

Activated carbon from cotton waste as an adsorbent in the purification process of azo-dyes

N. Djordjevic¹, D. Djordjevic^{1*}, M. Miljkovic², S. Urosevic³

¹University of Nis, Faculty of Technology, Leskovac, Serbia

²University of Nis, Faculty of Mathematics and Natural Sciences, Nis, Serbia

³University of Belgrade, Technical Faculty, Bor, Serbia

Received: April 1, 2013; revised: July 2, 2013

The treatment of azo dyes from the aqueous solution by adsorption process on activated carbon prepared from waste cotton fibers from weaving plants was investigated in this study. They are waste airborne fibers that arise as a by-product in the process of weaving. Waste cotton material is used for the production of activated carbon, which is then used for the reduction of textile azo dyes coloration in the solution. Qualitative and quantitative characterization of activated carbon shows that carbon is predominant in its chemical composition with the presence of several other elements. Based on the results, it can be said that the activated carbon produced from waste cotton fibers has potential as an adsorbent for the removal of azo dyes from aqueous solutions. Prolonged contact time means a greater amount of dye on the adsorbent, i.e. the dye concentration in the solution decreases with the duration of the adsorption. The percentage of removed dye decreases with the increase of initial dye concentration in the solution, but the actual amount of adsorbed dye increases with the increase of dye concentration.

Keywords: activated carbon, waste cotton fibers, azo-dye, adsorption.

INTRODUCTION

One of the main methods for removing pollutants from wastewater is the use of porous solid adsorbents. Porous materials properties that make them useful for the treatment of water are high porosity and surface area, as well as the physical and chemical nature of the internal adsorption surfaces. Large amounts of waste water polluted with dyes are discharged from the textile industry, leather and laundries. Pollutants include dyes, suspended solids, alkali, heavy metals and organic matters.

There are several studies on the adsorption of dye on different materials. These include the absorption of basic dyes on carbon, peat, wood and pith. Some studies indicate that the absorption rate is determined based on the adsorption equilibrium (unfavorable, linear, favorable or completely irreversible) and control mechanism (external diffusion, internal pore diffusion, inner solid-phase diffusion or longitudinal diffusion) [1-5].

Activated carbons are the most commonly used adsorbents in separation and purification processes. Lately, the efforts of scientists to find alternative adsorbent to replace the costly activated carbon

have been intensified. Some of the potential low-cost adsorbents for the removal of metals and organic substances are industrial waste materials. The purpose of activation is to obtain effective low-cost adsorbent. Activation can be carried out by chemical and physical methods. In chemical activation, the basic material is impregnated by various chemical substances, and then carbonized. Physical activation involves carbonization of carbonaceous feedstock, followed by gas processing of the obtained carbonizate, or direct activation of the initial material by activating agents (such as CO₂, water vapor, N₂, H₂, O₂ ...) [4-9].

Azo dyes are aromatic nitrogen compounds that dissolve in water due to existing sulfuric groups or other hydrophilic groups - carboxyl and hydroxyl. They are usually used for dyeing cellulose materials (cotton, viscose...) in the presence of electrolytes and wetting agents. Starting from the chemical frame of azo dyes, there are the carriers of free electrolyte pair groups that behave as electron donors, and carriers of hydrogen atom group - electron acceptor [10-14].

This paper deals with the adsorption process of azo dyes from aqueous solution on activated carbon produced from waste cotton fiber from the weaving plants. These airborne waste fibers are formed as a by-product in the weaving process using cotton yarns on looms. The aim is to use the waste cotton material, make it into activated carbon and use it

* To whom all correspondence should be sent:
E-mail: drag_64@yahoo.com

for coloration reduction, i.e. removal of textile azo dyes by adsorption on activated carbon.

EXPERIMENTAL

Materials

Activated carbon obtained by chemical and physical modification of waste cotton fibers from the weaving plants was used as an adsorbent. After the collection of waste fibers, they were washed in warm distilled water (40°C), dried and subjected to the treatment by concentrated sulfuric acid (1 g of waste fiber: 5 g H₂SO₄) for 24 h at room temperature. The samples were then heated at 180°C for 1 hour, followed by rinsing with distilled water and neutralization to pH=7 (with sodium bicarbonate). After drying, the obtained residue (activated carbon) was milled and then sieved to a particle size of 0.5 mm. Thus, prepared activated carbon was used in the experiment.

The dye used is a triazo class dye with 4 sulfo groups and one amino functional group. It is a dye that belongs to the group of azo dyes, CI Direct Blue 71, soluble in water, 10 g·dm⁻³ (60°C), 20 g·dm⁻³ (97°C) and exists in the anionic form, soluble in ethanol and insoluble in other organic solvents, Fig. 1.

Adsorption process

Adsorption test was performed in Erlenmeyer flasks in which the adsorbent (activated carbon) was suspended in azo dyes solution (adsorbate). Erlenmeyer flasks were placed on the shaker with 120 rpm·min⁻¹ at a temperature of 20°C and shaken for a given time. The amount of activated carbon was 3 g, while the solution in a constant volume of 100 cm³, contained dye concentrations of 10, 30, 50, 70 and 100 mg·dm⁻³. Processing time, with continuous stirring, was 10, 20, 30, 50 and 60 min. Experiments were conducted at neutral pH of the dye solutions, since there are no major variations in the wide range of pH.

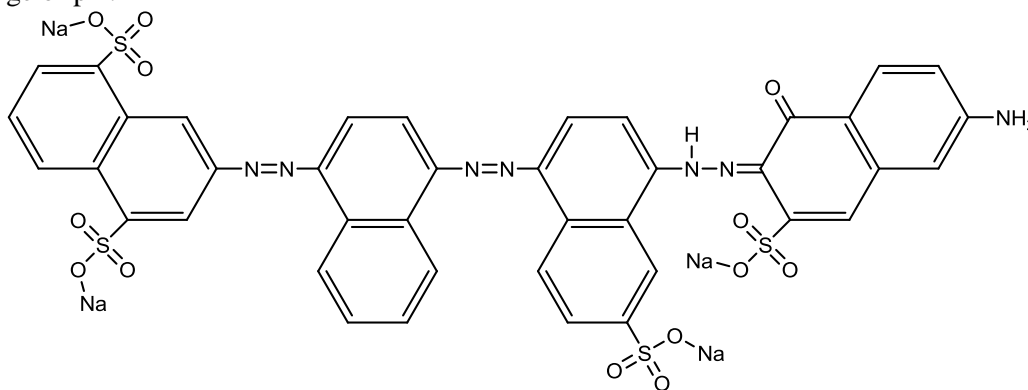


Fig. 1. Structure of the studied azo-dye.

The dye concentrations mentioned were taken for the simple reason that they mostly correspond to the amount of dye remaining in the waste solution after dyeing cotton textiles. It was found that the adsorption equilibrium time of dye adsorption on activated carbon was achieved in 60 min, and an extension of time of treatment did not significantly change the adsorption. Upon completion of the adsorption, dye solutions and activated carbon were passed through a filter paper.

Methods

Determination of the absorption of the solution was performed on a UV-VIS spectrophotometer (Cary 100 Conc UV-VIS, Varian) at 595 nm (maximum wavelength of the spectrum of the dye solution used).

SEM measurements were carried out on a JEOL JSM - 6610LV device using a secondary electron detector. In addition, as the SEM is equipped with Energy-dispersive spectroscopy (EDS) X-rays detector, characteristic X-rays of major elements (> 10 wt.%) were measured. EDS system enabled rapid assessment of the elemental composition of the sample - the adsorbent.

Analyses of specific surface area and pore distribution of the synthesized activated carbons were carried out by nitrogen adsorption at -196°C on a Sorptomatic 990 analyzer (Thermo Fisher Scientific Inc.). Before measurements, the samples were degassed for 12 h at 110°C. Determination of the specific surface area of samples was performed by Brunauer-Emmett-Teller (BET) method, the mesopore volume and surface area were determined by Barret-Joyner-Halenda (BJH) method, and the micropore volume was obtained by using the Dubinin-Radushkevich equation [7-9].

The degree of dye removal (dye exhaustion) was calculated based on the dye concentration

before and after treatment [7, 9]:

$$R = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (1)$$

where C_0 and C_t are the initial and final concentrations of dye solutions, respectively.

The amount of dye adsorbed (adsorbate) per unit mass of activated carbon (adsorbent), q_t (mg·g⁻¹), was determined as follows [7, 9]:

$$q_t = \frac{(C_0 - C_t) \cdot V}{M} \quad (2)$$

where: M , g - mass of adsorbent, V , dm³ - volume of solution from which adsorption is carried out.

RESULTS AND DISCUSSION

The activated carbon used is relatively fine bulk material with heterogeneous porous particles of diverse shapes and forms. Within larger particles, there are conspicuous cracks, cavities and channels that form the basis of the microporosity of materials. Otherwise, the inherent high porosity of activated carbons is provided by the presence of particles of irregular shape, a high degree of amorphization and a number of gaps in the structure. Micrograph in Figure 2 gives the appearance with $\times 750$ magnification. In addition to differences in shape, pores vary according to their availability for adsorbate molecules, which is associated with the fact that they can be closed, open at one end or both ends, they can be isolated or joined [4-7]. Taking into account the classification of pores according to their size, meso- and macropores can be said to be dominant in the sample used.

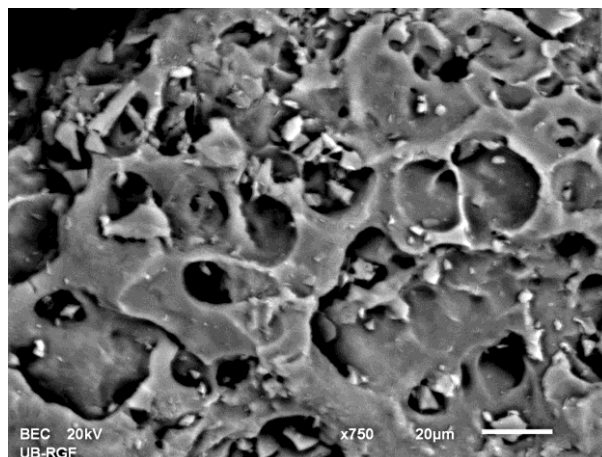


Fig. 2. Micrograph of the adsorbent used (activated carbon).

EDS system allows rapid assessment of the elemental composition of the sample. Sample analysis is non-destructive and quantitative analysis can be obtained by a spatial resolution of the order of magnitude of 1 μm . Table 1 shows the quantitative composition of active carbon, i.e., the percentage of one element in relation to the sum of all detected elements. All elements (e.g., C, O, Na, Al, Si, S, and Ca) detected in this analysis constitute 100 % and the individual percentages of each element means that 100 g of all detected elements contain that exact quantity in grams of each element.

Textural properties of activated carbon are given in Table 2. The results show different parameters, which by their numeric values characterize the specific surface area, pore volume, pore diameter, etc.

Table 1. Quantitative composition of the adsorbent used according to EDS spectrum analysis

Spectrum	C	O	Na	Al	Si	S	Ca	Total
Weight %	57.69	36.13	4.16	0.05	0.10	1.84	0.03	100.00
Mean	57.69	36.13	4.16	0.05	0.10	1.84	0.03	100.00
Std. deviation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.	57.69	36.13	4.16	0.05	0.10	1.84	0.03	
Min.	57.69	36.13	4.16	0.05	0.10	1.84	0.03	

Table 2. Activated carbon textural characteristics obtained by analyzing the adsorption and desorption of N₂.

S_{BET} (m ² ·g ⁻¹)	$V_{0.98}$ (cm ³ ·g ⁻¹)	V_{mic} (cm ³ ·g ⁻¹)	S_{mic} (m ² ·g ⁻¹)	V_p (cm ³ ·g ⁻¹)	D_{max} (nm)	D_{av} (nm)
2.14	0.0051	0.00085	2.40	0.0041	8.7	2.3

S_{BET} - specific area according to BET method;

$V_{0.98}$ - total pore volume at a relative pressure p/p_0 - 0.98 to Gurvich method;

V_{mic} and S_{mic} - micropore volume and specific surface area - by Dubinin and Raduskevich method

V_p , D_{max} , D_{av} - micropore volume, maximum porediameter and average pore diameter from the distribution according to Dollimore and Heal method for mesopore

The adsorption-desorption isotherm (Figure 3) represents a change in the amount of adsorbed gas (V_{ads}), on the solid material as a function of the equilibrium pressure (p/p_0), at constant temperature. Pore volume according to Gurvich for p/p_0 of 0.98 was $0.0051 \text{ cm}^3 \cdot \text{g}^{-1}$. The shape of adsorption-desorption isotherm depends on the porous structure of the solid material. According to IUPAC classification, there are six types of adsorption isotherms, which enable determination of the textural properties (specific surface area, pore volume, pore volume distribution by diameter).

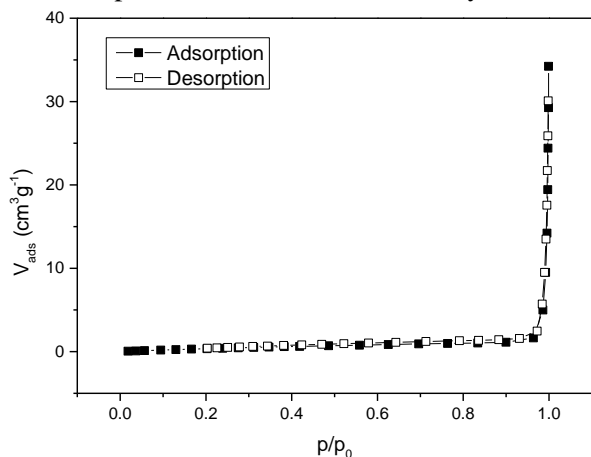


Fig. 3. Adsorption-desorption isotherms of activated carbon.

The curves shown in Figure 3 correspond to type III isotherms according to the IUPAC classification. The absence of a sharp decline in the area of low relative pressure indicates the absence of micropores. Isotherm has a reversible form throughout the range of the relative pressure. In type III the convexity to the x-axis extends along the entire isotherm. Isotherm convexity means that the particles that have been adsorbed tend to improve the adsorption of other particles from the depth of the phase. It is concluded that the interaction between the adsorbate particles is of primary importance here. Weak interactions at the beginning of adsorption (at low relative pressure) results in less pronounced adsorption. As the pressure increases, and new particles are adsorbed, the attraction between the adsorbate particles is increasingly favouring the adsorption, so the isotherm becomes convex.

The effect of contact time on the removal of azo dyes by the adsorbent is shown in Figure 4. The dye was quickly adsorbed in the first twenty minutes, and then the adsorption rate decreased gradually and reached equilibrium in about 60 minutes. At the beginning, the adsorption rate was high because the dye ions were adsorbed by the outer surface of

activated carbon. When the adsorption of the exterior surface reached saturation, dye ions were adsorbed by the interior surface of particles. This phenomenon has a relatively long contact time. It is believed that adsorption of matter on activated carbon also depends on the pore structure and chemical properties of the carbon surface as the adsorbate. From the point of view of the free energy of adsorption, the compounds are first adsorbed in the pores of similar size as the adsorbate due to the larger number of points of contact between the molecule and the adsorbent.

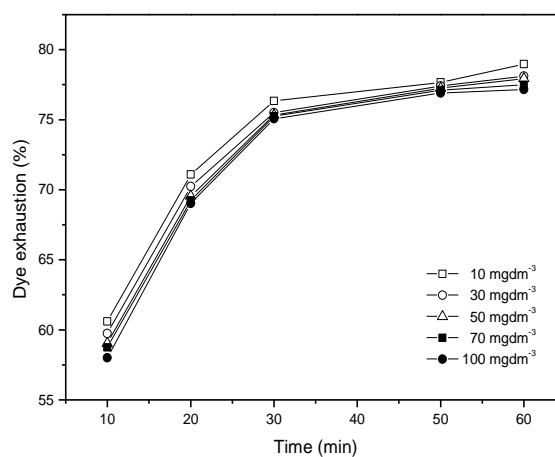


Fig. 4. The effect of adsorption time on the amount of exhausted azo-dyes .

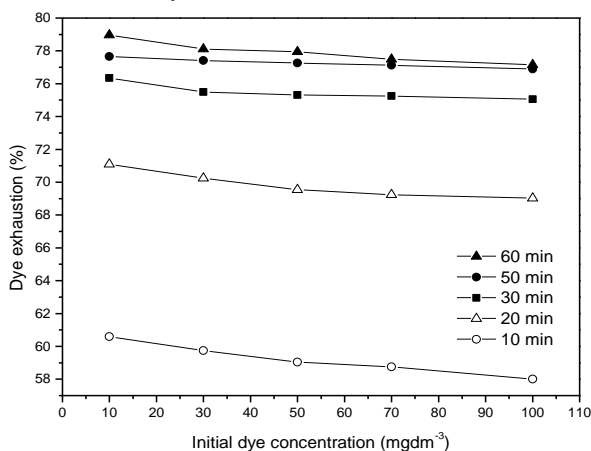


Fig. 5. The effect of the initial dye concentrations in the solution on the amount of azo dye removed.

Figure 5 shows the dependence of the degree of dye exhaustion on the initial dye concentrations for different times of adsorption. At lower dye concentrations, a slightly higher degree of dye removal is achieved. In reality, however, larger quantities of dye are adsorbed on activated carbon at largest initial concentration of azo dyes as will be explained further.

The results of the changed adsorbed amount of adsorbates on the adsorbent during time, for different starting dye concentrations, are showed on

diagrams on the figure 6. The continuity of changes in the period of time is present, i.e. longer time brings larger amount of adsorbed dye per adsorbent mass, i.e. there is the highest adsorption at the highest applied dye concentrations.

The continuous increase of the amount of exhausted dyes compared to the mass of adsorbent is also evident. At a given initial dye concentrations, a major change of the adsorbed dye occurs in the first 10 minutes of dyeing process, while in the later stage of adsorption these changes are minor.

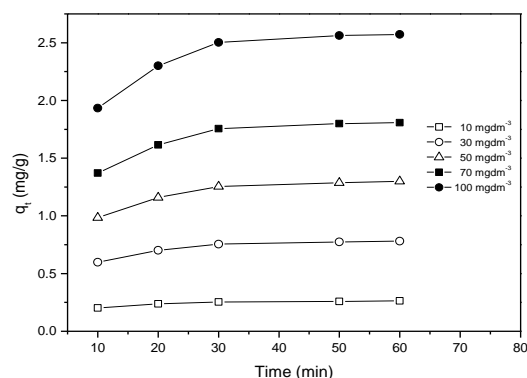


Fig. 6. Adsorbed amount of dye during time.

CONCLUSION

The thermochemical conversion of waste cotton fibers in powdered activated carbon was made with sulfuric acid as the activating agent. Activated carbon was investigated in terms of physical and chemical properties. A survey was done of azo dye adsorption onto activated carbon. In the elemental composition of the produced activated carbon dominated carbon, which was expected and in line with the theoretical data for activated carbon, which lead to conclusion that this material could be considered as a suitable carbon precursor for effective subjection to conversion into activated carbon.

Removal of azo dyes using activated carbon was investigated under various conditions. It was found that the adsorption depends on contact time and the initial dye concentration.

Based on the experimental results the following conclusions can be drawn:

- Activated carbon derived from waste cotton fibers can be an effective adsorbent for the removal of azo dyes from aqueous solutions with a logical tendency of application in industrial environments.
- Prolonged contact time means a greater amount of dye on the activated carbon, i.e. the dye concentration in the solution decreases with the duration of the adsorption.
- The percentage of the removed dye decreases with increasing the initial dye concentration in the solution, but the actual amount of the adsorbed dye increases with the increase of dye concentration.

The results obtained in this work indicate the possibility a practical application of removal of water coloration in the textile industry thus providing support of environmental protection both from economic and practical standpoint.

REFERENCES

1. B.H. Hameed, R.R. Krishni, S.A. Sata, J. Hazard. Mater. 162, 305 (2009).
2. P. Sharma, H. Kaur, M. Sharma, V. Sahore, Environ. Monit. Assess. 183, 151 (2011).
3. Y. Safa, H.N. Bhatti, Chem. Eng. J. 167, 35 (2011).
4. P.K. Malik, J. Hazard. Mater. B113, 81 (2004).
5. S. Wang, Z.H. Zhu, Dyes. Pigments. 75, 306 (2007).
6. H. Denga, G. Li, H. Yanga, J. Tanga, J. Tanga, Chem. Eng. J. 163, 373 (2010).
7. P.K. Malik, Dyes. Pigments. 56, 239 (2003).
8. B.S. Girgis, M.F. Ishak, Mater. Lett. 39, 107 (1999).
9. M. Ozdemira, T. Bolgaza, C. Sakab, O. Sahinc, J. Anal. Appl. Pyrol. 92, 171 (2011).
10. K. Sawada, M. Ueda, Dyes. Pigments. 58, 37 (2003).
11. M. Chairat, S. Rattanaphani, J. B. Bremner, V. Rattanaphani, Dyes. Pigments. 64, 231 (2005).
12. S.M. Burkinshaw, A. Gotsopoulos, Dyes. Pigments. 42, 179 (1999).
13. F. Carrillo, M.J. Lis, J. Valdeperas, Dyes. Pigments. 53, 129 (2002).
14. N.K. Amin, J. Hazard. Mater. 165, 52 (2009).

АКТИВЕН ВЪГЛЕН ОТ ПАМУЧНИ ОТПАДЪЦИ КАТО АДСОРБЕНТ ПРИ ПРЕЧИСТВЕАНИЕТО ОТ АЗО-БАГРИЛА

Н. Джорджевич¹, Д. Джорджевич^{1*}, М. Милькович², С. Урошевич³

¹*Факултет по технология, Университет в Ниш, Лесковац, Сърбия*

²*Факултет по математика и естествени науки, Университет в Ниш, Ниш, Сърбия*

³*Технически факултет, Университет в Белград, Бор, Сърбия*

Постъпила на 1 април; коригирана на 2 юли, 2013

(Резюме)

В настоящата работа е изследвано пречистването на азо-багрила от водни разтвори чрез адсорбция върху активен въглен, приготвен от отпадъчни памучни влакна. С получения активен въглен се намалява оцветяването на отпадъчните води от предачни предприятия. Количествените и качествените характеристики на активния въглен показват, че въглеродът преобладава в присъствие на няколко други елемента. На базата на получените резултати може да се заключи, че произведеният активен въглен има потенциала да адсорбира азо-багрила от водни разтвори. Продължителният контакт на активния въглен с водния разтвор води до по-висока степен на отстраняване на багрилата. Процентната част на отстранените багрила намалява с нарастването на началната концентрация на багрилото, но общото количество на адсорбираното багрило нараства с нарастване на началната му концентрация.