**99.0**
Reactive Yellow S-3R	+0.40 lighter	–0.04 greener	–1.12 bluer	**1.19**	**96.0**

* Color difference is a mathematical representation that allows you to express the difference between two colors in colorimetry numerically. dE should not exceed 2, which approximately corresponds to the minimally noticeable distinction among hues for the human eye [40, pp. 29–32].

The dyed fabric samples were tested for color resistance to dry crocking, washing with soap, and the influence of "sweat" (according to the current state standards of Ukraine and international ISO standards) (Table 5.). Qualitative indicators of the color fastness of dyed fabric samples were investigated by DSTU ISO 105-A02:2005 Gray standards scale, to dry crocking (DSTU ISO 105-X12:2016), washing with soap (DSTU EN ISO 105-C10:2020), influence of "sweat" DSTU ISO 11641:2012. The method uses a solution of artificial perspiration to simulate the effect of human sweat. Since perspiration varies greatly from one person to another, it is impossible to develop a method with universal validity. However, the alkaline perspiration solution in DSTU ISO 11641:2012 showed results similar to natural human perspiration in most cases.

Table 5

Qualitative indicators of the dyed with reactive dyes Coarse calico (art. 3461) fabric

Dye	Color fastness, points					
	dry crocking		washing with soap		influence of "sweat"	
	SPW*	PW*	SPW*	PW*	SPW*	PW*
Reactive Blue CB-RF	4–5	4-5	5	5	5	5
Reactive Red S-matrix	5	5	5	5	5	5
Reactive Yellow S-3R	5	5	5	5	5	5

SPW* - dyeing using softened process water
PW* - dyeing using purified water

Analysis of Tables 4 and 5 has shown that the intensity of dyeing of cotton fabric samples using purified wastewater is within 96–99 % compared to the standard (100 %) with a color difference of 0.45–1.19 (DE < 2). The stability of the studied samples practically does not differ from the stability indicators of dyed cotton fabric using softened process water.

Considering the current trends of water recycling as the leading resource of fabric dyeing, additional research on the possibility of using purified water in several technological cycles of fabric coloring appeared necessary. Three investigated cycles of cleaning the same volume of water with subsequent dyeing are proposed. The color characteristics of the studied samples were determined experimentally. The results are shown in Table 6.

Table 6

Color characteristics of the dyed with reactive dyes Coarse calico (art. 3461) fabric using adsorption purified water after the second (II) and third (III) treatment

Dye	Lightness dL		Hue (red-green) dA		Hue (yellow-blue) dB		Color difference dE*		Color intensity, % according to the standard (100 %)	
	II treatment	III treatment	II treatment	III treatment	II treatment	III treatment	II treatment	III treatment	II treatment	III treatment
Reactive Blue CB-RF	+0.39 lighter	+1.66 lighter	+0.52 redder	+2.63 redder	-0.18 bluer	-2.18 bluer	**0.88**	4.75	**96.1**	83.4
Reactive Red S-matrix	-0.44 darker	-1.25 darker	+1.1 redder	+1.96 redder	-0.73 bluer	-1.73 bluer	**1.44**	3.63	**95.6**	87.5

Continuation of the table 6

Reactive Yellow S-3R	+1.7 lighter	+2.52 lighter	-1.24 greener	-1.94 greener	-3.91 bluer	-5.91 bluer	4.44	6.44	83.0	74.8

* Color difference is a mathematical representation that allows you to express the difference between two colors in colorimetry numerically. dE should not exceed 2, which approximately corresponds to the minimally noticeable distinction among hues for the human eye [40, pp. 29–32].

Experimental studies have shown that the efficiency of dyeing intensity in the 95–96 % range is achieved with the double use of purified wastewater when dyeing with reactive coloring agents of dark colors (Reactive Blue CB-RF and Reactive Red S-matrix). However, for dyeing cotton fabric with the light-colored dye Reactive Yellow S-3R, purified wastewater must be used only once (after the first treatment).

Based on the results of these and other studies published in works [41–45], a basic technological scheme of dyeing cotton fabric process with repeated use of purified wastewater by the adsorption method was created for the first time (Fig. 4). Dyeing according to this scheme has been tested in the PJSC CSP's production conditions in automatic dyeing-roller machines of periodic action Jigger VN (Henriksen company, Denmark) and has practically significant results.

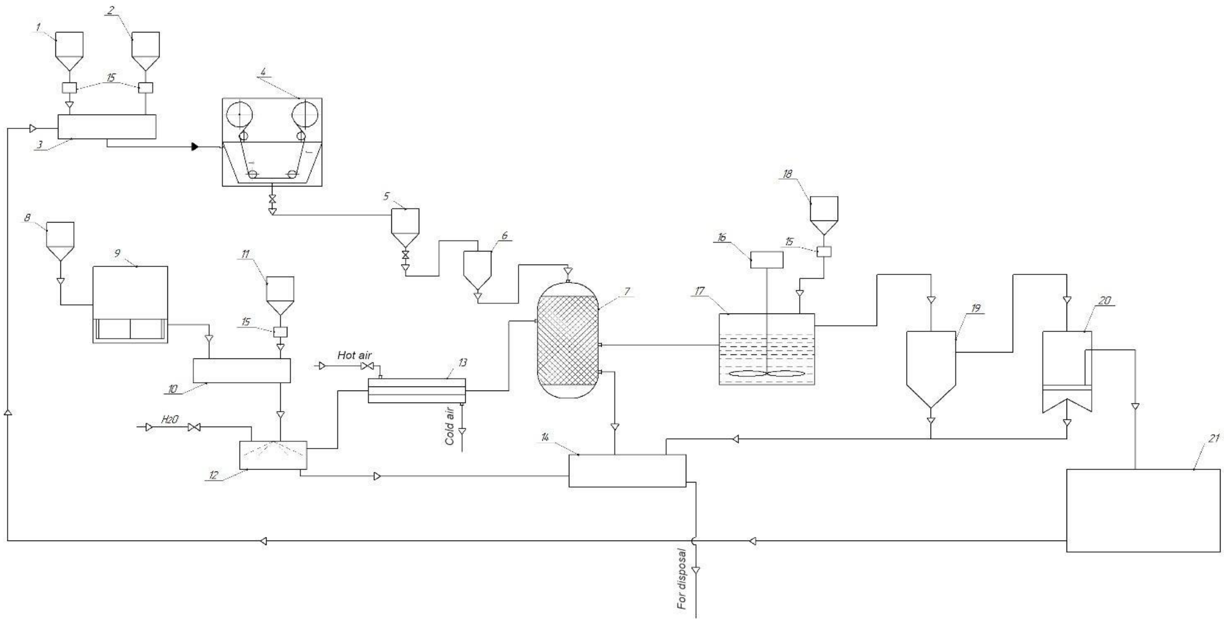

Fig. 4. Schematic diagram of the dyeing cotton fabric's resource-saving technology in a periodic way with repeated use of dyeing and finishing production's adsorption purified wastewater [46]: 1 - tank with process water; 2 – container with dye and auxiliary substances (table salt, crystal soda); 3 - container for the dyeing solution preparation; 4 – roller dyeing machine (jigger); 5 - wastewater collector (averager); 6 – pretreatment filter for wastewater; 7 – contact device for adsorption cleaning (adsorber); 8 – tank with zeolite; 9 – muffle furnace; 10 – tank for acid modification of zeolite; 11 – container with 10% sulfuric acid; 12 – tank for zeolite washing; 13 – dryer; 14 – sludge collector; 15 – dispensers; 16 – electric drive; 17 – mixer; 18 - tank with coagulant and flocculant; 19 - sump; 20 – vacuum filter; 21 – tank with purified water.

The method of wastewater treatment according to this scheme is as follows. The softened process water from container 1 and dye with auxiliary substances from container 2 are mixed in container 3 to become a dyeing solution. Then it's fed to the roller dyeing machine (jigger) 4, where the fabric dyeing process takes place. Wastewater is collected in the appropriate collector (averager) 5 after dyeing. Later, it enters the pretreatment filter 6, where dispersed particles are retained, and about 50 % of organic substances are removed. The filtered wastewater is fed into the contact apparatus of adsorption purification 7, where its purification is carried out. A zeolite adsorbent is also supplied to contact apparatus 7, which enters the muffle furnace 9 from tank 8. Then, zeolite adsorbent spends 4.5 hours at a muffle furnace (at 450 °C). It becomes thermally activated by calcination to release moisture from its pores, which improves the zeolites' adsorption properties. After the furnace, the zeolite is cooled to room temperature without access to air. The thermally activated sorbent is supplied into the tank for acid modification 10, into which 10 % sulfuric acid is fed from tank 11 for the acid modification

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of the mineral. The acid-modified zeolite is washed ten times in tank 12, then dried in dryer 13 at a temperature of 105 °C (30 minutes) until a constant mass is reached. This allows it to significantly increase its adsorption capacity, the number of macropores, and the efficiency of the adsorption process. The prepared zeolite is served into the adsorber (contact device) 7 for direct wastewater treatment. The absorption of dyes and auxiliary substances from wastewater by modified zeolite is performed in the contact apparatus. The spent zeolite is discharged into the sludge collector 14 and disposed of. Purified wastewater from the contact apparatus is sent for further purification (coagulation and flocculation) to mixer 17, into which solutions of aluminum sulfate coagulant and sodium alginate flocculant are fed from container 18. The resulting solution is mixed with the help of electric drive 16 (for 5 minutes). After intensive blending and coagulation in the mixer 17, the compound enters the settling tank 19, where the formation and precipitation of flakes occur. After settling, the mixture is fed to a vacuum filter 20 for more complete water purification from suspended impurities, removal of unsettled formed flakes, and impurities of clay rock – zeolite. As soon as filtering ends, the water fills tank 21 and is fed into container 3 to prepare a technological solution and further fabric dyeing. Dispensers 15 are used for dosing dyes and other substances.

The expense of water treatment was calculated by comparing the costs of softening process water and cleaning wastewater with a zeolite sorbent (Table 7) to implement the proposed new technology. PJSC CSP uses an ion exchange water softening system with KU-2-8 cationite to prepare water for dyeing. There is a well for extracting water on the enterprise's territory, which is softened and used later in technological processes.

Table 7

Cost of adsorption water treatment

Economic indicators	Extraction of 1 m^3 of water from a well	Softening and disposal of 1 m^3 of water	Purification of 1 m^3 of wastewater by adsorption method (without taking into account the electricity costs of the working agitator)
Prime cost*, UAH	2.2	119.1	107.3
Cost savings, %	10		

* the prime cost is calculated based on prices as of January 1, 2022

Implementing the adsorption method for wastewater treatment in dyeing and finishing production for reuse will save 10 % in cost.

Conclusions

For the first time, the possibility of reusing treated wastewater from the dyeing and finishing production with a natural sorbent zeolite in the technology of dyeing cotton fabric with reactive dyes was established and experimentally proved.

For the first time, wastewater purification using the adsorption method is one of the ways to reuse it as a secondary resource in fabric dyeing technology.

The possibility of using purified wastewater from dyeing and finishing production with zeolite as a natural sorbent in the dyeing cotton fabric with reactive coloring agents was investigated for the first time. Experimentally, it was determined that the use of purified wastewater in the technology of Coarse calico (art. 3461) dyeing, produced by PJSC CSP, ensures the color intensity of the dyed cotton fabric at the level of 96–99 % compared to the standard (100 %). According to the Gray standards scale, the obtained coloring stability is at the level of 4–5 points. Experiments have shown that the two-time purification of the same wastewater allows its use for dyeing cotton fabric with Reactive Blue CB-RF and Reactive Red S-matrix dyes (the intensity of the dyed fabric color is within 96 %). The color difference of all the examined fabric samples has the smallest value (DE < 2) between the reference and dyed samples, and the qualitative indicators of the obtained samples' color fastness are within the numerical limits of the reference ones.

Based on the obtained research results, a schematic diagram of the dyeing cotton fabric technology with reactive color agents and the repeated use of adsorption-purified wastewater was developed for the first time. According to this scheme, dyeing has been tested in the production conditions of PJSC CSP and has practically significant results.

The prime cost of water treatment is calculated by comparing the costs of softening process water and cleaning wastewater with a zeolite sorbent for its reuse. Cost saving is 10 %.

For the first time, a resource-saving technology for dyeing cotton fabrics with reactive dyes has been developed, based on the reuse of wastewater from the dyeing and finishing production treated by adsorption in the process of dyeing textile materials.

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