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Removal of Selected Dyes on Activated Carbons

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Abstract: Dyes are widely used in various industries such as those involving paper, food, plastics, and fibers. The produced wastewater has a specific character. Organic substances found in wastewater and when introduced into natural water bodies have a toxic effect on living organisms, causing increased chemical and biological oxygen demand. Some dyes, even in very low concentrations, cause intense colouring. To remove dyes from wastewater, methods such as flotation, oxidation, ozonation, filtration or coagulation with metal compounds are used. Unfortunately, when these methods are used, very large amounts of sludge are produced, which is another problem for the environment. Therefore, one of the methods that can effectively remove dyes from wastewater without creating large amounts of waste is activated carbon adsorption. Adsorption methods in the treatment of wastewater from the dye industry are of particular importance due to their high efficiency, ability to operate over a relatively wide range of concentrations, and availability. The most common adsorbent is activated carbon, which has a high adsorption capacity against many organic compounds. The aim of this study was to determine the effect of filtration rate and type of activated carbon on the removal efficiency of selected cationic (anilan yellow) and anionic (tartrazine) dyes from aqueous solutions.

Keywords: dyes; wastewater; activated carbon

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1. Introduction

Rapidly changing technologies and industrial products generate wastes that, if mismanaged, can threaten public health and the environment [1]. Among all industrial sectors, the textile industry is rated as one of the most polluting, in terms of discharge volume and wastewater composition. The most important exporters of all types of textiles are China, European Union countries, India and then the United States [2].

Textile industry is a chemical industry where dyes and pigments are used in very large quantities with very large amounts of water [3,4]. The total consumption of dyes in the textile industry alone exceeds 10^7 kg per year and it is estimated that 90% of this goes to textiles. Consequently, approximately 10^6 kg of dyes per year are discharged into waste streams by the textile industry. Dye manufacturers and users are interested in stability and durability and are constantly producing dyes that are more difficult to degrade after use [5].

It is estimated that approximately 200 L of water is used to produce 1 kg of textile [2]. This amount of water is required during the application of chemicals to fabrics and during the rinsing process of the finished products [6].

Wastewater from dyeing, textile, printing, leather and other industries contains many organic and inorganic pollutants in its composition. Among the organic substances, dyes are an important element due to the difficulties associated with their removal [7].

The presence of dyes in water, even at low concentration, causes its colouring, limitation of oxygen diffusion and negatively affects the photosynthesis process [8,9]. In addition, very often, dyes cause an increase in the pH value [10].

Some dye substances may cause dermatitis, allergies and mutagenic and carcinogenic effects. Therefore, before industrial effluents containing dyes are discharged to the aquatic environment, they should be treated [11].

The composition of most textile residual waters has high levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). More emphasis should be placed on the high amount of non-biodegradable organic compounds, especially textile dyes [12].

More than 100,000 dyes and pigments are currently used, and their annual production is estimated at more than 7×10^5 Mg, with about 10–15% of this amount becoming pollution degrading the aquatic environment [13,14].

Wastewater that arises during the dyeing process mainly contains dyes, but it can also contain substances that support the process. When the dye-containing effluent reaches the receiving medium, i.e., the aquatic environment, it causes a more or less noticeable change in the color of the water. The intensive colouring of the water means that its use for industrial and domestic purposes is greatly restricted.

The intensive colouring of water causes its use for industrial and household purposes to be limited to a large extent. Even in low concentrations, dyes can stain large areas of water, increasing the threat of oxygen deficiency because photosynthesis by algae and aquatic plants is hindered. The presence of dyes can have harmful effects on fish directly or indirectly [15].

The direct effect is due to the poisonous properties of a significant group of colouring agents. Even small concentrations of some aniline dyes in water can result in accumulation inside the fish's bodies and consequently lead to discoloration of their flesh. Indirect effects, on the other hand, occur through deterioration of living conditions for both fish and plankton due to changes in water chemistry and irradiation. The speed of the changes taking place means that microorganisms are unable to adapt [16].

Removal of dyes from wastewater is done by using chemical, physical and biological methods. These include flocculation, coagulation, reverse osmosis, dialysis, biological oxidation and adsorption on activated carbons [17]. More recently, biological methods have also been adopted for industrial wastewater treatment [18].

Among commercial adsorbents, activated carbon is the most widely used adsorbent. The use of activated carbons as adsorbents is possible due to their high adsorption capacity. It effectively removes various types of organic micropollutants as well as their secondary oxidation products and inorganic compounds, including chlorine resistant viruses [19–24]. Activated carbons are also characterized by selectivity towards the removed pollutants [25].

Studies in dynamic/fluidic conditions are performed less frequently than studies on adsorption properties of activated carbons in static conditions. It seems, from the point of view of the practical application of this adsorbent, that the studies should be extended, including their dynamics. Studies of synthetic dyes are carried out more often on biosorbents or waste materials [26,27].

The results obtained from laboratory scale adsorption columns can be used to determine various parameters characterizing the efficiency of dye removal from aqueous solutions. In this way, it is possible to determine the flow velocity of the solution through the adsorption column, the concentration of the dyes studied and the height of the sorption bed in the column. The study of adsorption dynamics is used, among other things, to determine to what extent a given adsorbent can be useful for water or wastewater treatment of various pollutants; this is called bed breakthrough time and bed saturation time.

The aim of this study was to investigate the dynamic adsorption of two dyes (tartrazine and anilan yellow) from aqueous solutions on two activated carbons.

The scope of the work included the preparation of activated carbons used for the study, and conducting the study under dynamic conditions—in a filter column filled with activated carbon.

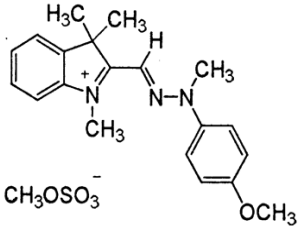
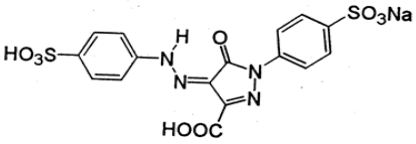
2. Materials and Methods

2.1. Sorbat

The anionic dye tartrazine and the cationic dye anilan yellow, produced by BORUTA—ZACHEM KOLOR (Poland), were selected for the study.

Table 1 shows the characteristics of the dyes used in the laboratory tests.

Table 1. Characteristics of dyes.

Type of Dye	Name of Dye	Application	Structural Formula
CATIONIC	anilan yellow	Used in industry for dyeing acrylic fibers by extraction methods. (Basic Yellow 28)	
ANIONIC	tartrazine	It is used in textile industry (dyeing of protein fibers—wool, natural silk), for dyeing wood, leather and household chemicals. This dye of light yellow color, with the trade symbol E 102, is also known as food yellow 5. It belongs to the group of food dyes.	

2.2. Sorbent

For the laboratory tests, two types of activated carbon were used as adsorbent material filling the filter columns:

- ROW 08 Supra—a granular and refined carbon that can be thermally regenerated. It is produced from peat by Dutch company NORIT,
- WG-12—granulated coal, produced from hard coal by the Polish company GRYF-SKAND sp. z o.o. from Hajnówka.

Activated carbons used in the study are obtained through the application of steam-gas activation. They are mainly used for drinking water treatment.

Table 2 presents the characteristics of the basic physical and chemical properties of used activated carbons, given by their manufacturers.

Table 2. Physicochemical properties of ROW 08 Supra and WG-12 activated carbons.

Indicator	Unit	Value	
		ROW 08 Supra	WG-12
Specific surface area	m^2/g	796	1005
External surface	m^2/m^3	3208	2292
Bulk density	g/L	380	420
Mechanical strength	%	98	98
Granule diameter	mm	0.8	1.2
Water absorption	mL/g	0.97	0.82
Ash content	%	5.94	11.00
pH of aqueous extract	-	8.6	10.1
Methylene number, LM	mL	30	30
Iodine adsorption, LJ	mg/g	1096	1050

2.3. Methodology of Study

Adsorption dynamics studies were conducted in a 2.6 cm diameter filter column filled with a 25 cm layer of activated carbon. Before the actual tests, distilled water

was passed through the carbon bed for 1 h, after which the bed was left saturated for 24 h. Only after this time, a solution of the appropriate dye was passed through the adsorbent layer. Filtration was carried out in the top-down direction at 3, 6, and 9 m/h, corresponding to volume fluxes of, respectively: 26.6; 53.1 and 79.7 mL/min. The initial concentration of the dyes tested was C_o = 100 mg/L. The filtrate was sampled at 30 min intervals. The concentration of dye in the filtrate was determined by Thermo Electron Corporation HELIOS α spectrophotometer using previously prepared standard curves. The wavelengths corresponding to the absorption maximum of a given dye were, respectively:

tartrazine − λ = 420 nm,

anilan yellow − λ = 428 nm.

Dynamic adsorption studies were carried out until the bed was saturated. As it is stated in literature [28], if dye concentration in the filter reaches 90% of the initial concentration, this moment is considered bed saturation. On the other hand, bed breakthrough occurs when the dye concentration in the filter reaches a concentration equal to 10% of the initial concentration.

Based on the laboratory results obtained, the velocity of displacement of the mass exchange zone along the height of the activated carbon layer was calculated using Equation (1):

$$u = \frac{h}{t_k - t_p} \quad (1)$$

where:

h—height of mass exchange zone, cm,

t_p—time to achieve breakthrough by the adsorbent bed, min,

t_k—time until the bed exhausts its adsorption capacity, min,

Formula (2) was used to calculate the dynamic adsorption:

$$a_d = \frac{C \cdot t_p \cdot Q}{V} \quad (2)$$

where:

a_d—dynamic adsorption, mg/L,

C—concentration, mg/L,

t_p—time to achieve breakthrough by the adsorbent bed, h,

Q—solution flow rate through the carbon bed, L/h,

V—volume in the activated carbon column, L.

3. Results

The results of dynamic adsorption studies of tartrazine on two porous carbon materials (ROW 08 Supra and WG-12) in the form of breakthrough curves are presented in Figures 1–6.

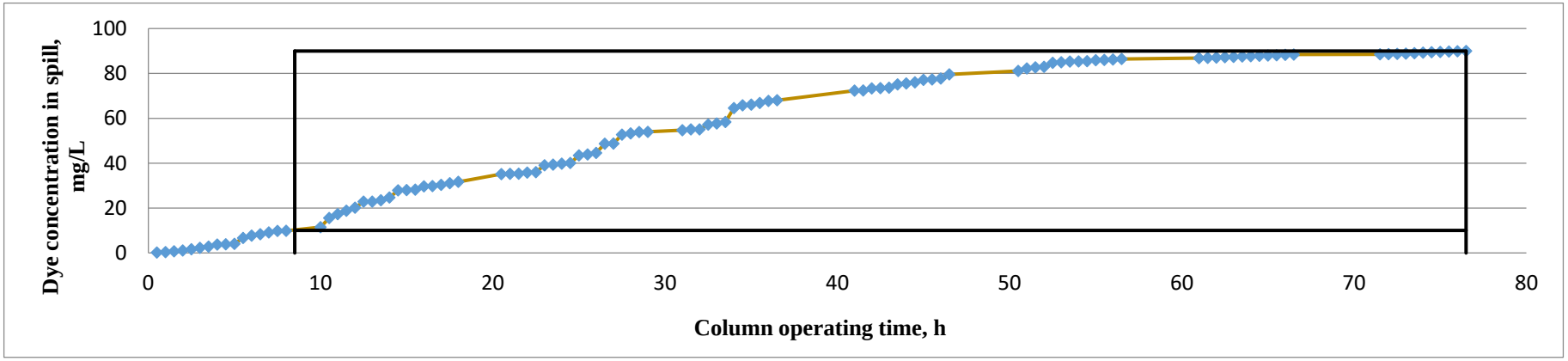


Figure 1. Breakthrough curve of ROW 08 Supra activated carbon bed for tartrazine at solution flow rate of 3 m/h.

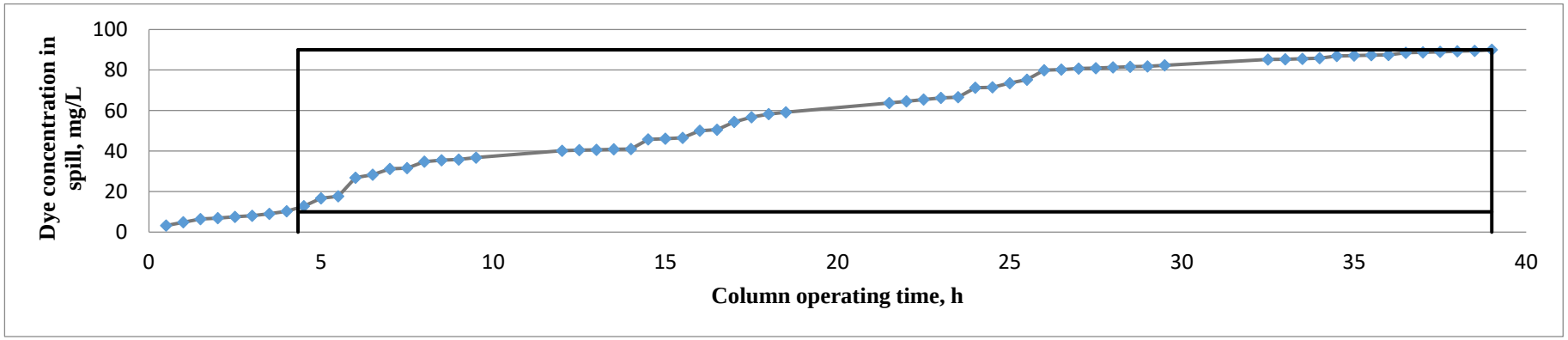


Figure 2. Breakthrough curve of ROW 08 Supra activated carbon bed for tartrazine at solution flow rate of 6 m/h.

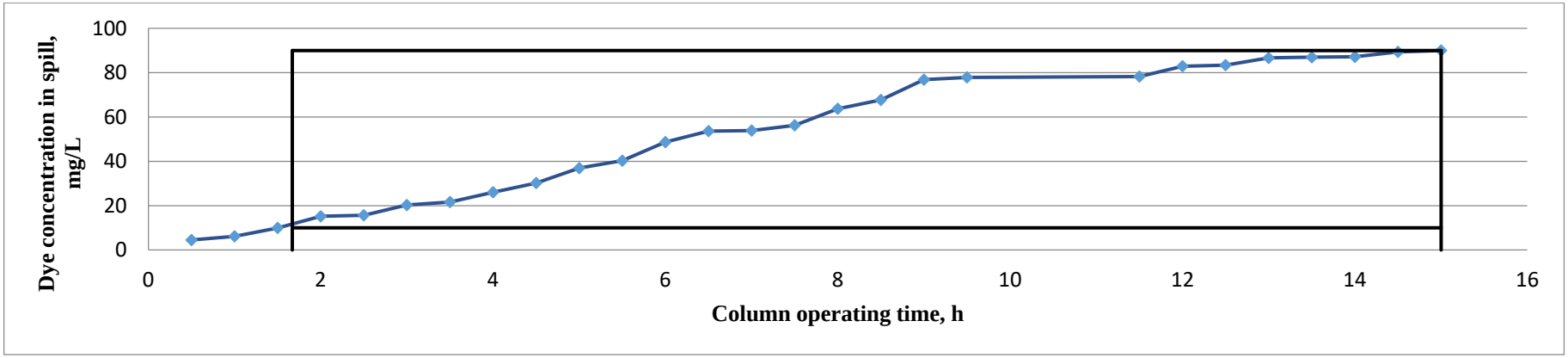


Figure 3. Breakthrough curve of ROW 08 Supra activated carbon bed for tartrazine at solution flow rate of 9 m/h.

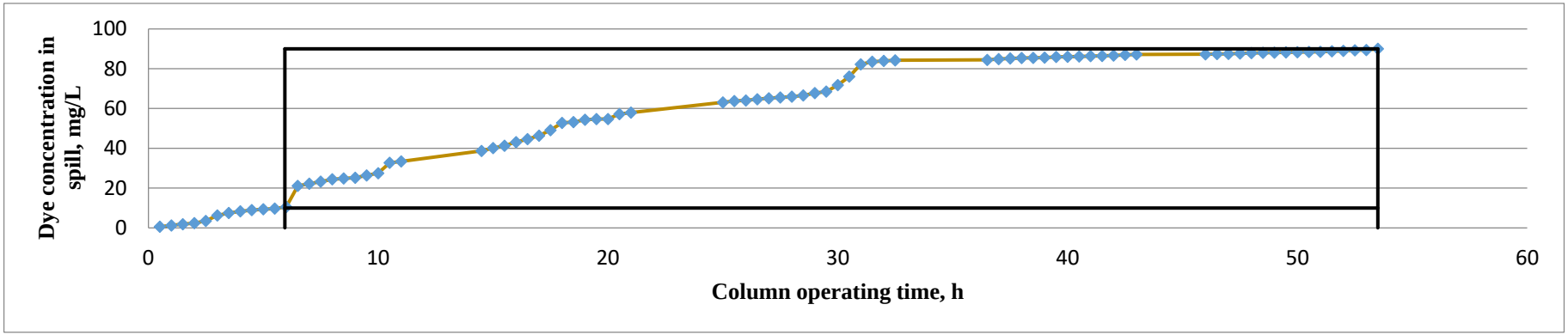


Figure 4. Breakthrough curve of WG-12 activated carbon bed for tartrazine at solution flow rate 3 m/h.

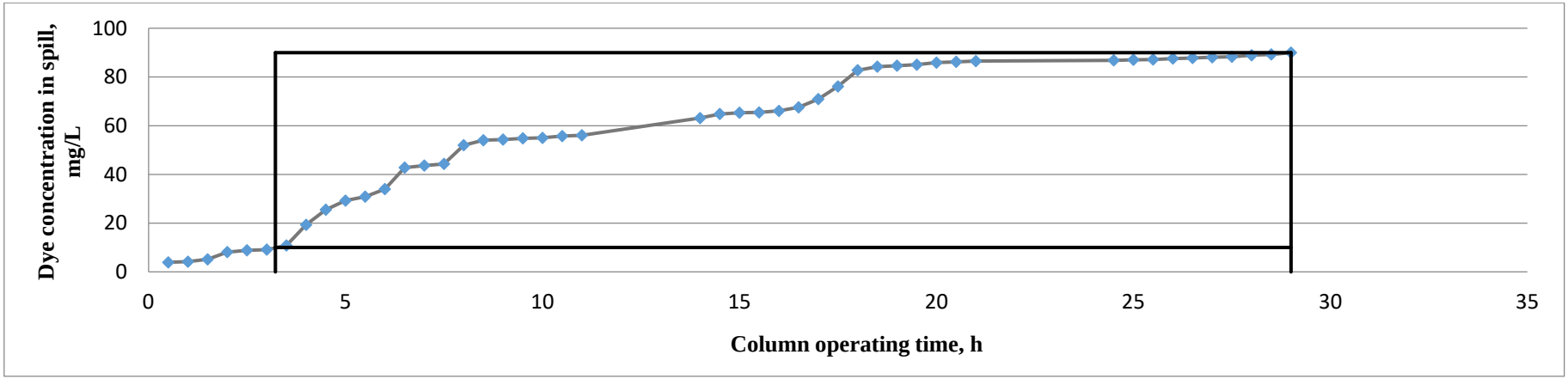


Figure 5. Breakthrough curve of WG-12 activated carbon bed for tartrazine at solution flow rate 6 m/h.

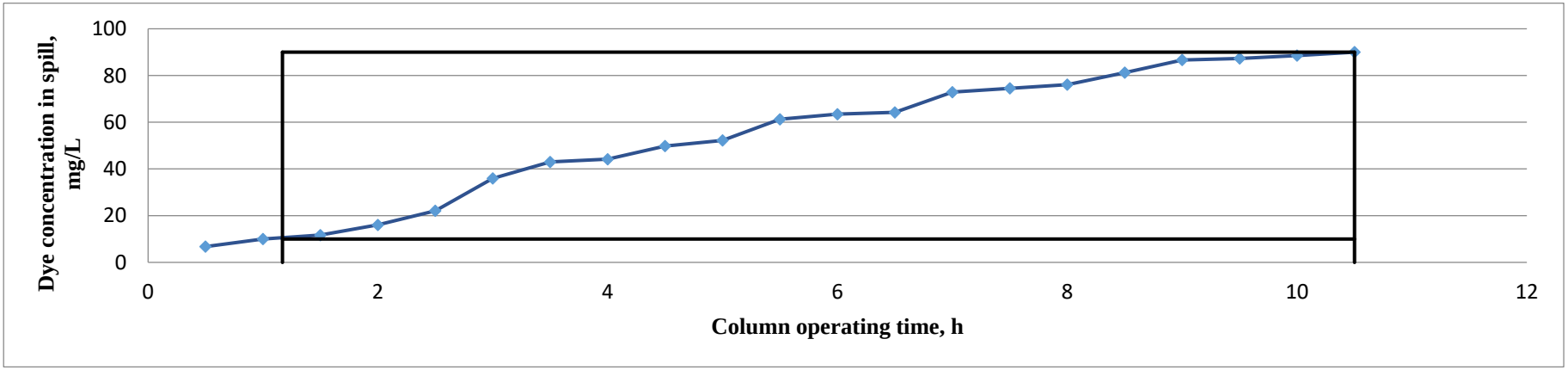


Figure 6. Breakthrough curve of WG-12 activated carbon bed for tartrazine at solution flow rate 9 m/h.

The obtained results for tartrazine adsorption show that the faster the flow rate the shorter the time until the bed reaches the exhaustion of its adsorption capacity. For activated carbon ROW 08 Supra, at the flow rate of 3 m/h, the time was 76.5 h, and when the flow rate was increased to 9 m/h, the time decreased to 15 h. The same can be observed for activated carbon WG-12, where for the lowest applied flow rate the time of adsorption capacity depletion was 53.5 h, while for the highest applied rate this time decreased to 10.5 h. For the anionic dyes used, tartrazine had the longest time to reach the adsorption capacity depletion point. The dynamic absorption for this dye was also higher. Adsorption of tartrazine is more efficient on ROW 08 Supra activated carbon due to its longer duration. The results of the calculations are shown in Table 3.

Table 3. Adsorption of tartrazine.

Type of Carbon	Flow Velocity m/h	Time to Adsorption Capacity Breakthrough		Time to Adsorption Capacity Depletion		Mass Exchange Zone Sliding Velocity cm/h	Dynamic Adsorption	
		h	min	h	min		g/L	mg/g
ROW 08 Supra	3	8.50	510.00	76.5	4590	0.37	10.20	27.40
	6	4.33	260.00	39	2340	0.72	5.20	13.70
	9	1.67	100.00	15	900	1.88	2.00	5.30
WG-12	3	5.94	356.67	53.5	3210	0.53	7.13	17.00
	6	3.22	193.33	29	1740	0.97	3.87	9.20
	9	1.17	70.00	10.5	630	2.68	1.40	3.30

Adsorption of Anilan Yellow Gold

The results of dynamic adsorption studies of anilan yellow gold on two porous carbon materials (ROW 08 Supra and WG-12) in the form of breakthrough curves are shown in Figures 7–12.

Table 4 shows the adsorption results showing that the velocity of mass transfer zone increases with increasing flow velocity. The depletion of adsorption capacity for ROW 08 Supra activated carbon at 3 m/h flow rate occurred after 86 h while for 9 m/h flow rate the time was 19.5 h. The second adsorbent used, WG-12, also showed faster wear of the bed with higher flow rate, for which the column operating time at 3 m/h was 62 h, while for the flow rate of 9 m/h this time decreased to 10.5 h. ROW 08 Supra activated carbon showed a longer wear time.

Table 4. Adsorption of anilan yellow.

Type of Carbon	Flow Velocity m/h	Time to Adsorption Capacity Breakthrough		Time to Adsorption Capacity Depletion		Mass Exchange Zone Sliding Velocity cm/h	Dynamic Adsorption	
		h	min	h	min		g/L	mg/g
ROW 08 Supra	3	9.56	573.33	86	5160	0.33	11.47	30.18
	6	5.11	306.67	46	2760	0.61	6.13	16.13
	9	2.17	130.00	19.5	1170	1.44	2.60	6.84
WG-12	3	6.89	413.33	62	3720	0.45	8.27	19.69
	6	3.78	226.67	34	2040	0.83	4.53	10.79
	9	1.17	70.00	10.5	630	2.68	1.40	3.33

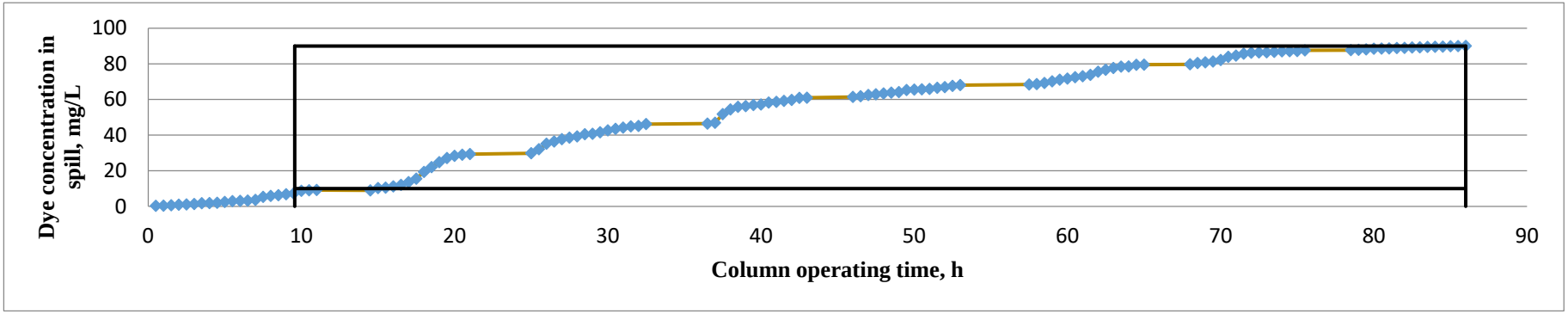


Figure 7. Breakthrough curve of ROW 08 Supra activated carbon bed for anilan yellow gold at solution flow rate 3 m/h.

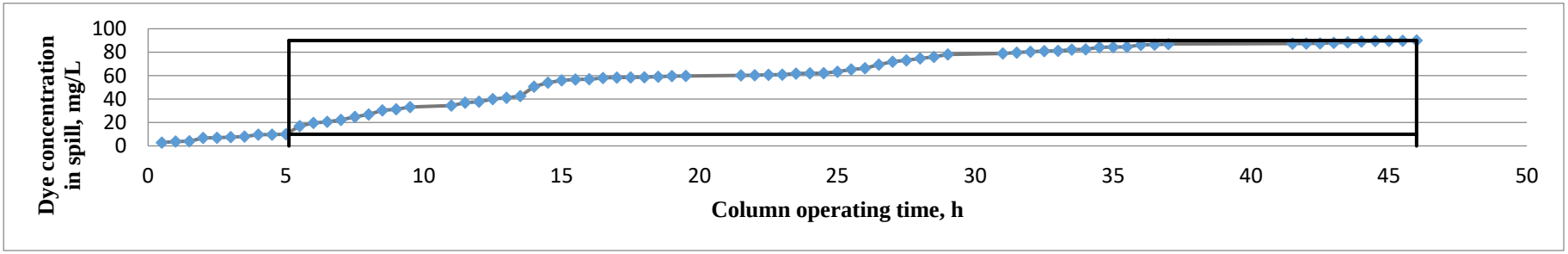


Figure 8. Breakthrough curve of ROW 08 Supra activated carbon bed for anilan yellow gold at solution flow rate 6 m/h.

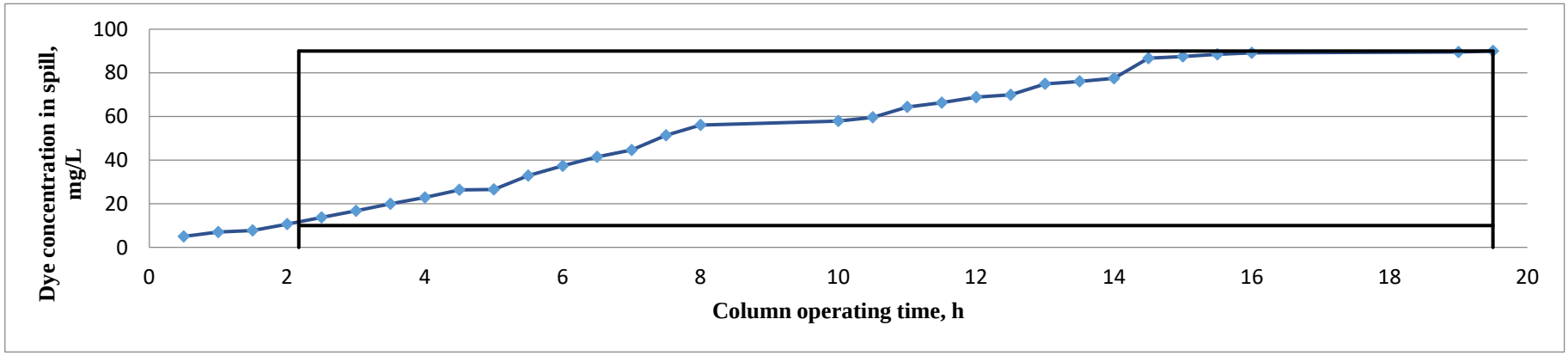


Figure 9. Breakthrough curve of ROW 08 Supra G-12 activated carbon bed for anilan yellow gold at solution flow rate 9 m/h.

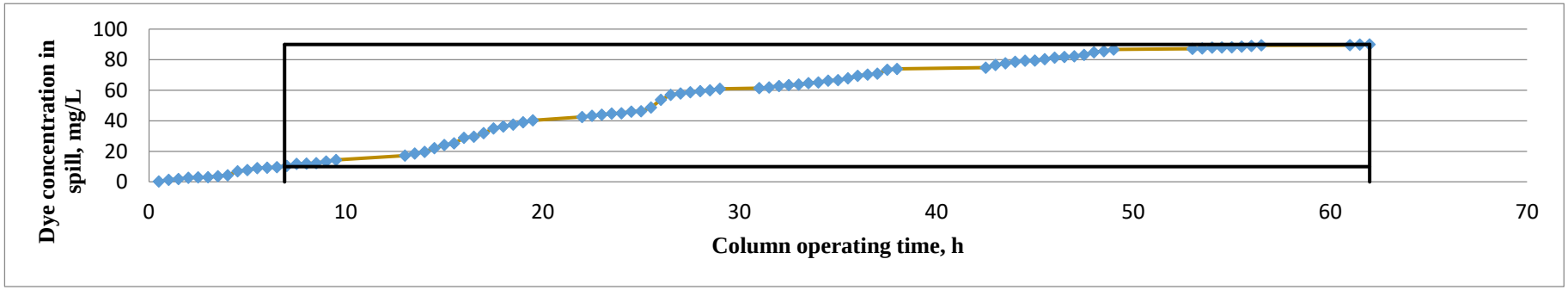


Figure 10. Breakthrough curve of WG-12 activated carbon bed for anilan yellow gold at solution flow rate 3 m/h.

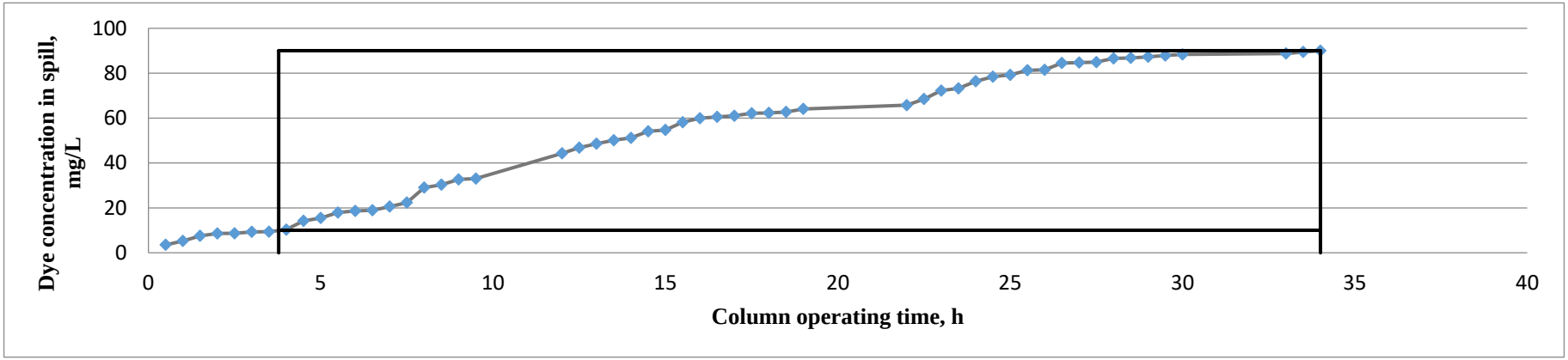


Figure 11. Breakthrough curve of WG-12 activated carbon bed for anilan yellow gold at solution flow rate roztworu 6 m/h.

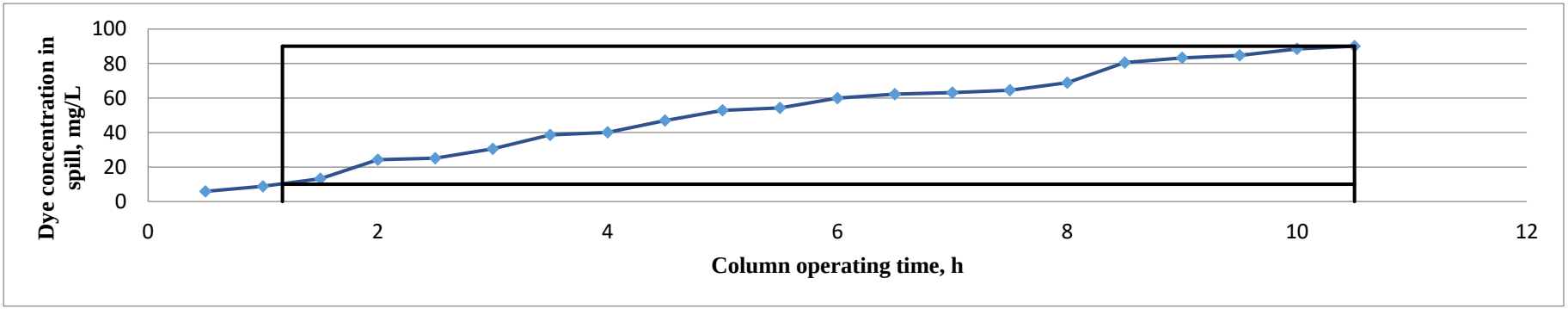


Figure 12. Breakthrough curve of WG-12 activated carbon bed for anilan yellow gold at solution flow rate 9 m/h.

4. Discussion

The carbon materials used in this study (ROW 08 and WG-12) effectively removed selected dyes (tartrazine and anilan yellow). The dynamic adsorption rates closely depend on many parameters, such as the water flow rate through the filter bed which has a direct effect on the contact time of the flowing solution with the activated carbon.

The authors of the paper [27] conducted adsorption studies of orange II, methyl orange and methylene blue dyes on carbon materials under flow-through conditions under the following conditions: initial concentration of dyes was 0.5 mg/mL, height of the bed in the column 0.5; 1 or 2 cm, volume flux 1 ml/min. It was shown that the highest dynamic adsorption values were obtained for sorption of orange II (669–706 mg/g). Slightly smaller dynamic adsorption values were obtained for methyl orange, the least for methylene blue.

The authors of the paper [29], who conducted studies on the sorption of a dye called Acid Orange 7 under dynamic conditions, found that increasing the flux of solution flowing through the filter column decreases the adsorption efficiency of the dye. Therefore, it is important to determine the correct flow rates through the adsorption bed to remove as much dye as possible. This was confirmed in their study by the authors of paper [30], who conducted adsorption studies of methylene blue on activated carbon obtained from agricultural waste. The concentration of this dye was 100 mg/L, the flux values were 5, 10 or 15 mL/min and the height of the carbon bed was 2, 3 or 4 cm. They found that the adsorption rate was affected by the flow rate, bed height.

Other researchers [31] conducted a study on the effect of the initial concentration of dye flowing through the adsorption bed, because it affects the working time of the bed. They investigated the adsorption of RB5 dye on activated carbon obtained from bamboo at the following parameters: initial concentration 50 ÷ 200 mg/L, volume flux 10 ÷ 30 mL/min, adsorption bed height 4 ÷ 8 cm. The highest removal efficiency of this dye (39.02 mg/g) was obtained when the dye concentration was 100 mg/L, the bed height was 8 cm and the volume flux was 10 mL/min.

5. Conclusions

Activated carbons are very effective at removing both anionic and cationic dyes, which were used in laboratory tests. The effectiveness of their removal depends on the type of activated carbon used. Among the activated carbons used in the study, the most effective adsorption under dynamic conditions was on ROW 08 Supra activated carbon. The longest time to complete depletion of sorption capacity was obtained on this activated carbon (76.5 h for tartrazine and 86 h for anilan yellow at flow rate of 3 m/h). An increase in filtration velocity results in a faster depletion of the adsorption capacity, while consequently, shorter lifetimes of activated carbons are obtained.

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