Repeated Use of Purified Wastewater in the Dyeing of Polyether Fabrics with Dispersed Dyes

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The article presents the results of reuse of treated wastewater from the dyeing and finishing production in the technology of fabric dyeing. The wastewater is purified by adsorption using natural zeolite, followed by coagulation and flocculation. The purified water is reused in the process of dyeing polyester fabric with dispersed dyes of Dark Blue Z, Red 2C, Yellow Stable 2K. They ensure the intensity of fabric coloring at 95-99.9% compared to 100%. The stability of the obtained color is at the level of 2-4 points according to the greyscale. The double treatment of the same wastewater makes it easy to dye Polyether fabric with dispersed Dark Blue Z dye.

Introduction

The textile industry ranks first in the use of coloring agents for dyeing fibers and textile materials among all branches of industry. Annually, about 7×10^7 tons of synthetic dyes are produced worldwide, and more than 10.000 tons of such dyes are used by the textile industry (1). According to recent data, India alone as one of the leading textile processing countries produces 100.000 tons of dyes and pigments per year (2). Along with dyes, water is one of the main resources of the textile industry. A textile enterprise with a daily production capacity of 8.000 kg of fabric has a daily water consumption of about 1.6 million liters. Almost 25% of the water from the total consumption is required for dyeing and filling processes (3) and about 80% of the used water is discharged as wastewater (4).

Dyes are not tightly bound to the fabric in the technological processes of textile processing and are discharged in the form of wastewater into the aquatic environment without preliminary treatment. Thus they create serious ecotoxicological threats with a toxic effect on living organisms (5). Azo dyes, which structurally contain one or more azo groups, are the largest class (more than 60%) among various groups of textile dyes and the most widely used dyes in the textile industry (6). Inefficient textile dyeing processes lead to the fact that 15–50% of azo dyes, which are not bound to fibers and fabrics, are released into the generated wastewater (7).

Therefore, it is urgent to develop cost-effective and ecological approaches to the proper treatment of industrial wastewater from dyeing and finishing production with expedient reuse in technological processes of textile production to avoid a negative impact on the environment, human health, and natural water resources, as well as to reduce significant water consumption in the textile industry.

The transition from a linear to a circular economy is relevant in the world economy of the water sector. There is no connection between waste management and resource use in the linear economy model since the main approach in the linear economy is “extraction-production-use-disposal” (8, 9). Here are the main advantages of treated wastewater reuse in technological processes of the textile industry: reduction of environmental problems; increasing production productivity; use of purified water in other industries that require significant water use; reducing dependence on freshwater (especially in drought-affected regions where there is a massive demand for freshwater); the minimum need for the number of labor resources, since the reuse of wastewater, is a mechanized process, so additional labor is not required (10). Water reuse is an important aspect of sustainable water management, especially when it is done to improve local water supply and reduce wastewater production (11). However, water used in textile processing, especially in the dyeing stage, must meet stricter quality requirements than that used to discharge into the environment (12). Therefore, it is necessary to develop effective purification processes aimed not only at the removal of color and organic matter but also at the recovery of salts and other components (13) for the reuse of purified wastewater to be economically beneficial; these processes have to lead to wastewater treatment with the maximum quality required for reuse (14).

Flocculation, filtration, coagulation, photodegradation, membrane processes, photocatalysis, reverse osmosis, and chemical oxidation are those modern physicochemical methods used for wastewater treatment. These methods are effective for color removal but they have a high cost, limited application, and problems of secondary pollution - formation of sludge, toxic gases, etc. (15, 16). There is a fairly simple and effective solution for sorption treatment among the methods that are successfully used to solve the complex task of dyeing and equipment industries’ wastewater treatment (17). The advantages of the sorption method include the possibility of removing pollutants of an extremely broad nature; the absence of secondary pollution; the use of inexpensive adsorbents; high cleaning efficiency; the short time required to remove dye from wastewater; the possibility of cleaning wastewater from such organic substances that could not be removed by other methods (18-20). The reuse of water obtained from the treatment of textile effluents with the help of adsorbents in new dyeing processes is increasing due to the high percentage of water that can be reused for fabric dyeing (21).

Researchers from many countries have studied the problem of cleaning industrial wastewater and the possibility of its reuse in technological processes, in particular, in fabric dyeing technology.

The document (22) describes the possibility of dyeing wastewater electrooxidation from the textile industry using a boron-doped diamond anode, which will ensure the quality of purified water required for reuse. The effect of current strength on the quality of treated wastewater and successive reuse in new dye baths was studied. It was determined that during the two cycles of purified wastewater reuse the samples of dyed cotton fabrics corresponded to the control ones, which indicates its effective sequential reuse. In addition to the reuse of water and complete saving of salts, electrooxidation allowed the reduction of ecotoxicity by 18.6 times.

The aim of the research described by scientists from Croatia (23) was to study the feasibility of a membrane hybrid process for real textile wastewater treatment and its potential reuse in the process of cotton-knitted fabric dyeing. The raw textile wastewater samples required for this study were collected from the discharge effluent of the GALEB d.d. textile factory (Zagreb, Croatia), specializing in the production of cotton clothing. Research on wastewater treatment was carried out in several stages: the first stage included preliminary treatment, sand filtration, and coagulation. The wastewater was treated on flat UF membranes in the second stage. The final stage was wastewater treatment with nanofiltration and reverse osmosis. The innovative aspect of this research consists of the full analysis of hybrid membrane separation processes for purified textile wastewater reuse, the proposal of a new reuse criterion for cotton-knitted fabric, and the economic feasibility of implementing the proposed technology.

Adsorption wastewater treatment was considered in the following work (24). The potential of using industrial waste “filtration earth” (composed of bentonite) provided by the Bunge company (USA), which was used for the clarification of soybean oil, was investigated. The adsorbent used in this study was not chemically treated. It was first dried for 24 hours at 60°C, and then calcined at 180°C. Treated industrial waste was used to purify aqueous solutions containing Direct Black 22 and Reactive Blue 222 dyes donated by DyStar (Singapore). The result of the study is a good adsorption potential of industrial waste, reaching 95.7% efficiency; using 1.0 g of calcined adsorbent at 60°C, and 95.7% decolorization of dye solutions. The purified water was reused in new dye baths for dyeing cotton fabric. The color characteristics of the dyed cotton fabrics were close to the standard ones, and the color difference index was DE<1; painted samples were resistant to washing and rubbing.

The main goal described in the study (25) was to reduce water consumption in the process of dyeing textile materials due to its purification and reuse of purified water in new dye baths. The cleaning efficiency of the chemical coagulation and electrocoagulation combined process with the removal of synthetic dyes Reactive Yellow 145 and Reactive Red 194 was evaluated. The wastewater produced in the dyeing process was decolorized with a mixture of alum and chitosan. The fabric's color was analyzed using washing, rubbing, and creasing fastness experiments. The combined treatment process was found to be very effective in decolorizing both dyes by 99.1% and 96.15%, respectively. The difference in color of the standard (dyed in freshwater) and serial samples for both dyes was 0.53 and 0.35, which is within the acceptable limit (≤1,0). The wash fastness test showed a range of 4-5 points for both standards. The conducted research allows us to conclude that the combined treatment of chemical and electrocoagulation is very effective for decolorizing wastewater containing dyes and the possibility of reusing purified wastewater in new technological processes of fabric dyeing.

The dyeing plant described in (26) by researchers from India dyed cotton fabric and generated a significant volume of wastewater containing inorganic chemicals and Reactive Green dye. For the dyeing process, the coloring agent was added at the rate of 0.1 – 3.0% of the fabric's weight. Dyeing was continued for 2-3 hours depending on the desired shade obtained. Wastewater samples were collected and characterized for the following parameters: pH, total hardness, dry residue, calcined residue, acidity, and alkalinity. Coagulation and flocculation with alum and chemical oxidation with bleaching powder were carried out separately in the first stage. Coagulation and flocculation showed low color removal - about 65%. Then, the wastewater, pre-treated with a 10% solution of bleaching powder, was purified by the adsorption method, using crushed burnt coal as an adsorbent. After several trials, this combination was found to be effective, removing 10% char content with an adsorption contact period of 90 minutes, showing a color reduction of 85-97%.

Paper (27) describes the reuse of wastewater in the dyeing of polyester fabrics with an encapsulated disperse dye. In this study, polyurethane-urea microcapsules were formulated by interfacial polymerization and encapsulated with C.I Disperse Blue 60 for the dyeing of polyester fabric without the use of dispersing agents and other auxiliaries. The dyeing was carried out in a high temperature dyeing machine with a very simple dyebath, in which there are only dissolved dye molecules, microencapsulated dyes and the fabric.

Additionally, the dyebath wastewaters were reused on a further dyeing as 100% bathwater and mixed with 50% distilled water. Colorimetric measurements show excellent colour removal in both samples.

The review and analysis of research by many scientists show the need to solve the problem of saving the main resource of the textile industry - water by creating a resource-saving technology for fabric dyeing with the repeated use of purified wastewater from the dyeing and finishing industry. The cyclical use of wastewater will lead to a reduction in the amount of emissions of toxic substances into the environment, which will improve the state of the environment and water resources, as well as reduce the cost of finished textile products. This is the basis for conducting laboratory and industrial research.

The purpose of the work is to experimentally investigate the possibility of reusing wastewater from the dyeing and finishing industry, purified by the adsorption method followed by coagulation and flocculation in the technology of dyeing Polyether fabric with dispersed dyes.

Experimental part

Material and methods

The main reason for the synthesis of dispersed dyes over the last two decades is a significant increase in the global production of polyether fibers since lots of these dyes are used mainly for dyeing Polyether fabrics (28, 29).

Disperse dyes are water-insoluble or slightly water-soluble azo dyes that dye textile fibres and fabrics from aqueous dispersions.

Anthraquinone derivatives are a common group of dispersed dyes which account for up to 30% of known dispersed dyes (30). They are used for dyeing all synthetic fibres (nylon, lavsan, nitron, polyester) and artificial acetyl cellulose fibres and fabrics made from them. Powdered (release forms) contain 10-15% dye, dispersants, and wetting agents (31, p. 112). All dispersed dyes have in common: the absence of sulfo-, carboxy- and other ionogenic groups in their structure, which give the dyes the ability to dissolve in water; small molecular weight and relative simplicity of the molecular structure; these dyes do not undergo any chemical changes in the process of dyeing, dyed fabrics have high light fastness, medium resistance to washing and soap action (32). Dispersed dyes are poorly soluble in water and aqueous solutions: from fractions of a milligram to several milligrams in 1 dm3 at room temperature and up to 50-350 mg/dm^3 at 80°C. The extremely low solubility of dispersed dyes in water makes it necessary to use them in dyeing processes only in the form of aqueous suspensions, usually with a particle size of 0.2 to 2 μm. In this regard, the degree of dispersion, homogeneity, and stability of the dispersion composition of these dyes in the final forms acquire special importance (33).

Disperse dyes are a versatile and valuable tool for the textile industry, with properties that make them ideal for use in fabric dyeing technologies. These dyes are able to penetrate so deeply into the fibres that they create a uniform, long-lasting colour that is resistant to fading and washing. Disperse dyes are known for their bright, intense colours and can be used to create a wide range of shades and tones. Disperse dyes have high heat resistance, making them ideal for textiles that are exposed to high temperatures.

Disperse dyes are known for their low environmental impact during the dyeing process, as they do not require the use of harsh chemicals or high temperatures. Unlike other types of dyes, disperse dyes do not contain heavy metals, so they are not toxic to the environment. As the textile industry continues to evolve and innovate, disperse dyes will play an important role in shaping the future of the industry (34). Disperse dyes are used to dye fabrics for use in automobiles, high visibility clothing, sportswear, inkjet and transfer printing. Dispersed dyes can be used to colour polyvinyl chloride, polypropylene cellulose and plastic (35). Dispersed dyes have no affinity for hydrophilic polymers such as cellulose, making them unsuitable for dyeing cotton and paper (36).

Dispersed dyes of three main colors were used in the work: dispersed Dark Blue Z, dispersed Red 2C, and dispersed Yellow Stable 2K (**Figure 1**).

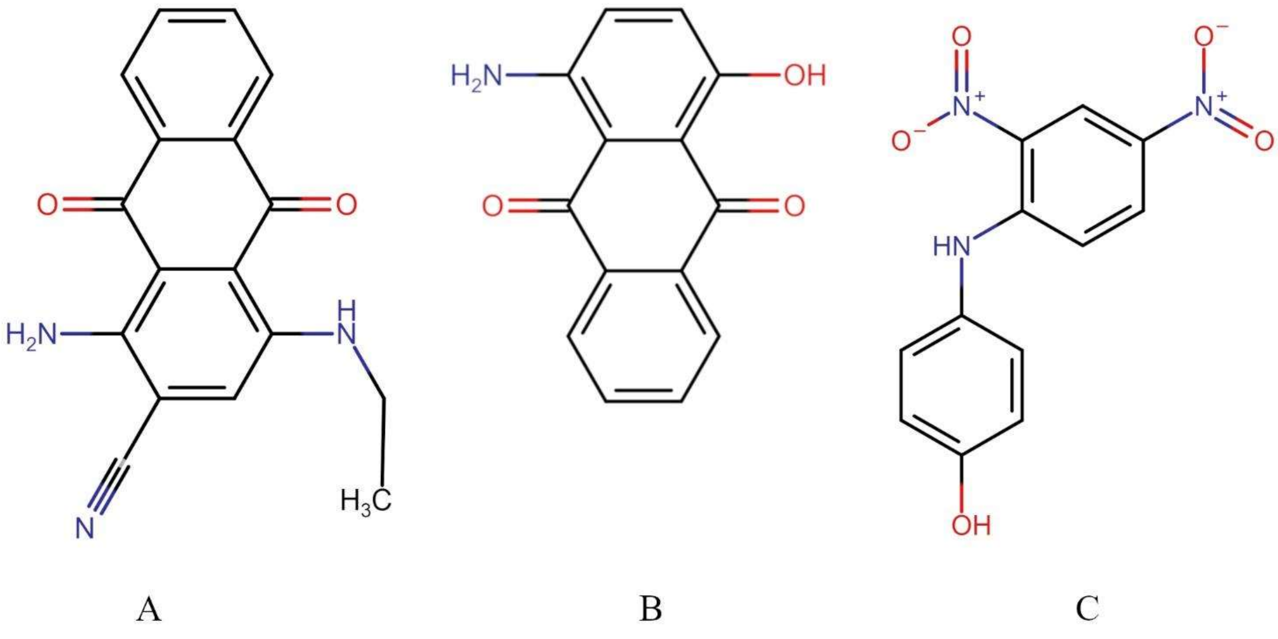


Figure 1. Molecular formulas of dispersed dyes: A – Dark Blue Z (dispersed Blue 359); [1-amino-4-(ethylamino)-9,10-dioxoanthracene-2-carbonitrile; 1-amino-4-(ethylamino)-9,10-dioxoanthracene-2-carbonitrile] (37); B – Red 2C (dispersed Red 15); [1-amino-4-hydroxyanthracene-9,10-dione; 1-amino-4-hydroxyanthracene-9,10-dione] (38); C – Yellow Stable 2K (dispersed Yellow 1); [4 (2,4-dinitroanilino) phenol; 4-(2,4-Dinitroanilino)phenol] (39).

Dispersed Dark Blue Z and Dispersed Red 2C are anthraquinone compounds by their molecular structure. Anthraquinone dyes are based on anthraquinone (**Figure 2**), whose molecular skeleton is a good chromophore due to its quinoid structure, which provides the colour of the dye.

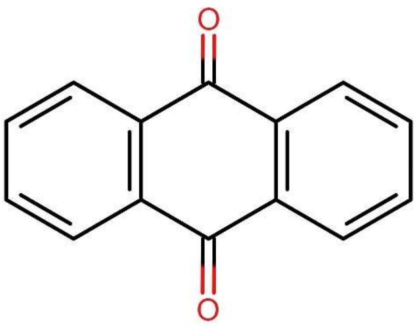


Figure 2. Structure of the anthraquinone molecule

Almost all of these dyes are modifications of known structures, which have been chemically synthesised with various substituents to increase or deepen the shades and improve the stability of colour characteristics (30).

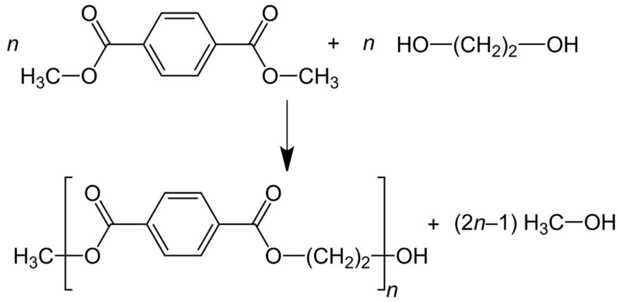
Dispersed Yellow Stable 2K dye is a molecular structure of Nitro diamines.

Upon entering the dye bath, a small portion of the dye passes into the solution, and this portion is gradually absorbed by the fabric during the dyeing process. It is accompanied by the simultaneous transition of the dye's appropriate amount from the dispersed state to the soluble state to maintain the equilibrium concentration in the solution and on the surface of the fabric. Dyeing with dispersed dyes takes place in the following stages (40):

- diffusion of a dispersed dye in the solid phase into water by disintegration into separate molecules. Diffusion depends on the dispersion and solubility of the dye and is caused by the presence of dispersing agents and an increase in temperature;
- adsorption of the dissolved dye from the solution onto the fabric surface. Dye adsorption by the fabric surface is affected by the solubility of the dye in the bath and in the fabric fibres;
- diffusion of the adsorbed dye from the surface of the fabric into the inner part of the fibrous substance. The rate of adsorption is always greater than the rate of diffusion in a normal state.

Polyether is one of the most widely used fabrics because it is inexpensive, strong, and elastic. Polyether is a synthetic material obtained from molten polyethylene terephthalate by the extrusion method (41).

The starting materials for the production of polyethylene terephthalate are terephthalic acid or its dimethyl ester (dimethyl terephthalate) and ethylene glycol (a dibasic alcohol). The synthesis is carried out in two stages: in the first stage, dimethyl terephthalate and ethylene glycol are transesterified in a melt at 150-200°C in the presence of a catalyst (zinc acetate, manganese (II) acetate) in a continuous process. Methanol is removed by distillation. Excess ethylene glycol is distilled off at a higher temperature under vacuum.



The second stage of transesterification is carried out at 270-280 °C under vacuum with stirring of the reaction mass for 4.5-6 hours. The by-product is ethylene glycol, which is removed from the reaction mass by continuous distillation (42, 43).

Polyether are characterized by a high degree of orderliness of the internal structure; there is an interaction between very elongated macromolecules due to van der Waals forces and hydrogen bonds between the oxygen atoms of the ester or carboxyl groups and the hydrogen in the benzene ring. The high density of the structure and the absence of reactive groups in the macromolecules determine the physical, mechanical, and chemical properties of these fabric. Polyether fibers are highly elastic. The elongation is completely reversed when stretched by 5-6%. Polyether fibers have higher friction resistance than natural fibers. The absence of active hydrophilic reactive groups in the molecules for attaching dyes leads to the fact that these fibers are hydrophobic, practically do not swell in water, and are very difficult to dye. Special high-temperature dyeing methods are used (at t = 120-135°C) for dyeing these polyester fabrics. They have high resistance to the action of oxidants and are characterized by high biostability (42, pp. 136-137). Polyether is strong and wear-resistant, light and thin, heat-resistant, and fireproof (the fabric is almost impossible to burn: it goes out when the source of ignition is removed). Tents and sleeping bags sewn from it do not let water pass and do not burn out. Polyether fabric is easy to care for, rarely wrinkle, and dries quickly without losing its shape after proper washing. Along with the advantages, polyester fabric and products made from it have a several disadvantages: artificial origin and low hygienic properties. Such a fabric can cause allergic reactions and does not support comfortable heat and air exchange during operation is stiff, highly electrified, products get dirty quickly, wash poorly, require antistatic treatment, with improper care (washing or ironing at high temperatures t > 50°C) fabrics are glued together, forming unattractive folds that cannot be ironed (44). The light industry widely uses this fabric for sewing bed linen, overalls, napkins, flags, and casual clothes for adults and children.

The paper presents the results of dyeing Polyether fabric (100%, article 033), the properties of which were investigated under the conditions of the Private Joint Stock Company Cherkasy Silk Plant (PJSC CSP) (Cherkasy, Ukraine) and are listed in **Table 1.**

Acetic (ethanoic) acid (CH_3COOH, DSTU ISO 753-1:2003; ISO 753-1:1981, IDT (45)), (98-99%) is an organic compound that belongs to the group of weak acids. It's a colorless transparent liquid with a sour taste and a sharp unpleasant smell; hygroscopic, flammable liquid, and miscible with water and ethyl alcohol in any ratio. When it gets on human mucous membranes, it causes a chemical burn.

Table 1. Indicators of physical and mechanical properties of Polyether fabric (100%, article 033)

Indicator		Numerical value of the indicator
Fabric width, cm		155
Surface density, g/m^3		105.6
Density, number of threads per 10 cm	warp thread	720
	weft thread	450
Breaking load, N	warp thread	1130
	weft thread	680
Elongation at break, %	warp thread	30
	weft thread	26
Air tightness, dm^3/m^2s		426
Fabric mass (1200 running meters (RMTs)), kg		201.358

The dye bath must be acidic for dispersed dyeing, pH = 4-5.5, so acetic acid is used to control the pH of the dyeing bath. This is necessary to maintain dye exhaustion and obtain a stable color of the dyed fabric (46).

The photocolorimetric method was used to study the analysis of dye baths and produced wastewater using a spectrophotometer UV-5800 PC (China). The color characteristics of the examined fabric samples were determined using 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 reference ones used by the PJSC CSP samples and by determining the color fastness by the current state standards of Ukraine and international ISO standards (DSTU 3998-2000 (47), DSTU ISO 105-X12:2016 (for dry crocking) (48), DSTU ISO 105-A02:2005 (Gray standards scale) (49), DSTU EN ISO 105-C10:2020 (washing with soap) (50).

Color fastness to dry crocking is measured on the Stainingtester device (Computex, Hungary) according to DSTU ISO 105-X12:2016 (48): according to a sample of the tested fabric with a length of 10 cm, the head of the device, which is covered with white cotton fabric, under a load of 9N makes 10 moves forward and back. At least three samples are taken for the test. The arithmetic mean of all measurements is taken 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

Averaged diluted (1:100) wastewater from the active dyeing and finishing production of PJSC CSP was subject to purification with a study of possible reuse. 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 was used. Wastewater treatment was carried out in the following sequence (51, 52):

- preparation of zeolite clays (sieving through a sieve, washing, drying, and thermal activation). Thermal activation was carried out in a muffle furnace of the SNOL - 1,6.2,5.1/9 - I4 type by baking at a temperature of 450ºC for 4.5 hours;

- chemical modification of zeolite was carried out by immersing the adsorbent in a 10% solution of sulfuric acid under normal conditions for 1 hour (volume ratio 1:2 solid phase: solution);

- wastewater treatment with thermally activated and chemically modified zeolite is one of the most common and effective methods of adsorption - long-term contact of liquid and solid phases at rest: loading a fixed layer of zeolite into the volume of wastewater being purified;

- coagulation and flocculation of wastewater (coagulant $Al_2(SO_4)_3$ (20 g/dm^3), flocculant $(C_6H_7O_6Na)_n$ (1%). The flocculant is sodium alginate, which is used to increase the efficiency of the coagulant and to provide more complete water treatment. Laboratory tests have shown that the optimal coagulant dose to achieve the maximum degree of water treatment is 2 mg/dm^3. The study was carried out using a continuously operating electric stirrer with a speed of 300 rpm. The resulting suspension was settled for 24 hours and filtered;

- physical and chemical analysis of purified wastewater was carried out and compared with the properties of PJSC CSP's technologically softened water (softening is carried out with the help of Cationite KU-2-8 GOST 20298-74 P.12 vol.2. The results of the study are shown in **Table 2** (53). Since the color of dyes is a consequence of their interaction with light, the quantitative assessment of the wastewater and purified watercolor was carried out by the spectrophotometric method, using the spectrophotometer UV-5800 PC (China). The result of the physico-chemical analysis of purified wastewater confirms its conformity to technologically softened water. The degree of wastewater purification is 91% (51), which indicates the possibility of its use in the dyeing textile materials technology and requires further research.

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 (0-0.25 mmol/dm^3) [54]. The dye is not fixed on the fabric at a hardness of more than 0.25 mmol/dm^3, which leads to the need for repeated processing and dyeing, and subsequently to the disposal of the scroll of defective fabric.

Spent zeolite phytotoxicity was determined by the method of laboratory phytotesting to its further disposal or use. Phytotoxicity was determined by a series of experiments on the germination of winter barley seeds of the «Devyaty Val» variety of Ukrainian selection with different initial conditions and on various research substrates: water extracts from native and spent zeolite, a mixture of soils with native and spent zeolite; substrate-concentrate – native zeolite and spent zeolite (55).

Three samples were tested as substrates for a mixture of soil with native and waste zeolites: 1- chernozem soil (control), 2 – a mixture of soil with native zeolite (the ratio of soil and zeolite by mass is 4:1, respectively (56)), 3 – a mixture of soil with spent zeolite (4:1 by mass, respectively). The soil is a typical chernozem (Chervona Sloboda village, Cherkasy district, Cherkasy region, Ukraine). The content of the humus is 2.4%. The weighted phosphorus content is 158 mg/kg, the nitrogen content is 90 mg/kg, and the potassium content is 62 mg/kg

(57). Since barley germinates at a 6-7.5 pH value, this value was determined in the studied soil samples by preparing water extracts that were tackled according to DSTU 7534:2014 "Greenhouse grounds. Method for preparation of water extract". It was found that the pH of the soil water extract is 7.5; the pH of the soil mixture with native zeolite aqueous extract is 7.7; The pH of the soil mixture with spent zeolite aqueous extract is 7.6. Pre-soaked barley seeds (for 12 hours) were planted in accordance with the international standards ISO 11269-1 and ISO 11269-2 and were grown directly in the soil and the studied mixtures (20 seeds in each sample). Maintaining constant humidity of the studied samples was a mandatory condition for the experiment. Plants have been growing at a temperature of 16°C for 12 days. Each version of the experiment was carried out in triplicate. The seed germination time was recorded in the course of the study, the same as the total number of seeds that emerged and the height of the stems. Similarity of winter barley grains for control is 95%, for native zeolite - 100%, and for spent zeolite - 85%. Photos of germinated seeds are presented in **Figure 3**.

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.

A B C

Figure 3. Photos of germinated winter barley seeds on soil substrates: A – soil (control), B – mixture of soil with native zeolite; C – mixture of soil with spent zeolite

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The phytotoxicity index is calculated according to the formula (58):

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

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.

Table 3. Average values of the winter barley stem height bioparameter and phytotoxicity on soil substrates

Investigated substrate	The average value of the winter barley stem height, cm	Phytotoxicity, %
Soil (control)	11.1	-
Mixture of soil with native zeolite	10.6	4.5
Mixture of soil with spent zeolite	10.4	6.3

As a result of the study, it was determined and mathematically calculated that the phytotoxicity (P) of spent zeolite does not exceed 20%, which, according to the existing criteria (when P <20% (59)), indicates the absence of toxicity (52). The obtained results make it possible to predict the possibility of its reuse as a secondary resource in the building materials creation (production of concrete solutions, foam, and aerated concrete, cement), for the traffic-bearing surface creation and ensuring its stability.

In this way, the problem of spent zeolite utilization as a solid by-product of wastewater treatment by the adsorption method is solved; this will contribute to reducing the ecological burden on the environment.

The reuse of wastewater purified by the adsorption method in fabric dyeing technology was studied experimentally in the production conditions of the PJSC CSP's dyeing and finishing production. Dyeing of Polyether fabric (100%, article 033) with dispersed dyes was carried out on an AHIBA NUANCE CH-6015 laboratory dyeing machine (Datacolor, USA). The composition of the dyeing solution and conditions are given in **Table 4**. Dyeing is carried out periodically according to the PJSC CSP's high-temperature technological mode. 2 g of Polyether fabric is immersed in the dye bath under laboratory conditions. Dyeing starts at a temperature of 40°C, the bath is heated to 130°C and dyed at this temperature for 40 minutes. After dyeing, the fabric is washed with tap water and neutralized with an alkaline solution of the reducing agent at a temperature of 70°C for 20 minutes (sodium hydroxide solution, 32%), the fabric is saponified with the detergent PERLAVIN OSGB conc. (1-2 g/dm^3) (manufactured by Dr. PETRY, Germany) stable in an alkaline environment.

Table 4. The composition of the dyeing solution used to dye the Polyether fabric (100%, article 033) (by a dye bath volume of 80 cm^3 for a laboratory dyeing machine)

Dye solution reagents	The amount of reagent according to the PJSC CSP's technology	The amount of reagent using purified wastewater
A solution (3%) of pre-boiled dispersed dye, cm^3	12	12
Ethanoic (acetic acid) (98-99%), cm^3	0.25	0.25
Process water (softened)*, cm^3	67.75	-
Wastewater purified by the adsorption method, cm^3	-	67.75

*softening is carried out at PJSC CSP with the help of Cationite KU-2-8 GOST 20298-74 P.12 vol.2.

Restorative treatment and subsequent washing of the dyed material ensure the most complete unfixed dye removal from the fabric's surface and improvement of color resistance to friction. Washed samples are dried in an oven at a temperature of 100°C for 5-7 minutes. The obtained dyed fabric samples (**Figure 4**) are examined for the intensity and stability of the color.

A B C
1 2 1 2 1 2

Figure 4. Samples of Polyether fabric dyed (100%, article 033) with dispersed dyes: A – Dark Blue dye Z, B – Red dye 2C, C – Yellow Stable 2K; 1 – with the use of softened process water, 2 – with the use of wastewater purified by the adsorption method.

The quality and stability of the obtained dyes were determined by comparing them with the reference ones, which served as samples dyed using softened water according to the PJSC CSP's technology (**Table 5**). When determining the indicators, the color of the sample is placed in the CIELab space and compared with the color standard for production.

Table 5. Color characteristics of the dyed Polyether (100%, article 033) with dispersed coloring agents using water purified by the adsorption method

Dye	Lightness dL	Hue (red-green) dA	Hue (yellow-blue) dB	Color difference dE*	Color intensity, % according to the standard (100%)
Dispersed Dark Blue Z (60)	-0.01 darker	+0.05 redder	-0.19 bluer	0.2	99.9
Dispersed Red 2C	-0.21 darker	-0.69 greener	-0.50 bluer	0.88	97.9
Dispersed Yellow Stable 2K	+0.47 lighter	-0.56 greener	+0.45 yellower	1.21	95.3

* Color difference is a mathematical representation that allows numerically expressing the difference between two colors in colorimetry. dE should not exceed 2, which approximately corresponds to the minimally noticeable difference between colors for the human eye (61, pp. 29-32).

The difference in color between the test sample and the standard is calculated and then compared to the limits (tolerances) of consumer acceptance for the colored product. Acceptance tolerances are established between the customer, who sets the requirement for color quality, and the production, which fulfills this order in the form of finished products (62, p. 2). The PJSC CSP's acceptance tolerances for the tested samples (compared to production reference ones) are the following: the deviation of color intensity is up to 5%, lightness (dL), hues of dA (red-green) and dB (yellow-blue) up to ± 2.

When analyzing **Table 5**, it can be concluded that with a color difference of 0.2-1.21 (dE < 2), the intensity of dyeing Polyether fabric samples using purified wastewater is within 95-99.9% compared to the standard (100%), the lightness and hue indicators of the reference and test samples have a difference within ± 2. Therefore, the values of the quality indicators and color intensity of the Polyether fabric dyed with dispersed dyes are within the acceptable limits of the PJSC CSP enterprise.

Since water is the main resource of dyeing, a task arose during the experiment to investigate the frequency of use of the same wastewater in dyeing processes. The same volume of water was cleaned and dyed three times in the course of the research. The color characteristics of the studied samples were determined experimentally. The results are shown in **Table 6.**

Table 6. Color characteristics of the fabric dyed Polyether (100%, article 033) with dispersed dyes using water purified by the adsorption method, 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	III	II	III	II	III	II	III	II	III
Dark Blue Z	+0.48 lighter	+1.18 lighter	-0.18 greener	-2.29 greener	-1.99 bluer	-3.99 bluer	1.99	2.65	95.2	88.2
Red 2C	-0.71 darker	-1.31 darker	-1.29 greener	-1.79 greener	-1.26 bluer	-2.26 bluer	1.94	2.94	92.9	86.9
Yellow Stable 2K	+0.62 lighter	+0.94 lighter	+0.08 greener	-1.80 greener	+0.02 yellower	+0.72 yellower	0.62	1.87	93.8	92.6

* Color difference is a mathematical representation that allows you to numerically express the difference between two colors in colorimetry. dE should not exceed 2, which approximately corresponds to the minimally noticeable difference between colors for the human eye (61, pp. 29-32).

A significant deterioration of the color characteristics of the dyed fabric is observed while analyzing Table 6. So, we can conclude that one volume of wastewater purified by the adsorption method can be used twice only for dyeing Polyether fabric (article 033) with dispersed Dark Blue Z dye. It is worth using wastewater only after a single adsorption cleaning for dyeing with dispersed dyes Red 2C and Yellow Stable 2K.

The deterioration of fabric colouring after two and three times of wastewater treatment can be explained by the chemical composition of wastewater and treated water presented in **Table 2**. The adsorption treatment of wastewater, including coagulation and flocculation stages, is not perfect in terms of complete removal of soluble mineral salt ions. After re-treatment of the same wastewater, mineral salt ions (SO_4^{2-}, Cl^-) and Fe salts accumulate, which can impair the adsorption capacity of the fabric (fibres) and the dye's fixation by the fibre. At the same time, due to the use of aluminium sulphate as a coagulant during treatment, not all Al^{3+} ions can be precipitated, so their accumulation in aqueous solution can lead to the formation of a dilute colloidal solution with the formation of the corresponding hardly soluble hydroxide $Al(OH)_3$ according to the scheme:

$$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+$$

An increase in the temperature of the dye bath at which dyeing is performed according to the technological regime (130°C) can contribute to the formation of a dilute colloidal solution due to the formation of a micelle of the composition $\{[Al(OH)_3]_m nAlO^{+}(n-x)Cl^{-}\}3xCl^{-}$. These factors can be the main reasons for the deterioration of the dyeing intensity with each repeated process, starting from the first. However, the first cycle of reuse (one-time treatment) of wastewater gives effective results in terms of intensity and durability of colours.

The dyed fabric samples were tested for color fastness to dry and wet crocking, washing with soap (according to the current state standards of Ukraine and international ISO standards) (**Table 7**). Qualitative indicators of dyed fabric samples' color fastness were studied by DSTU ISO 105-A02:2005 Gray standards scale, to dry and wet crocking (DSTU ISO 105-X12:2016), washing with soap (DSTU EN ISO 105-C10: 2020). Color fastness to dry and wet crocking is measured on the Staining Tester (Computex, Hungary) according to DSTU ISO 105-X12:2016 (48).

The durability indicators of the Polyether fabric (100%, article 033) investigated samples dyed with dispersed dyes using purified water practically do not differ from those of the dyed fabric using softened process water.

Table 7. Qualitative indicators of dyed fabric Polyether (100%, article 033) coloration with dispersed dyes after the first (I) and second (II) treatment of wastewater

Dye	Color fastness, points											
	Dry crocking				Wet crocking				Washing with soap			
	DPW*		PW*		DPW*		PW*		DPW*		PW*	
	I	II	I	II	I	II	I	II	I	II	I	II
Dark Blue Z	2	2	2	2-3	2	2	2	2	4	4	4	3-4
Red 2C	2	2	3	2-3	2	2	3	2	4	4	4	4
Yellow Stable 2K	3	3	3	2-3	3-4	3-4	3	3	4	4	4	4

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

The reuse of water purified by the adsorption method with natural zeolite was investigated during the dyeing of reactive (63) and direct dyes on Calico (article 3461) and Viscose (article 3324) fabrics. The colour intensity of the dyed fabric samples was within 96-99%. A basic flow chart of the process of dyeing cotton fabrics with active and direct dyes with the reuse of treated wastewater has been developed.

Since the adsorption method of industrial wastewater treatment is cheap, simple and effective, research is currently underway to use natural bentonite clay from the Dashukivske deposit in Cherkasy region (Ukraine) as an adsorbent and to reuse the water treated by this method in the fabric dyeing technology.

Conclusions

The possibility of reusing wastewater from the dyeing and finishing production was experimentally investigated for the first time. Wastewater purified by adsorption with natural zeolite, followed by coagulation and flocculation, is used in the process of dyeing polyester fabrics with disperse dyes.

It was experimentally determined for the first time that the reuse of purified wastewater in fabric dyeing technology Polyether (100%, article 033) ensures the intensity of fabric coloring at 95-99.9% compared to the standard (100%). The stability of the resulting color to dry and wet crocking, the action of the soap is at the level of 2-4 points according to the Scale of gray standards.

It was investigated through a series of experiments that the double purification of the same wastewater allows its use for dyeing Polyether fabric (100%, article 033) with dispersed Dark Blue Z dye. The color intensity of the dyed fabric is 95.2% and the color difference of the tested samples is significant DE < 2 between the reference and dyed samples. The quality indicators of the tested samples are within the reference range. It is worth using wastewater only after a single adsorption treatment for dyeing with Red 2C and Yellow Stable 2K dyes.

It has been determined that wastewater from dyeing and finishing production, which has a negative impact on the environment and pollutes it, can be a high-quality secondary raw material for the textile industry. The reuse of treated wastewater from dyeing and finishing production, i.e. its recycling, will reduce the consumption of fresh (tap) water and can be used in the technology of dyeing textile materials. The number (multiplicity) of repeated dyeing cycles using a secondary resource will reduce the amount of harmful substances emitted into the environment in proportion to the number of reuse cycles.

The results of the experimental studies highlighted in this article will be used to create a resource-saving technology for dyeing textile materials with the repeated use of purified wastewater.

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