DOI: 10.2428/ecea.2016.23(2)12 ECOL CHEM ENG A. 2016;23(2):161-171

Elżbieta BEZAK-MAZUR[1*] and Dagmara ADAMCZYK[1]

# ADSORPTION OF MIXTURE OF TWO DYES ON ACTIVATED CARBON

## ADSORPCJA MIESZANINY DWÓCH BARWNIKÓW NA WĘGLU AKTYWNYM

**Abstract:** Activated carbon is known as adsorbent of various contaminants from wastewater and air. The aim of the work was to estimate sorptive capacity of activated carbon in the removal of dyes, which are contaminants from textile wastewaters. The mixture of two dyes, methyl blue and naphthol green B was selected for investigations and WDex activated carbon, virgin and regenerated, was chosen as adsorbent. The dye concentration, in both cases, was 200 mg/dm$^3$. Sorptive capacities of activated carbon were expressed as values of surface sorption, which in case of fresh activated carbon was 60 mg/g, and after regeneration – ranged from 8 mg/g to 13 mg/g. The experimental data adsorption isotherms were defined and adsorption theoretical model, such as that of Freundlich or Langmuir, was selected. The highest removal efficiency in case of methyl blue was 94% for virgin carbon, the lowest – 75% (carbon after the fourth regeneration). The highest removal efficiency in case of naphthol green B was 78% for carbon after the fourth regeneration, the lowest – 55% (carbon after the first regeneration). The experimental data show that activated carbon can be used for the decontamination of dyes from textile wastewater. Model tests, however, need to be verified on real wastewater samples.

**Keywords:** Dye adsorption, activated carbon, Fenton reagent, methyl blue, naphthol green B

## Introduction

Water covers 71% of the Earth's surface and constitutes 65% of human body mass. Contaminated water becomes a health hazard and a threat to the whole water ecosystem. River, lake and sea pollution originate in man's activities [1]. Those result, among others, in the generation of wastewater from textile, paper-making and leather industries. It contains a lot of organic compounds, including dyes. The latter constitute a major problem in dyeing wastewater treatment because of their complex structure.

[1] Department of Environmental Engineering and Protection, Faculty of Environmental Engineering, Geomatics and Power Engineering, Kielce University of Technology, al. Tysiąclecia Państwa Polskiego 7, 25–314 Kielce, Poland, phone: +48 41 34 24 535.

* Corresponding author: ebezak@tu.kielce.pl

Additionally, physical and chemical properties of dyes make them sparingly biodegradable, toxic, carcinogenic and mutagenic compounds [2–4]. Dye is observable even at very low concentration, which is detrimental to the aesthetic value of waters [5].

Three types of methods: chemical, biological and physical, are used to remove dyes from wastewater. The methods include, among others, coagulation and /or flocculation, membrane technologies (dialysis, reverse osmosis), modern oxidation methods (Fenton reaction, hydrogen peroxide method, UV radiation), biochemical oxidation and adsorption (activated carbons, inorganic adsorbents) [6–9].

According to the literature on the subject, activated carbons are employed as adsorbents of gaseous and liquid contaminants of air and wastewater, also to purify water and as catalysts [10, 11]. The choice of activated carbon as a sorbent depends on its sorptive capacity which changes, depending mainly on the properties of pores, *ie* their surface area and size [12]. Spent activated carbons are regenerated by means of thermal and chemical processes. Oxidation is one of chemical regeneration methods. Presently, modern oxidation methods, termed Advanced Oxidation Processes (AOP), are used. One of them is Fenton reagent which oxidises organic pollutants with hydroxyl radical OH•, generated in the reaction medium, the oxidation potential of which amounts to 2.70 V. Activated carbons are catalysts of the formation of hydroxyl radicals. At the same time, carbons oxidize the pollutants adsorbed on carbon surface. Other oxidizing media include, among others, ozone, UV radiation, ultrasound, $TiO_2$ and hydrogen peroxide [13, 14].

Relying on the possibility of using activated carbons as sorbents of choice, reported in the literature on the subject, the authors undertook model investigations into selected dyes sorption on WDex activated carbon. The previous works [15, 16] of the authors concerned the possibility of sorption of naphthol green B and methyl blue, the present work deals with the sorption of the mixture of the dyes mentioned above.

The aim of the investigations, like in the earlier works, was to check the sorptive properties of activated, virgin and regenerated, WDex carbon, on which the mixture of two dyes, namely of methyl blue (C.I. 42780) and naphthol green B (C.I. 10020) was adsorbed. The spent WDex activated carbon was chemically regenerated with Fenton reagent, which is an excellent oxidizer.

## Material and methods of investigations

### Activated carbon characteristics

In the experiments, virgin WDex activated carbon, manufactured by Gryfskand company, was used. Activated carbon is employed, among others, in water purification. According to the literature [9], its sorptive capacity, *ie* specific surface area (1050 $m^2/g$), pore volume (1.20 $cm^3/g$) and iodine number (943 mg/g) indicate that this activated carbon can be an excellent sorbent.

## Dye characteristics

In the experiment, two dyes were used, namely methyl blue and naphthol green B, of which a mixture was made.

The first dye, methyl blue, alternatively called cotton blue, is one of triamino triphenylmethane dyes, of the following molecular formula: $C_{37}H_{27}N_3Na_2O_9S_3$. This compound is easily soluble in water but weakly soluble in ethanol. Depending on pH, the dye can be either acidic or basic (Fig. 1). The molar mass of the compound is 799.8 g/mol [17].

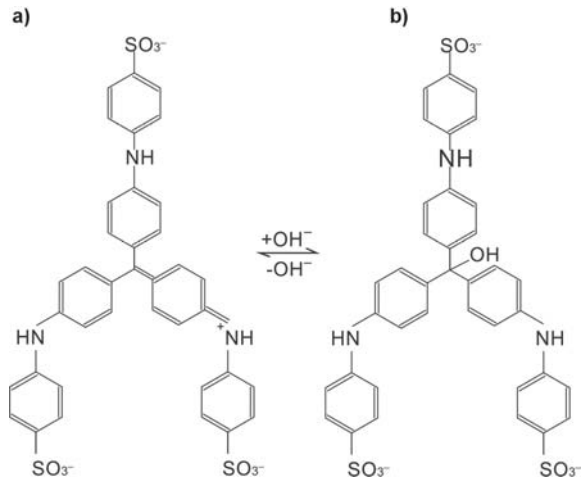


Fig. 1. Acidic a) and basic b) forms of methyl blue

Naphthol green B was the other dye (Fig. 2), the molecular formula of which is $C_{30}H_{15}FeN_3Na_3O_{15}S_3$. Its molar mass is 878.79 g/mol. This dye is very well soluble in water [18].

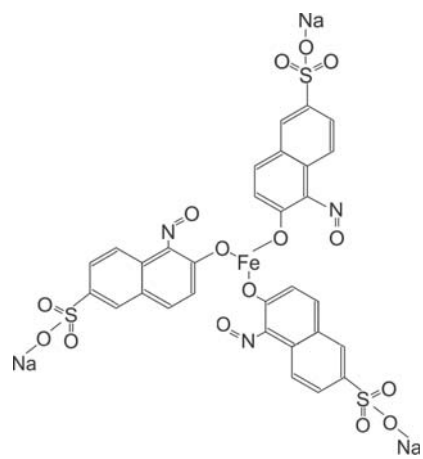


Fig. 2. Naphthol green B

## Course of the experiment

### Adsorption on virgin activated carbon

Virgin WDex activated carbon was placed in conical flasks (0.2 g, 0.5 g, 1 g, 1.5 g, 2 g, respectively). Then 100 $cm^3$ volumes of the solution of the mixture of the dyes, *ie* of methyl blue and naphthol green B, having the concentration of 200 $mg/dm^3$ each, were added to the flasks. The contents were shaken for six hours. After that time, the phases, *ie* the dye solution and the spent sorbent, were separated. WDex activated carbon was then washed with distilled water and dried in a dryer.

### Adsorption on regenerated activated carbon

Following the adsorption process, WDex 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 acid(VI) 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 activated carbon was used again to adsorb dyes mixture on it.

### 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 and methyl blue were recorded. Naphthol green B has the $\lambda$ = 715 nm wavelength maximum, whereas for methyl blue, the maximum is the $\lambda$ = 591 nm wavelength. Following the sorption process, samples of dyes were taken from a conical flask using a pipette and placed into a plastic cell. Then they were put into the spectrophotometer. The concentration of the dye, measured for pre-set wavelength, *ie* $\lambda$ = 715 nm and $\lambda$ = 591 nm for naphthol green B and methyl blue, respectively, was read on the computer monitor.

## Results and discussion

At the first stage of investigations adsorption, $A$, was computed following formula [19]:

$$A = \frac{(c_0 - c_i) \cdot V}{m_c}$$

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. 3–5). The highest surface sorption on virgin carbon for methyl blue and naphthol green B was 60 mg/g and 26 mg/g, respectively. As regards regenerated carbon, it ranged from 8 mg/g to 14 mg/g for methyl blue, and from 16 mg/g to 19 mg/g for naphthol green B.

Sorption isotherm presented in Figs. 3, 4, and 5 indicate that surface sorption for activated carbon decreased with subsequent regeneration cycles. After the first regeneration with Fenton reagent, surface sorption for methyl blue amounted to 12 mg/g, after the second regeneration cycle – to 9 mg/g. On the other hand, for naphthol

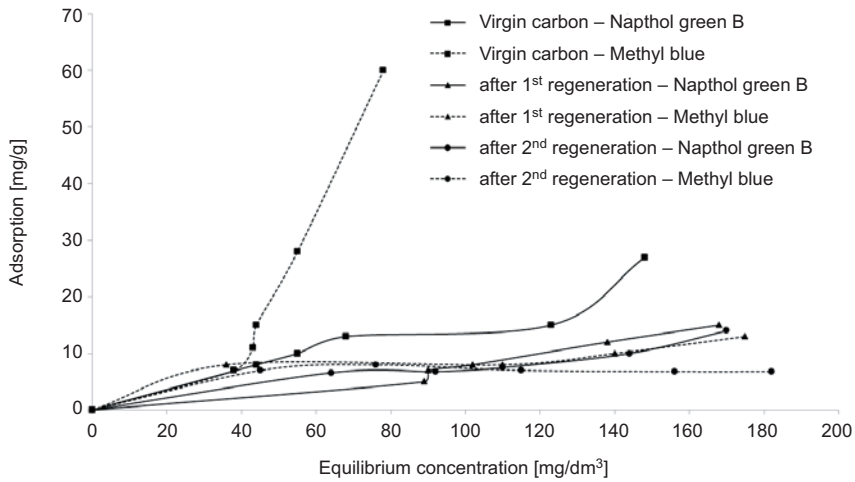


Fig. 3. Sorption isotherms for methyl blue and naphthol green B on virgin carbon and after the first and second regeneration

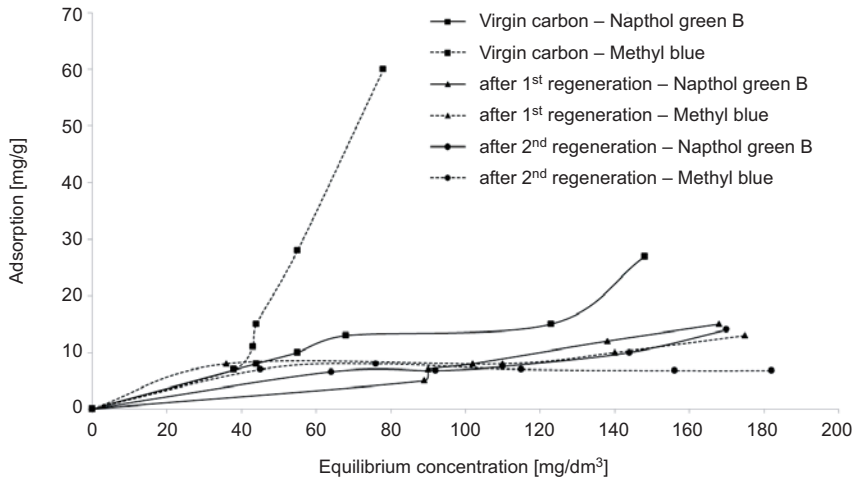


Fig. 4. Sorption isotherms for methyl blue and naphthol green B on virgin carbon and after the third and fourth regeneration

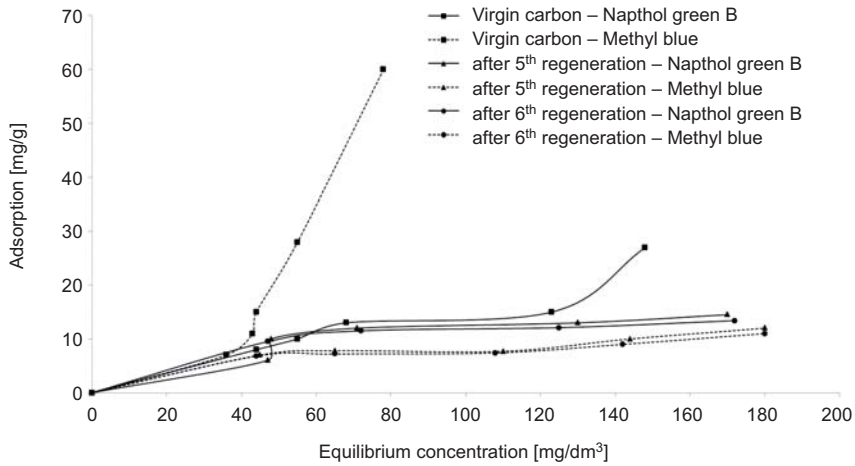


Fig. 5. Sorption isotherms for methyl blue and naphthol green B on virgin carbon and after the fifth and sixth regeneration

green B, after the first regeneration, surface sorption was 17 mg/g, after the second regeneration – it was 16 mg/g.

After the third and fourth regeneration cycle, surface sorption (Fig. 4.) for methyl blue was 12 mg/g and 11 mg/g, respectively, whereas for naphthol green B – 19 mg/g and 17 mg/g.

Sorption isotherms on virgin carbon and carbon after the fifth and sixth regeneration, presented in Fig. 5, showed that after the fifth and sixth regeneration, adsorption for methyl blue amounted to approx. 11 mg/g, and for naphthol green B – approx. 16 mg/g.

Experimental data indicate that WDex activated carbon has good sorptive properties. Regeneration with Fenton reagent, however, slightly deteriorates sorptive properties of activated carbon. A change in activated carbon sorptive properties after regeneration definitely must be related to the Fenton reagent oxidizing action on carbon surface, where modification of surface functional groups occurs.

It was also noted that regeneration process was significantly limited due to a loss of carbon mass. In the course of experiment out of the original sorbent mass of 15.057 g, only 11.159 g were left, which makes a loss of 25.89% (Table 1).

Table 1

Changes in carbon parameters during the experiment

| Sorbent type | Mass [g] | Mass loss [%] |
|---|---|---|
| Virgin carbon | 15.057 | |
| Carbon after the first regeneration | 13.562 | 9.93 |
| Carbon after the second regeneration | 12.295 | 18.34 |
| Carbon after the third regeneration | 12.034 | 20.07 |
| Carbon after the fourth regeneration | 11.667 | 22.51 |
| Carbon after the fifth regeneration | 11.498 | 23.64 |
| Carbon after the sixth regeneration | 11.159 | 25.89 |

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 [20], 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 [21] is the earliest developed relation that expressed sorption equation. The Freundlich model follows the formula:

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

where: $K$ – the Freundlich constant,
$1/n$ – the Freundlich exponent, or in the logarithmic form:

$$\log A = \log K + \frac{1}{n} \log c$$

An exemplary Langmuir isotherm for activated carbon after the fourth regeneration for methyl blue is presented in Fig. 6.

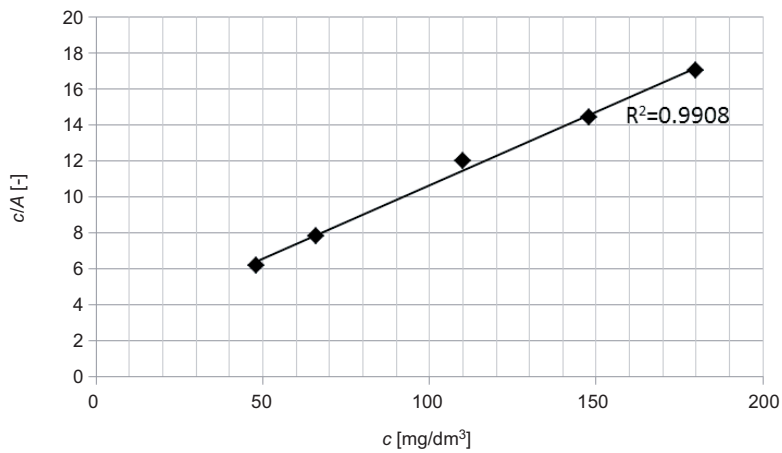


Fig. 6. Langmuir isotherm for WDex activated carbon after the fourth regeneration – methyl blue

An exemplary Freudnlich isotherm for activated carbon after the fourth regeneration for naphthol green B is shown in Fig. 7.

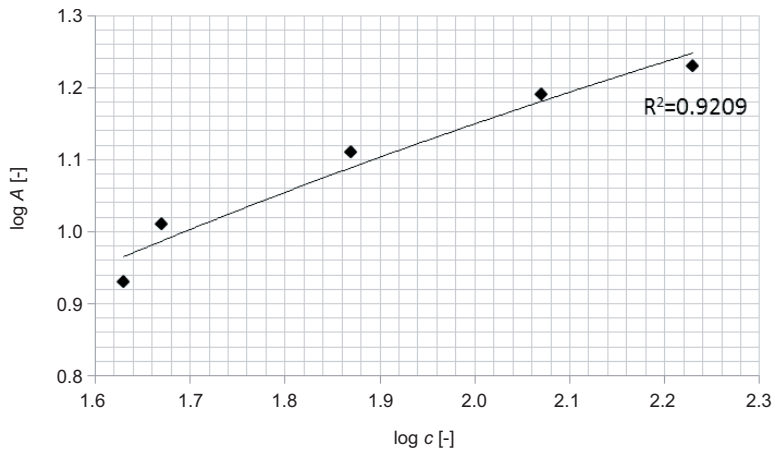


Fig. 7. Freundlich isotherm for WDex activated carbon after the fourth regeneration – naphthol green B

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 2, Table 3), it can be stated that for methyl blue adsorption on virgin carbon, the Freundlich model better describes experimental data. In turn, correlation coefficients of the Langmuir model indicate its better fit to the experimental data after successive regeneration cycles (from the first to the sixth one).

Table 2

Parameters of Freundlich and Langmuir isotherms for methyl blue

| Activated carbon | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| | $k$ | $n$ | $R^2$ | $a_m$ | $k$ | $R^2$ |
| Virgin | 0.0002 | 0.346 | 0.918 | –12.5 | –0.011 | 0.618 |
| After the first regeneration | 2.84 | 1.93 | 0.804 | 16.95 | 0.015 | 0.878 |
| After the second regeneration | 5.87 | 13.16 | 0.949 | 9.09 | 0.132 | 0.999 |
| After the third regeneration | 3.04 | 3.96 | 0.878 | 13.69 | 0.029 | 0.961 |
| After the fourth regeneration | 3.09 | 4.24 | 0.915 | 12.19 | 0.033 | 0.991 |
| After the fifth regeneration | 3.23 | 4.24 | 0.870 | 12.82 | 0.032 | 0.974 |
| After the sixth regeneration | 3.05 | 3.96 | 0.870 | 13.51 | 0.028 | 0.965 |

For naphthol green B, correlation coefficients show that the Langmuir model better describes the results after the fourth, fifth and sixth regeneration cycles. On the contrary, the Freundlich model is better fitted to the results of surface sorption on virgin carbon and on carbon after the first, second and third regeneration cycles.

It can be stated that both theoretical models are definitely capable of describing the experimental data obtained in the course of investigations.

Table 3

Parameters of Freundlich and Langmuir isotherms for naphthol green B

| Activated carbon | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| | $k$ | $n$ | $R^2$ | $a_m$ | $k$ | $R^2$ |
| Virgin | 0.28 | 1.13 | 0.911 | 125.00 | 0.001 | 0.137 |
| After the first regeneration | 0.007 | 0.66 | 0.910 | –20.40 | –0.003 | 0.459 |
| Aafter the second regeneration | 0.20 | 1.22 | 0.891 | 76.92 | 0.001 | 0.148 |
| After the third regeneration | 0.48 | 1.44 | 0.926 | 43.48 | 0.004 | 0.559 |
| After the fourth regeneration | 1.21 | 3.36 | 0.921 | 26.31 | 0.011 | 0.961 |
| After the fifth regeneration | 1.66 | 2.25 | 0.870 | 24.27 | 0.016 | 0.945 |
| After the sixth regeneration | 1.59 | 2.18 | 0.841 | 22.22 | 0.015 | 0.950 |

Dye adsorption on WDex activated carbon is also presented with a graph of the dependence of selected dye removal percentage on subsequent regeneration cycles g (Fig. 8.). The highest percentage of removal was 94% (virgin carbon) and 78% (carbon after the fourth regeneration), for methyl blue and naphthol green B, respectively. On the other hand, the lowest removal percentage was obtained for methyl blue in the fourth regeneration cycle (75%), and for naphthol green B in the carbon first regeneration cycle (55%).

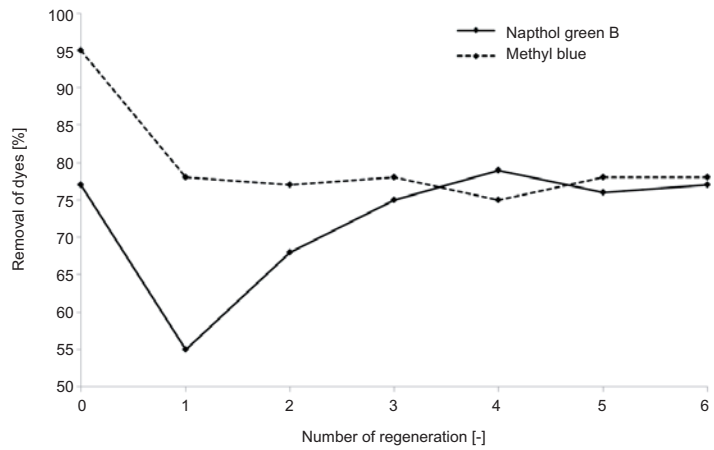


Fig. 8. Percentage of both dyes removal for virgin and regenerated activated carbon for $m_c$ = 2 g

## Conclusions

Summing up model investigations into selected dyes described above, that is naphthol green B and methyl blue, it can be stated that:

– WDex activated carbon demonstrates high sorptive capacity, which is implied by surface sorption values for virgin carbon: 60 mg/g (methyl blue) and 26 mg/g (naphthol green B),

– the maximum removal percentage for methyl blue amounted to almost 94% (virgin carbon), for naphthol green B that was 78% (carbon after the fourth regeneration),

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

– Fenton reagent causes the oxidation of the adsorbed substance and the carbon matrix, and also changes in the properties of carbon,

– a disadvantageous phenomenon that accompanies sorption on regenerated carbon is a sorbent mass loss, which after six regeneration cycles amounts to almost 26%.

## Acknowledgements

The work reported herein has been undertaken as part of project N N205 1993 33 funded by the Ministry of Science and Higher Education. The costs of the conference participation for the PhD student were covered from the budget of the Programme for the Development of Teaching Potential of the Kielce University of Technology – "Education to success", Contract UDA-POKL.04.01.01-00-175/08-02, co-financed from the European Social Fund, Priority 4, Measure 4.1, Activity 4.1.1.

## References

[1] Sonune A, Ghate R. Developments in wastewater treatment methods. Desalination. 2004;167:55-63. DOI: 10.1016/j.desal.2004.06.113.

[2] Pereira MFR, Soares SF, Órfão JJM, Figueiredo JL. Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon. 2003;41:811-821. DOI: 10.1016/S0008-6223(02)00406-2.

[3] Zhu M, Lee L, Wang H, Wang Z. Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud. J Hazard Mater. 2007;149:735-741. DOI: 10.1016/j.jhazmat.2007.04.037.

[4] Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigm. 2002;54:47-58. DOI: 10.1016/S0143-7208(02)00025-6.

[5] Kima T, Park Ch, Yang J, Kima S. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. J Hazard Mater. 2004;B112:95-103. DOI: 10.1016/j.jhazmat.2004.04.008.

[6] Demirbas A. Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review. J Hazard Mater. 2009;167:1-9. DOI: 10.1016/j.jhazmat.2008.12.114.

[7] Shen D, Fan J, Zhou W, Gao B, Yue Q, Kang Q. Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. J Hazard Mater. 2009;172:99-107. DOI: 10.1016/j.jhazmat.2009.06.139.

[8] Pengthamkeerati P, Satapanajaru T, Singchan O. Sorption of reactive dye from aqueous solution on biomass fly ash. J Hazard Mater. 2008;153:1149-1156. http://www.sciencedirect.com/science/article/pii/S0304389407013659.

[9] Attia AA, Rashwan WE, Khedr SA. Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment. Dyes Pigm. 2006;69:128-136. DOI:10.1016/j.dyepig.2004.07.009.

[10] Wang X, Zhu N, Yin B. Preparation of sludge-based activated carbon and its application in dye wastewater treatment. J Hazard Mater. 2008;153:22-27.

[11] Wang S, Zhu ZH. Effects of acidic treatment of activated carbons on dye adsorption. Dyes Pigm. 2007;75:306-314.DOI: 10.1016/j.dyepig.2006.06.005

[12] Tamai H, Yoshidaa T, Sasakib M, Yasudaa H. Dye adsorption on mesoporous activated carbon fiber obtained from pitch containing yttrium complex. Carbon. 1999;37:983-989. DOI: 10.1016/S0008-6223(98)80013-4.

[13] Dąbek L, Ozimina E, Picheta-Oleś A. Dye removal efficiency of virgin activated carbon and activated carbon regenerated with Fenton's reagent. Environ Protect Eng. 2012;38:5-13.DOI: 10.5277/epe.
[14] Dąbek L, Ozimina E. Usuwanie zanieczyszczeń organicznych z roztworów wodnych metodą pogłębionego utleniania.(Removal of organic pollution from methylene blue on activated carbon through advanced oxidation processes) Ochr Środ Zasob Natural. 2009;41:369-376.
[15] Bezak-Mazur E, Adamczyk D. Adsorpton Naphtol Green B on Activated Carbon F 300 (Investigation of adsorption methylene blue on activated carbon). Ecol Chem Eng A. 2012,19(9):1123-1131. DOI:10.2428/ecea.2012.19(09)108.
[16] Bezak-Mazur E, Adamczyk D. Badanie adsorpcji błękitu metylowego na węglu aktywnym [The investigation of adsorption methylene blue on activated carbon]. Zesz Nauk Polit Rzesz. 2011;58(4):17-26.
[17] http://stainsfile.info/StainsFile/dyes/42780.htm.
[18] http://stainsfile.info/StainsFile/dyes/10020.htm.
[19] Kumar KV, Kumaran A. Removal of methylene blue by mango seed kernel powder. Biochem Eng J. 2005;27:83-93. DOI: 10.1016/j.bej.2005.08.004.
[20] Malik PK. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. J Hazard Mater. 2004;B113:81-88. DOI: 10.1016/j.jhazmat.2004.05.022.
[21] Al-Degs YS, El-Barghouthi MI, El-Sheikh AH, Walker GM. Effect of solution pH, ionic strength, and temperature on adsorption behaviour of reactive dyes on activated carbon. Dyes Pigm. 2008;77:16-23. DOI: 10.1016/j.dyepig.2007.03.001.

## ADSORPCJA MIESZANINY DWÓCH BARWNIKÓW NA WĘGLU AKTYWNYM

Katedra Inżynierii i Ochrony Środowiska, Wydział Inżynierii Środowiska, Geomatyki i Energetyki
Politechnika Świętokrzyska w Kielcach

**Abstrakt:** Węgiel aktywny jest znany jako adsorbent różnych zanieczyszczeń znajdujących się w ściekach i powietrzu. W pracy podjęto próbę oceny zdolności sorpcyjnych węgla aktywnego w odniesieniu do barwników będących zanieczyszczeniami ścieków farbiarskich. Do badań wybrano mieszaninę dwóch barwników, błękitu metylowego i zieleni naftolowej B, a jako sorbent węgiel aktywny WDex świeży i regenerowany. Stężenie obu barwników wynosiło 200 mg/g. Zdolności sorpcyjne węgla świeżego wyrażone wielkością adsorpcji właściwej wyniosły 60 mg/g, a po regeneracji – od 8 mg/g do 13 mg/g. Z danych eksperymentalnych wykreślono izotermy sorpcji oraz dopasowano teoretyczny model adsorpcji tj. model Freundlicha lub Langmuira. Najwyższy procent usunięcia dla błękitu metylowego wyniósł 94% dla węgla świeżego, a najniższy – 75% (węgiel po IV regeneracji). Najwyższy procent usunięcia dla zieleni naftolowej B wyniósł 78% dla węgla po IV regeneracji, a najniższy – 55% (węgiel po I regeneracji). Uzyskane wyniki wskazują, iż zastosowany 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, błękit metylowy, zieleń naftolowa B