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DYE REMOVAL EFFICIENCY OF VIRGIN ACTIVATED CARBON AND ACTIVATED CARBON REGENERATED WITH FENTON'S REAGENT

The effectiveness of virgin and regenerated activated carbons was established for crystal violet removed from aqueous solutions. Granular activated carbon, WDex, saturated with the dye was regenerated using classic or modified Fenton's reagent, Fe^{2+}/H_2O_2 and Fe^{2+}/Ox, respectively. The application of modified Fenton's reagent resulted in the formation of hydrogen peroxide directly in the regeneration solution. The study was conducted under static and dynamic conditions. The sorptive capacities of virgin and regenerated WDex activated carbons for crystal violet were reported to be similar (approximately 42 mg/g). The results of the dynamic sorption show that under the predetermined conditions the regenerated activated carbons were better sorbents. The amount of dynamic sorption was approx. 17.6 g/dm^3. The longest breakthrough time (3970 min) and the longest saturation time (11 600 min) were observed for the carbon bed regenerated with modified Fenton's reagent.

1. INTRODUCTION

Current research studies concerning the treatment of wastewater show that advanced oxidation processes (AOP) are becoming a common procedure to remove dyes. The method ensures that hydroxyl radicals forming in the reaction environment are characterized by the highest oxidizing potential (2.70 V) [1, 2]. The radicals develop in the system containing hydrogen peroxide or ozone as a result of the exposure to UV irradiation or addition of Fenton's reagent being a mixture of Fe^{2+} and H_2O_2 in the presence or absence of UV irradiation [3–6]. The disadvantages include large amounts of reagents needed, sewage acidification and the formation of indirect oxidation products. On the other hand, it was found [7–10] that activated carbon can catalyze the conversion of hydrogen peroxide or ozone to hydroxyl radicals. For this reason, it may be possible to combine sorption with oxidation by AOP, the former as

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a method for removing a dye from a solution and increasing the concentration on the sorbent, and the latter as a method of the sorbent regeneration.

The objective of the study was to establish the adsorption efficiency of activated carbons (WDex) – virgin and regenerated by AOP – for crystal violet removed from aqueous solutions. The suitability of activated carbon to remove a dye was determined by analyzing the sorption under static and dynamic conditions. The results obtained under static conditions were used to estimate the total sorptive capacity of activated carbons at sorption equilibrium, while the results obtained under dynamic conditions were applied to determine the parameters and service life of the activated carbon bed. Classic Fenton's reagent, Fe^{2+}/H_2O_2, and modified Fenton's reagent, Fe^{2+}/Ox, were used as regenerating agents [11, 12]. When added to a reactive system, Fe^{2+}/Ox is an alternative source of hydrogen peroxide generated in the reaction environment. This ensures gradual development and effective use of hydroxyl radicals. As shown by the literature, this agent has been commonly used to oxidize organic compounds but it has not been applied to regenerate activated carbon.

2. EXPERIMENTAL

The materials used for the analysis were: commercially available granular activated carbon (GAC), WDex, produced by Gryfskand, whose physical and chemical parameters, and pore structure are shown in Tables 1 and 2.

Table 1

Physical and chemical properties of the WDex activated carbon [13]

Parameter	Value
Surface area, m^2/g	1050
Bulk density, g/dm^3	415
Water adsorption capacity, cm^3/g	0.80
Mechanical strength, %	96
Abrasion resistance, %	0.5
Ash content, %	21.8
Methylene blue index (MBI)	24
Iodine value, mg/g	980

Table 2

Capillary pore distribution in WDex carbon [13]

WDex	Capillary pore radius, nm					$\Sigma\Delta V$
	< 1.5	1.5–15	15–150	150–1500	1500–7500	
	Capillary pore volume, ΔV					
[cm^3/g]	0.3048	0.1727	0.1230	0.2716	0.0872	0.9530
[%]	32.0	18.1	12.9	28.5	8.5	100

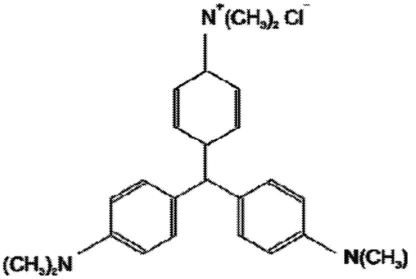

Fig. 1. Structural formula of crystal violet ($C_{25}H_{30}N_3Cl$)

Water solubility of crystal violet (hexamethyl *p*-rosaniline chloride, Fig. 1) at 20 °C is 16 g/dm^3. Its concentration was determined using a Marcel Media UV/VIS spectrophotometer at the wavelength λ of 590 nm.

Sorption of crystal violet under static conditions. The initial kinetic analysis showed that the adsorption equilibrium time in the crystal violet/WDex carbon system at 22 °C was 26 h. The adsorption isotherms were determined in the system composed of 0.3 dm^3 of the dye solution of the concentration of 165 mg/dm^3 and a carbon sample, the amount ranging from 0.10 g to 1.0 g. The amount of the adsorbed substance was determined from the difference in the concentrations of the adsorbate solutions before and after adsorption, according to the formula:

$$a_s = \frac{(c_0 - c_{eq})V}{m_c}$$

where: c_0 – initial concentration, c_{eq} – equilibrium concentration, V – solution volume, m_c – mass of the activated carbon.

Sorption under dynamic conditions. The analysis was conducted using a carbon adsorption column of the diameter of 1 cm and an active bed depth of 15 cm. The rate of the gravitational flow through the bed was 1.0 m/h, which ensured the contact time of 9 min. The concentration of crystal violet was approximately 40 mg/dm^3. The sorption process was continued until the breakthrough point was reached, i.e. when the violet concentration in the liquid leaving the carbon adsorption column c_p was $0.05c_0$, and until the adsorption capacity was exhausted, i.e. when $c_k = 0.7c_0$. The mass transfer zone height, L_0, was determined using the Michaels–Treybol equation [14, 15]

$$L_0 = L\frac{\tau_k - \tau_p}{\tau_k - (1-\varphi)(\tau_k - \tau_p)}$$

where: L_0 – mass transfer zone height, L – activated carbon bed depth, τ_p, τ_k –breakthrough and saturation times until the adsorption capacity of the activated carbon bed was exhausted, φ – symmetry coefficient for the activated carbon output curves, which is approximately 0.5 [16].

The rate at which the mass transfer zone passes through the activated carbon bed was calculated using the following formula:

$$\mu_0 = \frac{L_0}{\tau_k - \tau_p}$$

The dynamic adsorption capacity a_d was determined from:

$$a_d = \frac{c\tau_p Q}{V}$$

where: c – concentration, τ_p – time of the dynamic adsorption capacity, Q – rate of the solution flow through the activated carbon bed, V – volume of the activated carbon bed in the column.

Regeneration of the activated carbon after sorption of crystal violet. After sorption, the WDex activated carbon saturated with crystal violet was separated from the solution and treated with water in a reactor. 300 mg/dm^3 of H_2O_2 or Ox was then introduced at pH 3–4. Subsequently, iron(II) sulfate(VI) ($FeSO_4 \cdot 7H_2O$) was added, with the weight ratio being Fe^{2+}/H_2O_2 or Ox = 1:4. The reactor content was stirred for 20 min at room temperature while the carbon was rinsed with distilled water (5 × 100 cm^3). The regenerated carbon was dried and its pH was determined before the subsequent static and dynamic sorption processes.

Measuring the pH of the water extract of the activated carbon. 1.0 g of carbon was treated with 20 cm^3 of water, shaken for 1 h, and stored at room temperature for 24 h until used to measure the pH of the solution in contact.

3. RESULTS AND DISCUSSION

The research was conducted to analyze the removal of crystal violet from aqueous solutions by sorption on WDex activated carbons, virgin and regenerated, using classic or modified Fenton's reagent, Fe^{2+}/H_2O_2 and Fe^{2+}/Ox, respectively. As can be seen from Tables 1 and 2, WDex activated carbon is a micro-mesoporous carbon with a large surface area (1050 m^2/g), a high iodine value (980 mg/g), and a high methylene blue value (24cm). The parameters show that this carbon displays a very high sorptive capacity even for such large particles as those of crystal violet.

Crystal violet – a dye belonging to the group of aniline dyes – is commonly used for dyeing textiles, paper, and as a component of inks for printing. As the dye is considered hazardous to human health and the environment [17], it absolutely needs to be removed from wastewater. A particle of crystal violet is composed of three benzene rings with a multiple bond system. In aqueous solution, it acts as a cation, and the positive charge is delocalized over the whole particle. This indicates that the interactions between a crystal violet particle, electrons π of the graphite structures, and oxygen functional groups present on the activated carbon surface should facilitate the sorptive removal of the dye from the solution.

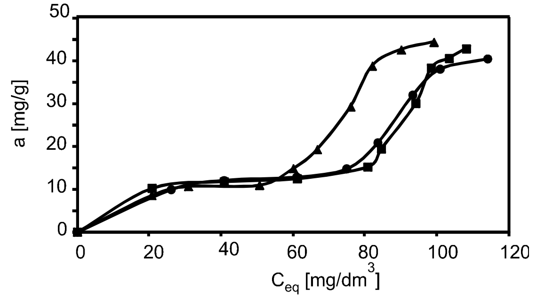

Fig. 2. Sorption isotherms of crystal violet on virgin and regenerated activated carbons: ● –WDEx, × – WDex/Fe^{2+}/H_2O_2 and ■ – WDex/Fe^{2+}/Ox

The sorption isotherms in Fig. 2 show that the sorption of crystal violet up to 12 mg/g can be described by the Langmuir isotherm, above that value it increases significantly to 43 mg/g. The isotherms suggest that a change in the spatial orientation of the sorbed particles may occur after some surface area of the activated carbon was covered, i.e. some active centres were used. The sorptive capacity of the activated carbon saturated with crystal violet regenerated with classic or modified Fenton's reagent was similar to that of virgin activated carbon. The similarity refers to both the amount and mechanism of sorption.

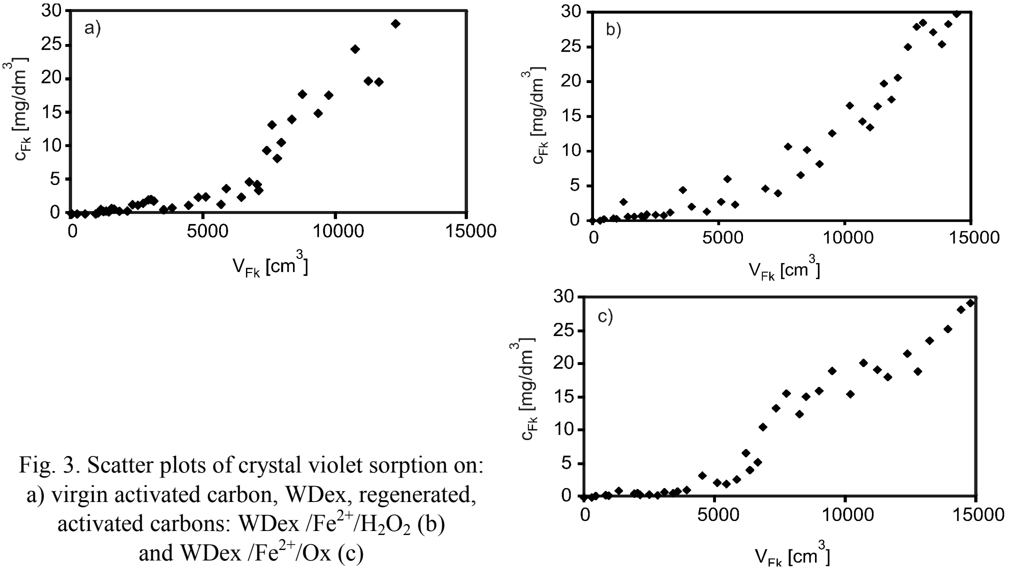

Fig. 3. Scatter plots of crystal violet sorption on: a) virgin activated carbon, WDex, regenerated, activated carbons: WDex /Fe^{2+}/H_2O_2 (b) and WDex /Fe^{2+}/Ox (c)

The next stage of the analysis focused on the dynamic sorption on virgin activated, WDex, which was then saturated with crystal violet and regenerated in the same way as under static conditions. Figure 3 and Table 3 illustrate the measured and calculated parameters of dynamic sorption. Under pre-determined conditions, activated carbons regenerated by oxidation of the adsorbent dye were found to be better sorbents. The dynamic sorption amounted to approximately 17.6 g/dm^3. The breakthrough time τ_p for WDex/Fe^{2+}/H_2O_2 was 3953 min, while for WDex/Fe^{2+}/Ox it was 3970 min. The saturation times τ_k were 11 400 and 11 600 min, respectively. The shift rate of the mass transfer zone determined for the regenerated carbons was 0.11 cm/h and it was ca. 20% lower than that obtained for the virgin carbon.

Table 3

Parameters of dynamic adsorption of crystal violet on virgin activated carbon and regenerated carbons

Activated carbon	Time [min]		Dynamic sorption [g/dm^3]	Height of mass transfer zone [cm]	Shift rate of the masstransfer zone [cm/h]
	τ_p	τ_k			
WD-extra	3512	9620	15.60	13.95	0.14
WD-extra/Fe^{2+}/H_2O_2	3953	11400	17.56	14.55	0.12
WD-extra/Fe^{2+}/Ox	3970	11600	17.60	14.70	0.11

The results obtained under static and dynamic conditions show that sorption is an effective means of removing dyes from solutions. The proposed method for the regeneration of spent activated carbon using Fenton’s reagent is suitable for multiple cycles. The regeneration procedure applied to activated carbons caused that the recovered sorbent had sorptive capacity similar to or even slightly better than that of the virgin carbon. The different amounts of sorption obtained for virgin carbon and regenerated carbons were probably due to the changes in the porous structure and the chemical surface characteristics. The data presented in Refs. [18] and the experimental data obtained by the authors show that the action of oxidants (from the AOP group) on the activated carbon with an adsorbed organic substance does not lead to significant changes in the distribution or size of pores, but it does affect the change in the chemical surface characteristics. It was impossible to determine the functional groups on the analyzed activated carbons because of the presence of ash, iron and residues of non-oxidized crystal violet. The external surfaces of the granules were observed using an optical microscope at magnification 80×.

As can be seen from Fig. 4, the external surfaces of virgin and regenerated granular activated carbons (WDex, WDex/Fe^{2+}/H_2O_2, and WDex/Fe^{2+}/Ox) are different. The surface of the virgin GAC, WDex, was slightly porous with several bright points of mineral substances (Fig. 4a). Once the carbon was saturated with crystal violet, the external surface of the granules (Fig. 4b) changed slightly. In a colour image, there were traces of crystal violet on the surface of the mineral substances. The contact of the crystal violet solution with the activated carbon resulted in the sorption of the dye on the internal surface and the attachment to/reaction with the mineral substances, e.g. ash, present in the activated carbon.

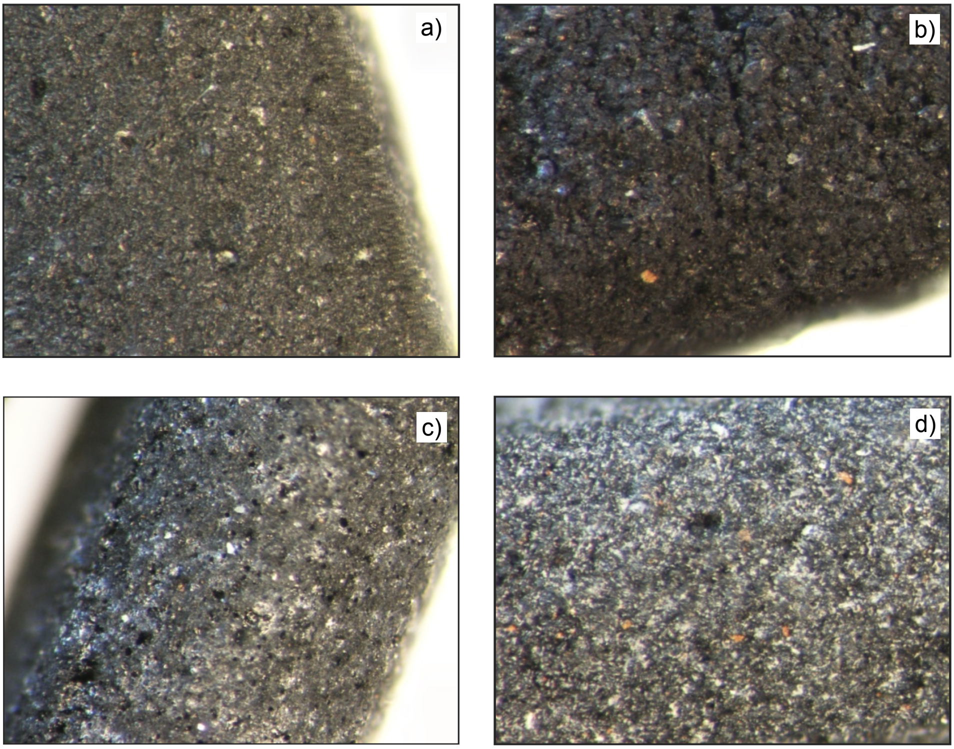

Fig. 4. Images of the external surfaces of: virgin granulated activated carbon, WDex (a), regenerated carbons, WDex/Fe^{2+}/H_2O_2 (b) and WDex/Fe^{2+}/Ox (c), magnification 80×

A completely different image of the external surface of the granules was obtained after applying Fenton's reagent (Figs. 4c and 4d). The surface of the GAC regenerated by oxidation with classic Fenton's reagent (Fig. 4c) was similar to that of the virgin carbon. The different character, i.e. higher roughness of the carbon surface after regeneration with modified Fenton's reagent was due to the increase in the content of the additional substance. For this reason, pH of the water extract of the activated carbons had to be determined. It was found that the the solution after extraction of the virgin activated carbon, WDex, was basic (pH = 8.60). Water extract of the activated carbon after regeneration with classic Fenton's reagent was acidic (pH = 4.0). Finally, the water extract of the activated carbon regenerated with modified Fenton's reagent was almost neutral (pH = 6.5), despite the fact that the regeneration was performed in a solution of pH 3.0. This suggests that the sorption of crystal violet on activated carbon was dependent on both the sorbent pore structure and its pH. The process mechanism, however, was different.

4. CONCLUSIONS

The results of investigation indicate that sorption on virgin and regenerated WDex activated carbons is an efficient method for removing crystal violet from aqueous solutions. The process is thus well suited for treating wastewater containing this dye. The study suggests that activated carbon saturated with crystal violet can be regenerated effectively using advanced oxidation processes at the presence of Fenton's reagent. The results obtained under static conditions indicate that the sorptive capacity of the virgin activated carbon for crystal violet was comparable to that of the regenerated carbons (approximately 43 mg/g). Under dynamic conditions, modified Fenton's reagent was found to be a more efficient oxidant used for the adsorbed crystal violet. The bed of the WDex activated carbon regenerated with modified Fenton's reagent had the dynamic adsorption capacity of 17.6 mg/dm^3, which was higher than that of the virgin carbon, i.e. 15.6 g/dm^3. Moreover, the bed of the WDex activated carbon regenerated with modified Fenton's reagent was characterized by the longest breakthrough and saturation times. This was attributable to the effective oxidation of the adsorbed crystal violet as well as the favourable chemical character of the external and internal surfaces of the regenerated activated carbon.

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