Original Scientific Paper
UDK 628.316.12 : 551.217
DOI: 10.46793/NovelTDS16.143JP

DECOLORIZATION OF AQUEOUS SOLUTION OF TEXTILE DYE USING VOLCANIC ASH-BASED ADSORBENT

Jelena Jovićević Pavković* ID, Dragan Đorđević ID
University of Niš, Faculty of Technology, Leskovac, Serbia

This study investigates the potential application of modified volcanic ash as an adsorbent for the removal of textile direct dye from wastewater. The aim of the research was to optimize the decolorization process of model solutions using volcanic ash previously modified through physical and chemical treatments. Various process parameters were examined, including the pH value, initial dye concentration, contact time, temperature, and adsorbent dosage. The highest adsorption efficiency was achieved at a pH value of 3, while maximum dye removal efficiency was reached after 60 minutes of treatment. The maximum adsorption capacity was 7 mg/g, and the dye removal rate exceeded 82%, positioning the modified volcanic ash as a competitive adsorbent. In conclusion, modified volcanic ash represents a low-cost and effective material for the decolorization of aqueous solutions of textile direct dyes, with potential application under industrial conditions for the treatment of colored wastewater from the textile industry.

Keywords: volcanic ash, adsorption, decolorization, textile direct dye, wastewater.

INTRODUCTION

The modern textile industry is facing serious environmental challenges, among which the problem of water pollution due to the discharge of colored effluent stands out [1,2]. During the dyeing process of textile materials, especially natural fibers such as cotton, a large number of synthetic dyes are used, which are characterized by high chemical stability and complex molecular structure [3].
Textile direct dyes are a type of synthetic dye that is directly applied to cellulosic fibers, such as cotton, flax, etc. They are water-soluble and bind to the fibers mainly through

* Author address: Jelena Jovicevic, University of Nis, Faculty of Technology in Leskovac, Bulevar oslobođenja 124, 16000 Leskovac, Serbia
e-mail address: jejchin@gmail.com

hydrogen bonds and van der Waals forces. The main characteristics of textile direct dyes are: good solubility in water, which allows for a simple dyeing process; a simple dyeing procedure, usually carried out in neutral or slightly alkaline conditions; an affordable price and ease of application make them suitable for use in small productions and for home dyeing; lower fastness to light and washing compared to reactive or sulfur dyes, which makes them less suitable for textiles that are frequently washed; a wide range of colors, which enables diverse application in decoration and less demanding textile products [4]. The main ecological problems of direct dyes in waters are: low degradability – these dyes are often of complex structure (e.g. based on azo or anthraquinone cores), which makes them difficult to biodegrade; they decompose very slowly in nature; coloration of water – even in small concentrations (e.g. <1 ppm), direct dyes cause strong coloration of watercourses, which affects light penetration and disturbs photosynthesis in aquatic ecosystems; toxicity and mutagenicity – some azo derivatives formed by dye degradation can be toxic, carcinogenic, or mutagenic to aquatic organisms and humans; accumulation in living organisms – direct dyes can adsorb onto sediments and enter the food chain, accumulating in fish and other aquatic organisms [7].

Methods of removing direct dyes from wastewater: physico-chemical processes – adsorption (e.g., activated carbon), coagulation/flocculation, membrane technologies (e.g., nanofiltration); biological processes – aerobic and anaerobic bioreactors, microorganisms modified for dye degradation; advanced oxidation processes – ozonation, Fenton reaction (Fe^{2+} + H_2O_2), UV/H_2O_2 or UV/O_3 systems [8].

The use of direct dyes without adequate wastewater treatment represents a serious threat to the environment. The introduction of more environmentally friendly dyes (e.g., reactive dyes with better fixation) and efficient wastewater treatment systems is crucial for the sustainable development of the textile industry.

Volcanic ash as an adsorbent is increasingly being investigated as an environmentally friendly and economically acceptable material for the removal of various pollutants from water, including dyes from textile wastewater, heavy metals, and organic compounds. As a natural mineral waste material, it is always an interesting subject of research in the field of adsorption, primarily because of its heterogeneous mineral structure, porosity, and the possibility of chemical modification to increase its adsorption capacity [5,6]. Although volcanic ash is not soluble in water, its physical and chemical properties allow it to act as a natural adsorbent in various purification and environmental protection applications. The mode of application, in this sense, is that the ash is mixed with wastewater or used in filter systems, and it can be activated with acid or base for greater efficiency [9].

Advantages of using volcanic ash are [10]:

- Environmentally friendly (natural material).
- Economical compared to synthetic adsorbents.
- High efficiency for removal of cationic dyes and metals.

This paper investigates the potential of chemically modified volcanic ash as an adsorbent for the removal of textile direct dye from model wastewater. The aim of the research is to, through systematic experimental analysis, examine the influence of key parameters – solution pH value, contact time between adsorbent and adsorbate, as well as initial dye concentration – on adsorption efficiency, along with determining kinetic and equilibrium characteristics of the process. Based on the obtained results, the potential application of this system in textile effluent treatment was assessed, thereby contributing to the development of environmentally acceptable, technically feasible, and economically sustainable solutions in the field of water protection.

MATERIALS AND METHODS

For the modification and application in the process of decolorization of model dyed waters, waste volcanic ash collected from the foothills of the active volcano Etna, Italy, was used. Models for wastewater, after dyeing, were prepared using the direct dye designated as C.I. Direct Green 26. The commercial name is Solophenyl Green BLE, from the company Huntsman, Germany. The molecular formula of the dye is $C_{50}H_{33}N_{12}Na_5O_{18}S_4$ (Fig. 1), with a molar mass of 1,333.08 g/mol. The dye fastness ratings are 6 for light, 4 for perspiration, and 4 for washing, according to the relevant ISO standards.

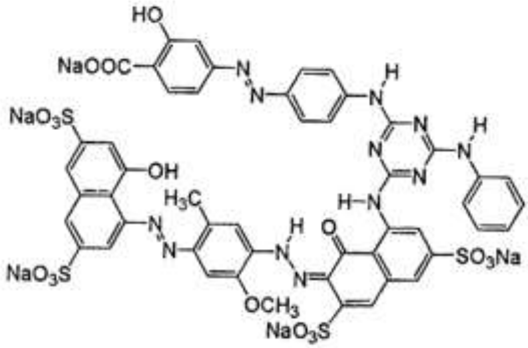

Figure 1. Structural formula of the direct green dye C.I. Direct Green 26

Preparation of the active agent from volcanic ash was carried out as follows: Collected waste volcanic ash (precursor) was washed in hot distilled water (60 °C, 30 min), then dried and treated with 5% sulfuric acid for 48 hours (bath ratio 1:100) at room temperature (18–20 °C), with occasional stirring. The resulting product was rinsed with distilled water until a neutral pH of 7 was reached. After drying (100 °C), the obtained active agent was manually ground. The material prepared in this way was used in experiments for the adsorption of direct green dye from aqueous solution.

In a reaction vessel (200 cm^3), the adsorbent (active agent – volcanic ash) was suspended in a solution of direct green dye (adsorbate). The vessel was placed on a shaker with orbital motion (125 min^{-1}) at 20 °C and kept for a defined time. The amount of active agent was always 2 g, while the green dye solution was maintained at a constant volume of 50 cm^3 with concentrations of 10, 20, 30, 40, 50, and 60 $mg \cdot dm^{-3}$. The treatment time, with continuous shaking, was 5, 10, 15, 30, 40, 50, and 60 minutes. All experiments were performed at a solution pH of 3, adjusted using a diluted aqueous solution of H_2SO_4.

It was determined that the equilibrium adsorption time of the dye on the active agent was achieved after 60 minutes, after which no significant change in adsorption was observed. After the adsorption process was completed, the absorbance of the solution was measured using a spectrophotometer, Varian Cary 100 UV-Vis Spectrophotometer (at 680 nm). The obtained values were used to construct a calibration curve: absorbance vs. dye concentration, from which the unknown dye concentrations during and after adsorption were calculated.
The efficiency of dye removal, or the degree of dye exhaustion from the solution, was defined by the expression [7]:

$$Degree\ of\ exhaustion = \frac{(C_O - C_e)\cdot V}{w} \quad (1)$$

Where: C_O and C are the initial and final dye concentrations in the solution (mg/dm³), w – mass of adsorbent (g), and V – volume of solution for adsorption (dm³), respectively.
The amount of dye (adsorbate) adsorbed per unit mass of adsorbent was determined by the expression [7]:

$$q_e = \frac{(C_0 - C_e)\cdot V}{w} \quad (2)$$

Where: C_O - is the initial adsorbate concentration (mg/dm³), C_e - is the equilibrium adsorbate concentration after adsorption (mg/dm³), w - is the mass of the adsorbent (g), and V - is the volume of the adsorption solution (dm³), q_e – adsorption capacity at equilibrium (mg/g or mmol/g).

RESULTS AND DISCUSSION

To describe the process of adsorption of the direct dye onto the volcanic ash adsorbent, it is important to emphasize that direct dyes in aqueous solution exhibit a pronounced anionic character. In order to achieve effective adsorption, it is necessary to reduce or eliminate the negative charge on the surface of the adsorbent, thereby enhancing its ability to bind anionic dye molecules. In the dyeing solution, the dye can be present in various forms—such as individual molecules, micelles, aggregates, or solid particles—with smaller forms, like molecules and micelles, being much more easily adsorbed onto the surface of the active agent.
During the preparation process of the adsorbent, a mass loss of 15–25% was recorded after washing the raw ash, while the yield of the active agent after chemical modification with acid was 60–70%.
The analysis of the pH effect showed that the maximum efficiency of dye removal was achieved at a pH value of 3. Under these conditions, protonation of the acidic sites on the adsorbent occurs, making its surface positively charged and allowing strong electrostatic binding with the anionic sulfo-groups of the dye. In neutral and alkaline media, deprotonation of these sites takes place along with an increased presence of OH^- ions, which reduces the number of available active sites and significantly decreases the adsorption efficiency. These results are in agreement with earlier studies on similar materials, which confirm the key role of pH in adsorption processes [13,14].

The analysis of the effect of contact time (Figures 2–4) showed that the dye was adsorbed more rapidly in the later stage of the experiment, especially after 30 minutes, until reaching equilibrium concentration after 60 minutes. The efficiency of adsorption depends on several factors, including solution temperature, pH value, degree of mechanical stirring, and the diffusion rate of the dye molecules. For example, an increase in temperature can accelerate diffusion but may simultaneously reduce the final degree of exhaustion due to weaker binding. In the initial phase of the process, the mass transfer rate is limited by the thickness of the boundary layer around the adsorbent particles, while increasing the stirring speed reduces this resistance and accelerates dye transfer. Once a critical speed is reached, further increases in stirring no longer have a significant impact, as the process then becomes limited by the rate of diffusion of dye molecules into the internal pores of the adsorbent.
Figure 2 shows the dependence of the amount of adsorbed dye (q_t) on contact time using 2 g of adsorbent at a temperature of 20 °C. As expected, the amount of bound dye increases with prolonged contact time.

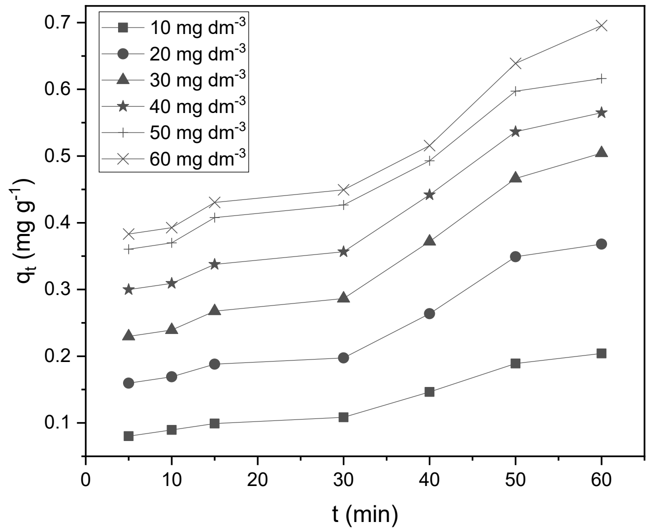

Figure 2. Change in the amount of direct green dye during adsorption

Figure 3 shows the degree of dye exhaustion, which increases over time and is particularly pronounced for solutions with lower initial dye concentrations. After 30 minutes, a sharp rise in exhaustion is evident, which is explained by the onset of dye absorption into the interior of the particles after accumulation on the surface of the volcanic ash-based adsorbent.

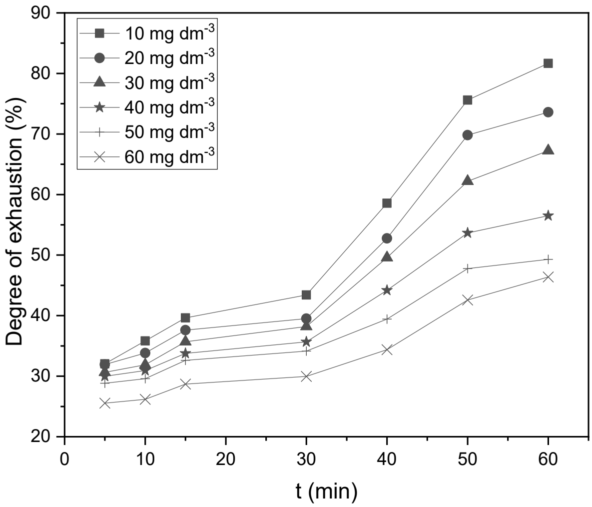

Figure 3. Change in the degree of exhaustion of direct green dye during adsorption

Figure 4 shows the change in the initial dye concentration (C_0) in the solution over time, where a clear, continuous, and monotonic decrease in dye concentration is observed during adsorption, indicating effective and uniform dye removal.

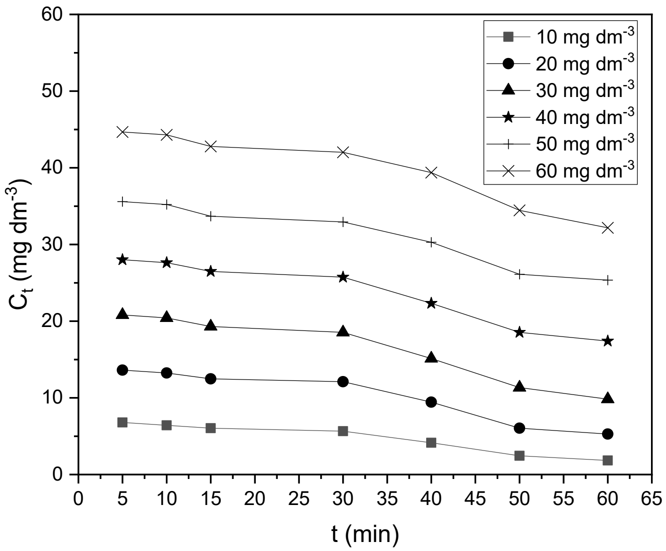

Figure 4. Change in the initial concentration of direct green dye during adsorption

The investigation of the effect of the initial dye concentration (Figures 5 and 6) was carried out in the concentration range from 10 to 60 mg/dm³. According to the results, with an increase in the initial dye concentration, the relative degree of exhaustion decreases in all cases, while the absolute amount of dye adsorbed per unit mass of adsorbent (q_t) increases and reaches a maximum at 60 minutes. The initial dye concentration in the solution represents an important driving force that enables overcoming the mass transfer resistance between the aqueous and solid phases. Although the initial dye concentration does not significantly affect the time required to reach equilibrium, it substantially determines the mass transfer rate, as a higher concentration gradient ensures a more intense transport of molecules toward the adsorbent surface.

It is important to emphasize that at first glance, dye exhaustion appears highest at lower initial concentrations, which is an apparent effect. More detailed calculations show that the actual amount of dye adsorbed, expressed in mg/g, is greatest at the highest initial concentrations, while q_t values are the lowest for solutions with the smallest C_0.

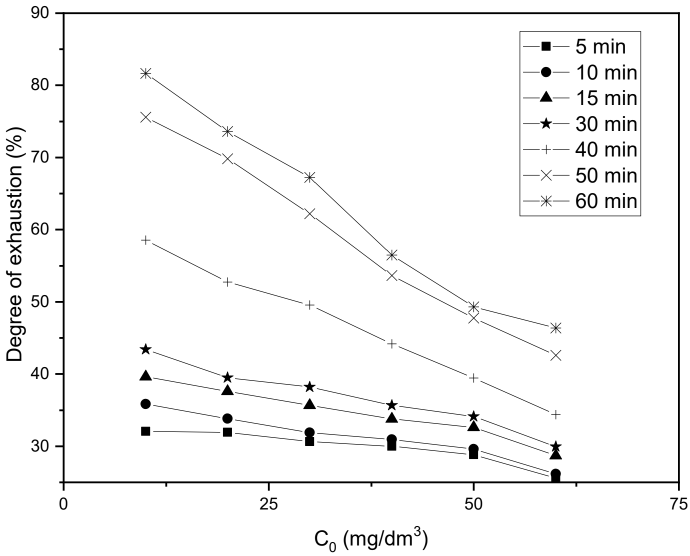

Figure 5. Degree of removal of direct green dye during adsorption as a function of initial dye concentration

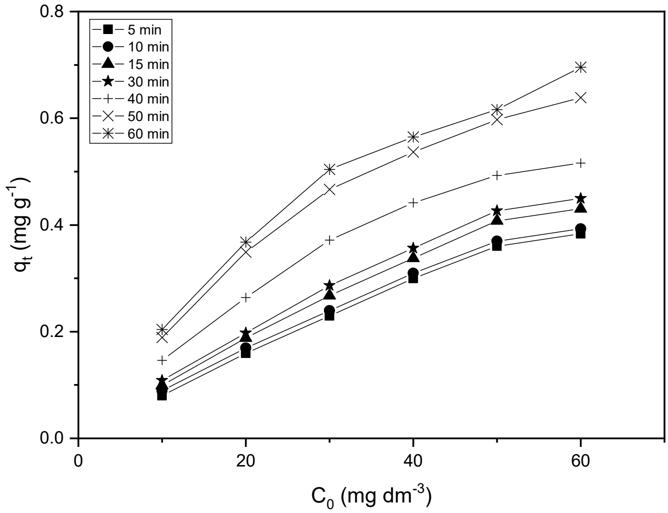

Figure 6. Amount of adsorbed direct green dye during adsorption as a function of initial dye concentration

In general, the results indicate that the adsorption mechanism involves multiple stages: initial diffusion of molecules through the solution, transfer across the boundary layer, adsorption on the surface of the adsorbent, and penetration into the internal pores. The key contribution to dye removal comes from physicochemical interactions, including ionic bonds, hydrogen bonds, and Van der Waals forces. When the obtained data are compared with literature results for other natural and synthetic adsorbents [11], the modified volcanic ash demonstrates competitive performance, with an adsorption capacity of 7 mg/g and a dye removal efficiency exceeding 82% under optimal conditions. These results confirm that natural waste materials, with appropriate chemical modification, can provide sustainable and economically viable solutions for wastewater treatment, contributing to environmental protection and the implementation of circular economy principles.

CONCLUSION

The study on the application of modified volcanic ash as an adsorbent for the removal of the direct dye C.I. Direct Green 26 from aqueous solutions showed that this natural waste material, after chemical modification, can be effectively used for the treatment of textile industry wastewater. The experimental results clearly demonstrated that the adsorption process is significantly influenced by pH value, contact time, and initial dye concentration.

The maximum adsorption capacity was 7 mg/g, while the dye removal efficiency exceeded 82%, placing modified volcanic ash among competitive adsorbents compared to more expensive commercial materials. Analysis of the process mechanism indicates a complex multi-phase course, involving surface adsorption and internal diffusion, with dominant roles played by physicochemical interactions, including ionic bonds and electrostatic forces.

These findings confirm that modified volcanic ash represents a sustainable, cost-effective, and environmentally friendly solution for dye removal from wastewater, with the additional benefit of incorporating the recycling of a natural waste material. Further research should focus on investigating the regenerative potential of the adsorbent, process scaling, and testing under real industrial conditions to confirm its applicability in large-scale wastewater treatment systems.

Acknowledgment

The authors express their gratitude to the Academy of Technical and Art Applied Studies Belgrade for the support provided, which contributed to the realization of this research.

References

[1] Robinson T., McMullan G., Marchant R., Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 2001, 77(3), 247–255. https://doi.org/10.1016/S0960-8524(00)00080-8

[2] Crini G. Non-conventional low-cost adsorbents for dye removal: a review. Bioresource Technology. 2006, 97(9), 1061–1085. https://doi.org/10.1016/j.biortech.2005.05.001

[3] Forgacs E., Cserháti T., Oros G. Removal of synthetic dyes from wastewaters: a review. Environment International. 2004, 30(7), 953–971. https://doi.org/10.1016/j.envint.2004.02.001

[4] Yıldız, M., & Başaran, B. (2024). Sustainable cationic cotton with keratin hydrolysate. Fibers and Polymers, 25, 403–411. https://doi.org/10.1007/s12221-024-00626-0

[5] Allen S. J., Koumanova B. Decolourisation of water/wastewater using adsorption. Journal of the University of Chemical Technology and Metallurgy. 2005, 40(3), 175–192. https://dl.uctm.edu/journal/node/j2005-3.html

[6] Gupta V. K., Suhas. Application of low-cost adsorbents for dye removal: a review. Journal of Environmental Management. 2009, 90(8), 2313–2342. https://doi.org/10.1016/j.jenvman.2008.11.017

[7] R. Saadi, Z. Saadi, R. Fazaeli, N. E. Fard, Monolayer and multilayer adsorption isotherm models for sorption from aqueous media, Korean J. Chem. Eng., 32(5), 787-799 (2015).

[8] Yaseen, D. A., & Scholz, M. (2019). Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *International Journal of Environmental Science and Technology*, 16(2), 1193–1226. https://doi.org/10.1007/s13762-018-2130-z

[9] Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17(1), 145–155. https://doi.org/10.1007/s10311-018-0785-9

[10] Shikuku, V. O., Tome, S., Hermann, D. T., & Tompsett, G. A. (2022). Rapid adsorption of cationic methylene blue dye onto volcanic ash–metakaolin based geopolymers. *Silicon*, 14, 9349–9359. https://doi.org/10.1007/s12633-021-01637-9
[11] Prajaputra, V., Abidin, Z., & Widiatmaka. (2019). Methylene Blue Removal Using Developed Material From Volcanic Ash Soils. *International Journal of Scientific & Technology Research*, 8(7), 706–710.
[12] Etana, R., Angassa, K., & Getu, T. (2025). Dye removal from textile wastewater using scoria-based vertical subsurface flow constructed wetland system. *Scientific Reports*, 15, Article 949.
[13] Lim, S., Kim, J. H., Park, H., Kwak, C., Yang, J., Kim, J., Ryu, S. Y., & Lee, J. (2021). Role of electrostatic interactions in the adsorption of dye molecules by Ti_3C_2-MXenes. *RSC Advances*, 11(12), 7060–7070. https://doi.org/10.1039/D0RA10876F
[14] Vojnović, B., Cetina, M., Franjković, P., & Sutlović, A. (2022). Influence of Initial pH Value on the Adsorption of Reactive Black 5 Dye on Powdered Activated Carbon: Kinetics, Mechanisms, and Thermodynamics. *Molecules*, 27(4), 1349. https://doi.org/10.3390/molecules27041349

Izvod

DEKOLORIZACIJA VODENOG RASTVORA TEKSTILNE BOJE POMOĆU ADSORBENTA NA BAZI VULKANSKOG PEPELA

Jelena Jovićević Pavković ID, Dragan Đorđević ID
Univerzitet u Nišu, Tehnološki fakultet, Leskovac, Srbija

Ovaj rad istražuje mogućnosti primene modifikovanog vulkanskog pepela kao adsorbenta za uklanjanje tekstilne direktne boje iz otpadnih voda. Cilj istraživanja bio je optimizacija procesa dekolorizacije modelnih voda korišćenjem vulkanskog pepela prethodno modifikovanog fizičkim i hemijskim tretmanima. Razmatrane su različite varijante parametara, uključujući pH vrednost, početnu koncentraciju boje, vreme kontakta, temperaturu i količinu adsorbenta. Najefikasniji stepen adsorpcije postignut je pri pH vrednosti od 3, dok se maksimalna efikasnost u uklanjanju boje postiže nakon 60 minuta tretmana. Maksimalni kapacitet adsorpcije iznosio je 7 mg/g, dok je stepen uklanjanja boje premašio 82%, što modifikovani vulkanski pepeo svrstava među konkurentne adsorbente. U zaključku, modifikovani vulkanski pepeo predstavlja jeftin i efikasan materijal za dekolorizaciju vodenih rastvora tekstilne direktne boje, sa potencijalnom primenom u industrijskim uslovima za obradu obojenih otpadnih voda tekstilne industrije.

Ključne reči: vulkanski pepeo, adsorpcija, dekolorizacija, tekstilna direktna boja, otpadna voda.