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ADSORPTION NAPHTOL GREEN B ON ACTIVATED CARBON F-300

ADSORPCJA ZIELENI NAFTOLOWEJ B NA WĘGLU AKTYWNYM F-300

Abstract: In the present study, the sorptive capacity of activated carbon F-300 in the removal of dyes from textile wastewaters, was estimated. Dye – naphtol green B – were chosen to study, and as adsorbent we have chosen the activated carbon F-300, virgin and regenerated. Fenton reagent, which is good oxidant, was used for activated carbon regeneration. The iodine number, which was measured according to the directive PN-83 C-97555.04, was used to evaluate sorptive capacity of regenerated activated carbon. Dye concentration was 400 mg/dm^3. Sorption abilities of activated carbon were expressed by mass balance relationship in case of fresh activated carbon it was 21 mg/g, and after regeneration – from 22 mg/g to 33 mg/g. The highest removal efficiency was 88 % (carbon after 4th regeneration), the lowest – 74 % for virgin carbon. The experimental data adsorption isotherms were defined. Adsorption theoretical models Freundlich or Langmuir were selected. The value of the correlation coefficient (r^2) showed better fit to Langmuir model. The experimental data shows that chosen activated carbon can be used for the decontamination of dyes from textile wastewater. However, model tests need to be verified on real wastewater samples.

Keywords: dye adsorption, activated carbon, Fenton reagent, naphtol green B

1. Introduction

Dyes are natural or synthetic colorants used in various industries such as textiles, tanneries, paints, pulp and paper [1]. Synthetic dyes are indispensable to the textile and dyeing industries. The use of dyes, as most chemicals, can be hazardous [2]. Physical and chemical properties of dyes make them sparingly biodegradable, toxic, carcinogenic and mutagenic compounds [3]. Dyes are classified on a few groups such as acid dyes, basic dyes, disperse dyes, direct dyes, reactive dyes, solvent dyes, sulphur dyes, vat dyes and others [4]. The colour of dyes is provided by the presence of a chromophore groups. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalised electrons. The chromogen, which is the aromatic structure usually containing benzene, naphthalene or anthracene rings, is part of chromogen – chromo-

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phore structure along with an auxochrome. Common chromophore groups are azo (-N=N-), nitroso (-NO or N-OH), nitro (-NO_2 or =NO-OH), sulfur (C=S) and others [5].

The removal of contaminants from the effluents is problematic with established technologies often unable to adequately reduce contaminant concentrations. This has initiated a search for more effective, economic treatment techniques, of which adsorption processes appear to offer significant potential. The conventional wastewater treatment such as biological treatment process is not very effective in treating a dyes wastewater. It is also treated by physical or chemical processes, but these processes are very costly and cannot effectively be used to treat the wide range of compounds [6]. Methods used to treat wastewater containing dye include coagulation-flocculation [7], advanced oxidation process [8], adsorption[9] and membrane technology [10]. The adsorption process is one of the effective methods for removal dyes from the textile wastewater [6].

Adsorption is a flexible process that may be fully automated, incur significantly lower capital costs than, for example, ozone, membrane or biological processes [11].

Activated carbons are mainly used to remove organic and inorganic compounds from the water [12–13]. The various kinds of activated carbons are used in Polish waterworks such as granulated activated carbon, for example WD-extra, WG-12, or granular one PICA, F-300 [14]. The sorptive capacity of activated carbon depend on the properties of pores, *ie* their surface area and size, chemical nature of the surface, structure and chemical properties of dissolved organic substances and other substances, which can be absorbed by activated carbon [15].

Activated carbons can be regenerated during a various processes such as thermal and chemical methods [16]. Oxidation of organic chemical pollutants by Fenton reagent with hydroxyl radical OH is one of chemical regeneration methods [17]. The Fenton reagent is defined as a mixture of hydrogen peroxide and iron(II) ion ($H_2O_2 + Fe^{2+}$) and it is effective for color and COD removal of dye effluent [18–19]. The one of the regeneration's advantage is fact that it is cheaper than changing the deposit on new one.

According to the previous works [20–23] concerned possibility of sorption of dyes on activated carbon, the present work deals with checking sportive capacity of virgin and regenerated by Fenton reagent activated carbon F-300 with reference to dye – napthol green B.

2. The material and methods of investigations

2.1. Activated carbon characteristics

Activated carbon called F-300 is used for removal of organic pollutants (detergents, petrochemicals, grease, amines, oils) from municipal or industrial (production of bearings) wastewaters. Exhausted activated carbon was regenerated by Fenton reagent.

2.2. Dye characteristics

Napthol green B (Acid green 1) belongs to nitroso group dyes (Fig. 1). This dye is very well soluble in water and its molar mass is 878.79 g/mol. Industrial napthol green

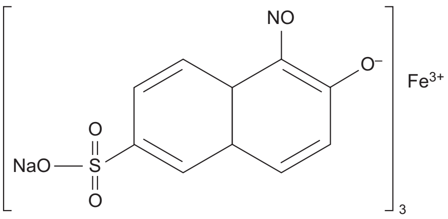

Fig. 1. Naphthol green B

B is a product which contain 50 % of clean dye. Dye as an anion is ranked as acidic dyes [24]. Naphthol green B is used to dye cotton, nylon and paper. It can be found in textile and printing wastewater.

2.3. Course of the experiment

2.3.1. Adsorption on virgin activated carbon

Virgin F-300 activated carbon (0.2 g, 0.5 g, 1 g, 1.5 g, 2 g, respectively) was placed in conical flasks (300 cm^3). Then 100 cm^3 volumes of the solution of napthol green B, having the concentration of 400 mg/dm^3, were added to the flasks and the contents were shaken for ten hours. After that time, the phases, *ie* the dye solution and the spent sorbent, were separated. F-300 activated carbon was then washed with distilled water and dried in a dryer.

2.3.2. Adsorption on regenerated activated carbon

Following adsorption, F-300 activated carbon was regenerated using Fenton reagent. The latter was prepared in the following way: distilled water was poured into 1 dm^3 beaker, then concentrated sulphuric(VI) acid was added, in such a way so that pH ranged around 3. To so prepared solution, 10 cm^3 of $FeSO_4 \cdot 7\ H_2O$ (the amount of ferrum ions 9.27 mg) and 1.5 cm^3 of hydrogen peroxide were added. WDex activated carbon was treated with Fenton reagent solution (500 cm^3) prepared in a way described above, then it was stirred for 15 min. Activated carbon was then washed with distilled water, afterwards the regeneration process was repeated. Thus regenerated F-300 activated carbon was used again to adsorb dyes mixture on it.

2.3.3. Determination of dye concentration

Spectrophotometric method was used to determine the concentration of dyes. Marcel Media UV/VIS Spectrophotometer was employed. First, spectra of naphthol green B were recorded and it has the λ = 715 nm wavelength maximum. Following the sorption process, samples of dyes were taken from a conical flask using a pipette and placed into a plastic cell and then they were put into the spectrophotometer. The concentration of dye was read on the computer and measured at determined concentration.

2.3.4. Changes in carbon parameters during the experiment

The process of adsorption and regeneration of activated carbon was also evaluated during an experiment. It was noted that regeneration process was significantly limited due to a loss of carbon mass. The mass of the virgin activated carbon has decreased from 15.000 g to 10.021 g (Table 1).

Table 1

Changes in carbon parameters during the experiment

Sorbent type	Mass	Mass loss [%]
Virgin carbon	15.000	
Carbon after the first regeneration	13.742	8.39
Carbon after the second regeneration	12.485	16.77
Carbon after the third regeneration	11.801	21.33
Carbon after the fourth regeneration	11.167	25.55
Carbon after the fifth regeneration	10.698	28.68
Carbon after the sixth regeneration	10.021	33.19

The sorptive capacity of regenerated carbon was measured by changes of iodine number (Table 2), which was evaluated according to directive no. PN-83 C-97555.04. Iodine number was the highest after the 1st regeneration, and it was the lowest for virgin carbon F-300.

Table 2

Iodine number

Activated carbon	Iodine number
Virgin carbon	507.68
After the first regeneration	666.33
After the second regeneration	656.811
After the third regeneration	634.6
After the fourth regeneration	647.119
After the fifth regeneration	644.119
After the sixth regeneration	644.119

3. Results and discussion

At the first stage of investigations surface sorption was calculated from following formula [25]:

$$A = \frac{(C_0 - C_i) \cdot V}{m_c},$$

where: C_0 and C_i – dye initial and equilibrium concentration, respectively;
V – solution volume,
m_c – mass of dry activated carbon.

On the basis of calculated values of surface sorption, it was possible to plot sorption isotherms (Fig. 2).

The highest surface sorption on virgin carbon for naphthol green B was 21 mg/g. As regards regenerated carbon, it ranged from 22 mg/g to 32 mg/g. Experimental data indicate that F-300 activated carbon has good sorptive properties according to

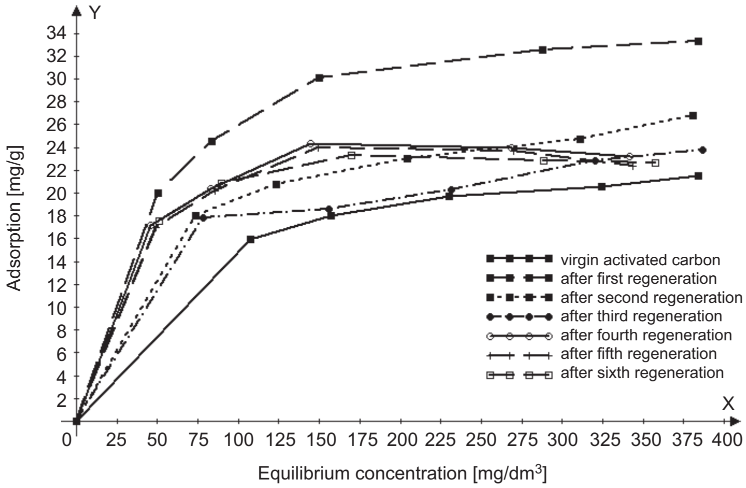

Fig. 2. The isotherms of naphthol green B on virgin and regenerated active carbon F-300

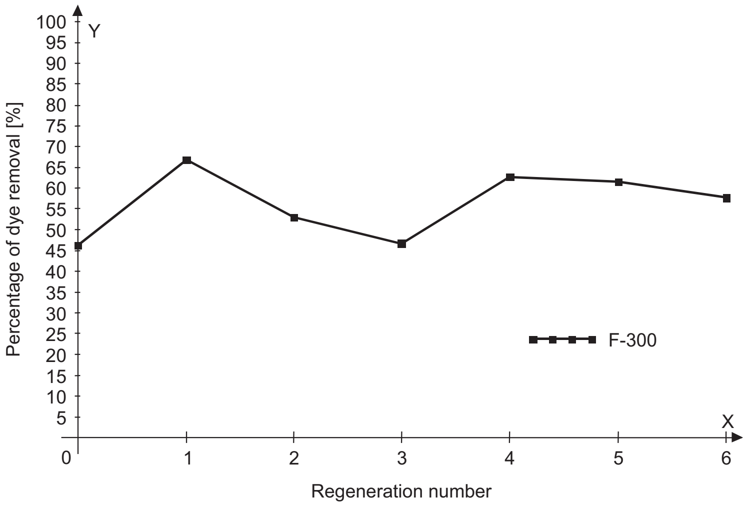

Fig. 3. Percentage of naphtol green B removal for virgin and regenerated activated carbon for $m_c = 1$ g

experimental models. Regeneration with Fenton reagent, however, slightly improves sorptive properties of activated carbon.

The experimental data allowed to evaluate dependence of selected dye removal percentage on subsequent regeneration cycles (Fig. 3). The percentage removal of virgin activated carbon F-300 was 46 % (carbon mass equal 1 g). As regards regenerated carbon (carbon mass equal 1 g), the percentage of removal ranged from 46 % to 66 %.

At the next stage of investigations, an attempt was made to fit an adsorption model to experimentally obtained isotherms. Two models, *ie* Freundlich equation and Langmuir equation, were used to analyse adsorption isotherms.

The Langmuir equation [26], applied to determine adsorption results, is based on the assumption that the adsorption maximum corresponds to the sorbent surface being saturated with adsorbed molecules of constant energy, and additionally, no migration of adsorbed substance on the sorbent plane takes place. The Langmuir equation can be presented in the following form:

$$\frac{C}{A} = \frac{1}{a_m \cdot k} + \frac{1}{a_m} \cdot C$$

where: C – dye concentration in the solution,
A – adsorption,
k – a constant related to adsorption heat,
a_m – adsorbed surface.

The Freundlich isotherm [27] is the earliest developed relation that expressed sorption equation. The Freundlich model follows the formula:

$$A = k \cdot c^{1/n}$$

where: a – adsorption,
C – concentration,
k – the Freundlich constant,
$1/n$ – the Freundlich exponent,

or in the logarithmic form:

$$\log a = \log k + \frac{1}{n} \log C$$

It should be noted that the higher is the value of the correlation coefficient (r^2), the better is the fit of the theoretical model to the experimental isotherm.

On the basis of calculated correlation coefficients (Table 3), it can be stated that for naphtol green B adsorption on virgin and regenerated carbon F-300, the Langmuir model better describes experimental results.

An exemplary Freundlich isotherm for activated carbon F-300 after the second regeneration for naphthol green B is shown in Fig. 4 and an exemplary Langmuir isotherm after the sixth regeneration is presented in Fig. 5.

Table 3

Parameters of Freundlich and Langmuir isotherms

Activated carbon	Freundlich isotherm			Langmuir isotherm		
	k	r^2	*n*	*k*	r^2	a_m
Virgin	5.69	0.979	4.464	0.044	0.988	22.222
After the first regeneration	8.016	0.93	4.048	0.044	0.991	34.483
After the second regeneration	6.807	0.99	4.386	0.039	0.985	27.027
After the third regeneration	7.603	0.899	5.347	0.041	0.983	24.39
After the fourth regeneration	10.069	0.755	6.452	0.122	0.996	24.39
After the fifth regeneration	10.162	0.697	6.711	0.147	0.994	23.256
After the sixth regeneration	11.376	0.763	8.000	0.146	0.0998	23.256

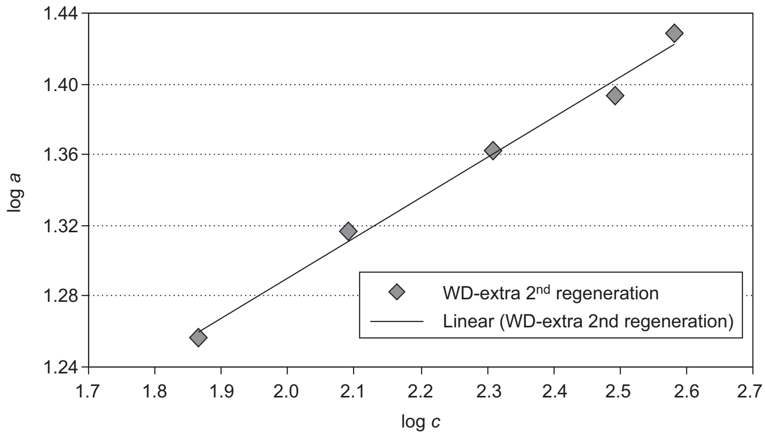

Fig. 4. Freundlich isotherm for F-300 activated carbon after the 2nd regeneration – naphthol green B

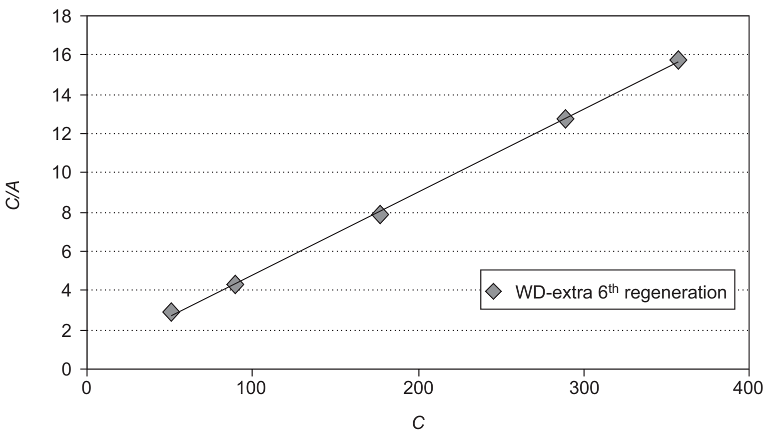

Fig. 5. Langmuir isotherm for F-300 activated carbon after the 6th regeneration – naphthol green B

4. Conclusions

The most important task of experiment was to check sorptive capacity of virgin and regenerated granular activated carbon F-300.

Summing up model investigations into selected dye described above it can be stated that:

– F-300 activated carbon demonstrates high sorptive capacity, which is confirmed by experimental results,

– Fenton reagent used for regeneration made it possible to maintain carbon sorptive capacity,

– a disadvantageous phenomenon that accompanies sorption on regenerated carbon is a sorbent mass loss,

– iodine number confirms better sorptive capacity for regenerated activated carbon than for virgin one,

– the Langmuir model better describes experimental results.

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ADSORPCJA ZIELENI NAFTOLOWEJ B NA WĘGLU AKTYWNYM F-300

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Abstrakt: W pracy podjęto próbę oceny możliwości użycia węgla aktywnego F-300 do usuwania barwników ze ścieków farbiarskich. Do badań wybrano barwnik – zieleń naftolową B, a jako sorbent zastosowano węgiel aktywny F-300 świeży i regenerowany. Regeneracja została przeprowadzona za pomocą odczynnika Fentona, który jest doskonałym utleniaczem. Zdolności sorpcyjne węgla po regeneracji oceniano poprzez zmiany wartości liczby jodowej, która została wyznaczona zgodnie z normą PN-83 C-97555.04. Stężenie barwnika wynosiło 400 mg/dm^3. Zdolności sorpcyjne węgla świeżego wyrażone wartością adsorpcji właściwej, która wynosiła 21 mg/g, a po regeneracji – od 22 mg/g do 33 mg/g. Na postawie danych eksperymentalnych wykreślono izotermy sorpcji. Najwyższy stopień usunięcia zieleni naftolowej B z roztworu wodnego wyniósł 88 % (po IV regeneracji), a najniższy – 74 % (węgiel świeży). Dopasowano teoretyczny model adsorpcji, tj. model Freundlicha lub Langmuira. Wartość współczynnika korelacji wskazuje na lepsze dopasowanie modelu Langmuira. Otrzymane wyniki wskazują, iż wybrany sorbent zarówno w postaci świeżej, jak i zregenerowanej może być stosowany w procesach usuwania barwników ze ścieków farbiarskich. Jednak badania modelowe muszą zostać sprawdzone na realnych próbkach ścieków.

Słowa kluczowe: adsorpcja barwników, węgiel aktywny, odczynnik Fentona, zieleń naftolowa B