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Adsorption of Methylene Blue and Malachite Green from Aqueous Solutions on Mesoporous Carbon-Nickel and Carbon-Zinc Composites

Adsorpcja błękitu metylenowego i zieleni malachitowej z roztworów wodnych na mezoporowatych kompozytach węglowo-niklowych i węglowo-cynkowych

In this work adsorption of methylene blue and malachite green on mesoporous carbon-nickel and carbon-zinc composites (ST-A-Ni, ST-A-Ni(NO$_3$)$_2$-imp and ST-A-Zn, ST-A-Zn(NO$_3$)$_2$-imp) were investigated. These materials were obtained by the soft-templating method in presence of various precursors containing nickel or zinc. Nanoparticles of nickel or zinc and solutions of nickel nitrate(V) or zinc nitrate(V) were used as a source of nickel and zinc.

Low-temperature nitrogen adsorption isotherms were determined for investigated materials and they were used for porous structure parameters calculation. Obtained isotherms can be classified as IV-type in order to IUPAC classification. Adsorbents have large surface area S_{BET}: 674 m^2/g (ST-A-Ni), 651 m^2/g (ST-A-Ni(NO$_3$)$_2$-imp) and 511 m^2/g (ST-A-Zn), 654 m^2/g (ST-A-Zn(NO$_3$)$_2$-imp), large total volume of pores V_t: 0.65 cm^3/g (ST-A-Ni), 0.63 cm^3/g (ST-A-Ni(NO$_3$)$_2$-imp) and 0.32 cm^3/g (ST-A-Zn), 0.64 cm^3/g (ST-A-Zn(NO$_3$)$_2$-imp). Participation of mesoporosity in the total porosity of carbon composites is from approx. 44% to approx. 78%. This means that studied carbons are in fact mesoporous materials, with considerable domination of mesoporosity over the microporosity. The exception is composite ST-A-Zn were the microporosity value is a little bit higher than mesoporosity. The mesopores dimension for the maximum of the distribution function (in the range of mesopores) was determined by Kruk-Jaroniec-Sayari (KJS) method. This dimension was approx. 7 nm for all investigated adsorbents.

SEM photos confirmed the presence of ordered mesopores, particularly in materials obtained as a result of zinc nitrate impregnation. Also the presence of nickel nanoparticles, with different dimensions and shapes (ST-A-Ni), was confirmed by SEM photos.

The concentrations of adsorbates, before and after adsorption, were determined by spectrophotometric method. Adsorption experiments were carried out at 25°C temperature. The adsorption equilibrium for investigated in this work mesoporous compositions (carbon--metal-composite - colorant solution) was settled after 90 minutes (ST-A-Ni(NO$_3$)$_2$-imp-MB and ST-A-Zn(NO$_3$)$_2$-imp-MB), after 120 minutes (ST-A-Ni-MB), after 240 minutes (ST-A-Ni-MG) and for the rest of investigated compositions after 360 minutes. The studies of adsorption process velocity showed that in most cases adsorption kinetics proceeded according to pseudo II-order reaction model. Only in one case according to pseudo I-order reaction model: for ST-A-Zn (malachite green). Obtained adsorption isotherms were substituted into the Langmuir equation and Freundlich equation. Adsorption process of methylene blue and malachite green on all studied carbon-metal composites proceed in accordance to adsorption model described by Langmuir equation. Adsorption ability of studied mesoporous carbon materials is significantly higher for methylene blue than for malachite green. The best adsorbent for methylene blue was carbon ST-A-Zn(NO$_3$)$_2$-imp (q_m = 104.17 mg/g), the worst

adsorbent was carbon ST-A-Zn (q_m = 6.65 mg/g). In the case of malachite green the best adsorbent was carbon ST-A-Ni (q_m = 58.82 mg/g) and the worst adsorbent was carbon ST-A-Zn (q_m = 4.25 mg/g). On the basis of K constant from Langmuir equation the value of free enthalpy ΔG was calculated. Obtained values change in the range from –28.06 to –36.78 kJ/mol. Negative values of ΔG mean that investigated process is spontaneous.

Keywords: methylene blue, malachite green, adsorption, mesoporous carbon-nickel composites, mesoporous carbon-zinc composites

Introduction

Carbon-metal composites enjoy growing interest of the scientific community in consideration of a wide range of opportunities for their application, e.g.: adsorption, catalysis, energy storage, separation, etc. [1-3]. These material contain mesoporous, ordered carbon with dispersed, in their structure, metal and metal oxides nanoparticles. This structure causes the carbon materials have unusual properties: determined pore dimensions (2÷50 nm) and presence, in their structure, of metals and their oxides with nanometric dimensions [4, 5]. In consideration of high adsorption ability of investigated materials, they are used more and more often for organic colorants adsorption from aqueous solutions [6-8].

Methylene blue (MB) and malachite green (MG) can be treated as cation colorants that have the negative influence on living organism. The MB colorant is used most often in industry, e.g. textile industry, paper industry, fishkeeping equipment and also medicine (microbicide). MG colorant is very important for textile industry, e.g. for staining silk, leather, cotton, wool. Furthermore, MG is used as the microbicide, fungicide, and parasiticide. MG has a negative influence on immune and reproductive systems, thus it is necessary to remove MG and MB from wastes [9, 10].

Authors of work [6] studied adsorption properties of ordered mesoporous carbon (Fe-CMK-3), containing magnetic nanoparticles of iron, concerning MB. Adsorption process equilibrium data of MB showed the best adjustment to Langmuir model. The maximum adsorption capacity was 316 mg/g. The kinetic data of MB adsorption were better described by pseudo II-order reaction model. On the basis of received thermodynamic data, it was found that MB adsorption process was spontaneous and exothermic. However, another authors [7] applied mesoporous carbons, containing magnetic nanoparticles Fe/Ni, for MB colorant removal. The adsorption kinetic was described by pseudo I-order reaction model. The adsorption equilibration complied with Langmuir equation and the maximum adsorption was 959.5 mg/g. Thermodynamic studies showed that adsorption process was spontaneous and endothermic. In another work [8] carbon composite with zinc nanoparticles (ZnO-NRs-AC) was applied for MB removal. The influence of pH on MB adsorption was presented. It was shown that the biggest amount of colorant was adsorbed with pH = 7, for the quantity of adsorbent 0.02 g, time = 20 minutes (adsorbed amount: 558.8 mg/g). MB adsorption on studied

adsorbent carried out in order to Langmuir model. The rate of adsorption was described by pseudo II-order reaction equation. The intramolecular diffusion process had an influence on adsorption rate. Determined thermodynamic functions ΔG, ΔH, and ΔS showed that adsorption process was spontaneous and endo-thermic. The positive sign of ΔS value can be explained that adsorption process was performed through electrostatic interaction between adsorbent surface and adsorbate. In work [11] composite TiO_2/carbon was applied for MB removal. The kinetic, in this case, was better described by the pseudo II-order reaction. The equilibration data were described by Freundlich model, the process was endothermic. The MB maximum adsorption in various temperatures were: 25°C - 20.48 mg/g, 40°C - 21.94 mg/g, 55°C - 25.73 mg/g.

The authors of work [12] applied magnetic nanocomposites, containing various content of Fe_3O_4 (2÷10% weight) (MCS-2, MCS-4, MCS-7, MCS-10), for MG removal from aqueous solutions. The maximum of adsorbed amount: MCS-2 (159.1 mg/g), MCS-4 (283.2 mg/g), MCS-7 (324.5 mg/g), MCS-10 (86.8 mg/g). In work [13] mesoporous carbon with cobalt nanoparticles was applied for MG colorant adsorption. Carbon material with cobalt had magnetic properties and it was obtained by the soft-templating method. The addition of TEOS, during the synthesis, then silica etching by NaOH had an influence on improvement of adsorption properties of carbon composite. The maximum amount of adsorbed MG was 1151 mg/g. However in work [14] composite carbon material with ZnO nanoparticles ($S_{BET} > 603$ m^2/g), was used for MG adsorption (maximum adsorption capacity - 322.58 mg/g, time of contact - 30 minutes, adsorbent amount - 0.005 g). Another authors [15] applied carbon composite (MAC) with magnetic Fe_3O_4 nano-particles ($S_{BET} = 721$ m^2/g) for MG removal (maximum adsorption - 333 mg/g).

A lot of works indicate scientists interest of other colorants adsorption on carbon-metal composites, e.g.: orange II [6], methyl orange [7, 16], Congo red and indigo carmine [12], reactive orange 16 and reactive red 120 [17].

In presented work the adsorption kinetic and adsorption equilibrium were inves-tigated, concerning colorants: methylene blue and malachite green from aqueous solution on mesoporous carbon-nickel and carbon-zinc composites, obtained by the soft-templating method.

1. Materials and methods

1.1. Adsorbents and adsorbates

As adsorbents, mesoporous carbon-nickel and carbon-zinc composites (ST-A-Ni, ST-A-Ni(NO$_3$)$_2$-imp and ST-A-Zn, ST-A-Zn(NO$_3$)$_2$-imp) were applied. Adsorbents were obtained by the soft-templating method in presence of various precursors containing nickel or zinc. Composites were obtained using resorcinol and formal-dehyde as carbon precursors and triblock copolymer Lutrol 127 as the soft matrix. The source of nickel or zinc were nanoparticles of nickel or zinc (added at the carbon composite synthesis stage in amount of approx. 10 % weight) and solutions

of nickel nitrate(V) or zinc nitrate(V) (obtained pure carbon was impregnated after synthesis using 10% weight aqueous solutions of salts in terms of Ni and Zn). Adsorbents were obtained according to recipes presented in works [18, 19].

As adsorbates methylene blue ($C_{16}H_{18}ClN_3S$, $M_{mol} = 319.85$ g/mol) and malachite green ($C_{23}H_{25}ClN_2$, $M_{mol} = 382.93$ g/mol) were applied, both from Sigma-Aldrich (Germany).

1.2. Porous structure of adsorbents

The porous structure of applied adsorbents was determined on the basis of low-temperature nitrogen adsorption isotherms (–196°C), using volumetric adsorption analyzer ASAP 2020 by Micromeritics (Norcross, GA, USA) - Structural Research Laboratory of Jan Kochanowski University in Kielce. Before adsorptive measurements, all the samples were degassed in temp. 200°C for 2 hours. On the basis of experimental low-temperature nitrogen adsorption isotherms for investigated adsorbents, standard parameters of the porous structure were determined [20-25]. The specific surface area of investigated carbon composites was determined by Brunauer-Emmett-Teller (BET) method. S_{BET} was determined in the range of relative pressure from 0.05 to 0.2, considering the surface occupied by a single molecule of nitrogen in adsorptive monolayer (cross-sectional area) equal 0.162 nm^2 [20]. Total pore volume (V_t), being the sum of micropores volume (V_{mi}) and mesopores (V_{me}) was determined from one point of nitrogen adsorption isotherm, corresponding to the relative pressure p/p$_0$ equal 0.99 [21]. The functions of pore volume distribution of mesoporous carbons were determined on the basis of nitrogen adsorption-desorption isotherm adsorptive curve by Kruk-Jaroniec-Sayari (KJS) method [26]. KJS method is based on Barrett-Joyner-Halenda (BJH) method [25]. The maximums of pore volume distribution functions of mesoporous carbons determined by KJS method were used for mesopores dimension (w_{me}) determination.

Photos, of investigated materials, were obtained by scanning electron microscope (SEM) Zeiss mod. Ultra Plus, EDS Bruker Quantax 400. It is high resolution low energy microscope with field emission Shotkky's cathode. The voltage applied during the measurements was 5 kV.

1.3. Adsorption studies from aqueous solutions

For adsorption studies, mesoporous carbon-metal materials were applied, with grain size from 0.2 to 0.8 mm. Therefore samples of synthesized carbon material composites were crushed in the mortar and next sifted on sieves. Before proceeding into the proper studies, carbons were dried in the laboratory dryer in temp. 100°C until constant masses of adsorbents were obtained. Concentrations in solutions of organic colorants before and after the adsorption were determined by the spectrophotometric method, using spectrophotometer SP-830 Plus from Metertech. The wavelengths applied during the concentrations determination for both

adsorbates were determined from literature data [10, 27] and absorption spectra performed using spectrophotometer HITACHI U-2900 in the visible light range 400-800 nm. During the investigations following wavelength were applied: 665 nm (MB) and 615 nm (MG). Adsorption studies were carried out in 100 ml Erlenmeyer's flask. To each flask 0.1 g of mesoporous carbon was added, then 50 ml of colorant solution, with defined concentration, was transferred. Next flask with adsorbents and colorant solutions were transferred into the incubator for defined time: ST-A-Ni (MB): 15, 30, 45, 60, 90, 120, 240 and 360 minutes; ST-A-Ni (MG): 30, 60, 90, 120, 180, 240, 360, 480 and 600 minutes; ST-A-Ni(NO$_3$)$_2$-imp (MB): 15, 30, 45, 60, 75, 90, 120, 240 and 360 minutes; ST-A-Ni(NO$_3$)$_2$-imp (MG): 30, 60, 90, 120, 240, 360, 480 and 600 minutes; and ST-A-Zn (MB): 15, 30, 45, 60, 90, 120, 240, 360 and 460 minutes, ST-A-Zn(NO$_3$)$_2$-imp (MB): 15, 30, 45, 60, 75, 90, 120, 240, 360 minutes; ST-A-Zn (MG): 60, 90, 120, 240, 300, 360, 480, 600 minutes; ST-A-Zn(NO$_3$)$_2$-imp (MG): 15, 60, 75, 120, 240, 260, 480 and 600 minutes.

The measurements were carried out in constant temp. 25°C and mixing rate 150 rpm. After removing samples from the incubator, carbon was separated from colorant. Next, the absorbance of the colorant was measured by the spectro-photometer. The kinetic data of BM and MG adsorption on all studied adsorbents was determined for initial concentration 15 mg/dm^3.

On the basis of calibration curve concentrations of colorants before and after adsorption were calculated. Next the value of adsorption q$_t$ (mg/g) was calculated from formula [28, 29]:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where:
C$_0$ - concentration of colorant in solution before adsorption, mg/dm^3;
C$_t$ - concentration of colorant in solution after adsorption, after time t, mg/dm^3;
V - volume of the solution used for adsorption, dm^3;
m - adsorbent mass, g.

Adsorption measurements in equilibration conditions - adsorption isotherms were determined for initial concentrations of colorants: ST-A-Ni (MB) and ST-A-Ni(NO$_3$)$_2$-imp (MB): from 29.67 to 398.28 mg/dm^3; ST-A-Ni (MG): from 51.14 to 300.82 mg/dm^3 and ST-A-Ni(NO$_3$)$_2$-imp (MG): from 50.51 to 190.56 mg/dm^3; ST-A-Zn (MB): from 4.49 to 23.41 mg/dm^3; ST-A-Zn(NO$_3$)$_2$-imp (MB): from 99.42 to 301.02 mg/dm^3; ST-A-Zn (MG): from 3.15 to 24.50 mg/dm^3 and ST-A-Zn(NO$_3$)$_2$-imp (MG): from 34.28 to 222.33 mg/dm^3.

Prepared Erlenmeyer's flask with studied adsorbent was filled with 50 cm^3 of adsorbate (with appropriate concentration) and placed in the incubator for 90 min (ST-A-Ni(NO$_3$)$_2$-imp-MB and ST-A-Zn(NO$_3$)$_2$-imp-MB), 120 min (ST-A-Ni-MB), for 240 min (ST-A-Ni-MG) and four remaining samples for 360 min. Applied time of measurements was a result of previous kinetic investigations.

The adsorbate amount, that was adsorbed on the adsorbent surface q_e (mg/g), was calculated from the formula [28, 29]:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_e - equilibrium concentration, mg/dm^3.

2. Investigation results and discussion

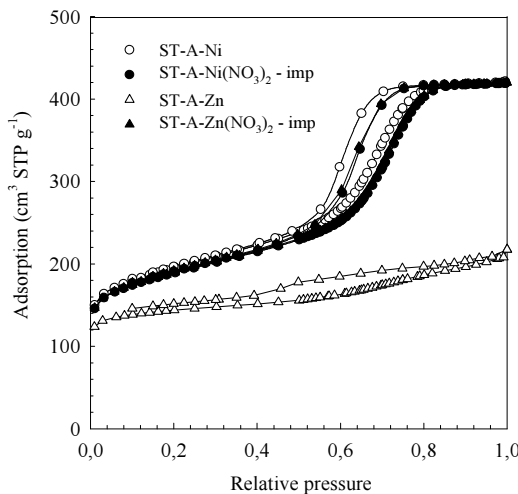Experimental nitrogen adsorption-desorption isotherms are shown in Figure 1.

Fig. 1. **Low-temperature nitrogen adsorption isotherms of mesoporous carbon composites**
Rys. 1. **Niskotemperaturowe izotermy adsorpcji azotu dla mezoporowatych kompozytów węglowych**

Following the IUPAC classification [30] obtained isotherms are type IV with good shaped hysteresis loops type H1. Structural parameters were calculated on the basis of nitrogen adsorption isotherms, using methods described above, are shown in Table 1.

Investigated adsorbents (Table 1) have specific surface area 511 m^2/g for carbon ST-A-Zn to 674 m^2/g for carbon ST-A-Ni. Total pore volume V_t assumed value: 0.32 cm^3/g for carbon ST-A-Zn to 0.65 cm^3/g for carbon ST-A-Ni. Micropores volume V_{mi} change in the range from 0.14 cm^3/g (ST-A-Ni(NO$_3$)$_2$-imp) to 0.18 cm^3/g (ST-A-Zn). It affects, of course, the mesoporosity expressed in percentage, which indicates the mesoporosity participation in the total porosity of studied carbons. This means that studied carbons are in fact mesoporous, with the significant advantage of mesoporosity over microporosity. The exception is carbon ST-A-Zn, which is microporous material (Fig. 1 and Table 1). Similar parameters of the porous structure were obtained in work [19] for the material with zinc nanoparticles obtained according to the same recipe. Mesopores dimension is approx. 7 nm.

Table 1. **Structural parameters of mesoporous carbon composites determined from low-temperature nitrogen adsorption isotherms**

Tabela 1. **Parametry struktury porowatej mezoporowatych kompozytów węglowych wyznaczone z niskotemperaturowych izoterm adsorpcji azotu**

Carbon composite	S_{BET} m^2/g	V_t cm^3/g	V_{me} cm^3/g	V_{mi} cm^3/g	w_{me} nm	Mesoporosity %
ST-A-Ni	674	0.65	0.50	0.15	7.03	77
ST-A-Ni(NO$_3$)$_2$-imp	651	0.63	0.49	0.14	6.86	78
ST-A-Zn	511	0.32	0.14	0.18	6.82	44
ST-A-Zn(NO$_3$)$_2$-imp	654	0.64	0.50	0.14	6.94	78

S_{BET} - specific surface area; V_t - single-point total pore volume calculated at $p/p_0 = 0.99$; V_{me} - mesopore volume calculated by subtracting V_{mi} from V_t; V_{mi} - volume of micropores obtained by α_s-method; w_{me} - mesopore width at the maximum of the PSD curve obtained by the KJS method; Mesoporosity - the percentage of the volume of mesopores to the total pore volume

In Figure 2 are shown SEM photos of the studied adsorbents surface. In photo 2A, a mesoporous structure of carbon ST-A-Ni can be seen, with noticeable Ni nanoparticles, on carbon surface, with various dimensions and shapes. In photo 2B interesting mesoporous structure of the sample ST-A-Ni(NO$_3$)$_2$-imp is presented, visible canals are mesopores. Photo 2C presents ST-A-Zn carbon surface, with visible Zn nanoparticles (white fragments). In this photo, it can be seen that carbon structure is microporous-mesoporous. Photo 2D, for ST-A-Zn(NO$_3$)$_2$-imp sample, shows ordered, mesoporous, the layered structure of this material.
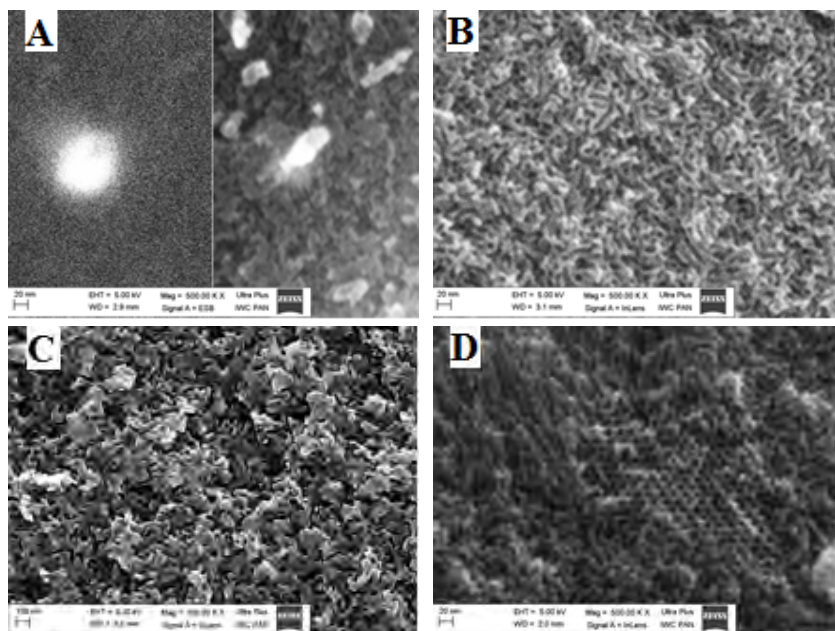
Fig. 2. **SEM photos of mesoporous carbon composites: ST-A-Ni (A), ST-A-Ni(NO$_3$)$_2$-imp (B), ST-A-Zn (C), ST-A-Zn(NO$_3$)$_2$-imp (D)**

Rys. 2. **Zdjęcia SEM mezoporowatych kompozytów węglowych: ST-A-Ni (A), ST-A-Ni(NO$_3$)$_2$-imp (B), ST-A-Zn (C), ST-A-Zn(NO$_3$)$_2$-imp (D)**

The kinetics of MB and MG adsorption process on studied mesoporous carbon-
-metal composites (ST-A-Ni, ST-A-Ni(NO$_3$)$_2$-imp, ST-A-Zn, ST-A-Zn(NO$_3$)$_2$-imp)
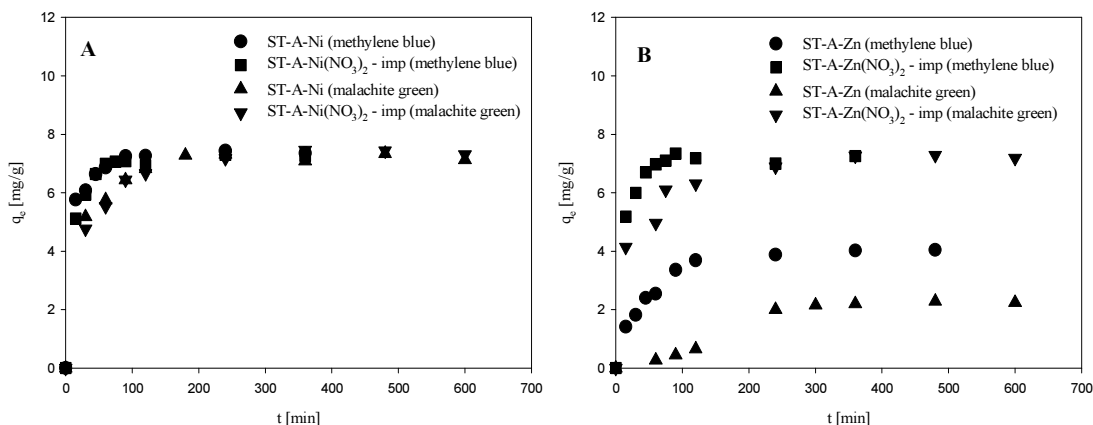are shown in Figure 3A and B.

Fig. 3. **The adsorption kinetics of methylene blue and malachite green on mesoporous carbon-
-metal composites for C$_0$ = 15 mg/dm^3**

Rys. 3. **Kinetyka adsorpcji błękitu metylenowego oraz zieleni malachitowej na mezoporowa-
tych kompozytach węglowo-metalicznych dla C$_0$ = 15 mg/dm^3**

Adsorption equilibrium settled after 90 min (ST-A-Ni(NO$_3$)$_2$-imp-MB and
ST-A-Zn(NO$_3$)$_2$-imp-MB), after 120 min (ST-A-Ni-MB), after 240 min
(ST-A-Ni-MG) and 360 min for remaining four cases.

In order to describe more precise the adsorption kinetics on phase boundary
solution/solid phase in compliance to literature data [31-33] pseudo I-order and
pseudo II-order reaction equations were applied, with linear forms are shown
in equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where:
k$_1$, k$_2$ - reaction rate constants, min^{-1}, g mg^{-1} min^{-1};
t   - time, min;
q$_e$ - adsorption value after the equilibrium stabilization, mg/g;
q$_t$ - adsorption value in given time t, mg/g.

In Table 2 calculated reaction rate constants are collected, for pseudo I-order
and pseudo II-order reactions and also correlation coefficients R^2.

Table 2. **Reaction rate constants for pseudo-I order and pseudo II-order reactions, describing adsorption of MB and MG on mesoporous carbon composites**

Tabela 2. **Stałe szybkości równań pseudo I- i pseudo II-rzędu opisujące adsorpcję MB oraz MG na mezoporowatych kompozytach węglowych**

Adsorbent	Adsorbate	q_e mg/g	Pseudo I-order		Pseudo II-order	
			k_1 min^{-1}	R^2	k_2 $g\ mg^{-1}\ min^{-1}$	R^2
ST-A-Ni	MB	7.263	0.065	0.875	0.021	0.998
	MG	7.316	0.027	0.924	0.007	0.997
ST-A-Ni(NO$_3$)$_2$-imp	MB	7.077	0.084	0,951	0.018	0.999
	MG	7.454	0.022	0.967	0.007	0.999
ST-A-Zn	MB	4.018	0.014	0.938	0.007	0.991
	MG	3.202	0.012	0.950	0.0009	0.855
ST-A-Zn(NO$_3$)$_2$-imp	MB	7.341	0.038	0.993	0.017	0.999
	MG	7.258	0.009	0.936	0.008	0.993

Analyzing data shown in Table 2 it can be found that adsorption process of MB on studied mesoporous carbon-metal composites proceeds as pseudo II-order reaction, which is confirmed by higher values of correlation coefficients R^2 than for pseudo I-order reaction. Similar as in the case of MB adsorption, for MG adsorption process can be described by pseudo II-order reaction for all investigated materials, except ST-A-Zn, where adsorption process rate can be described by the pseudo I-rate reaction. At this stage of work, there is no data, which could explain why adsorption process of colorants on carbon ST-A-Zn is described by various kinetic equations.

In Figure 4A and B adsorption isotherms of investigated colorants, on mesoporous carbon composites, in temp. 25°C are shown.
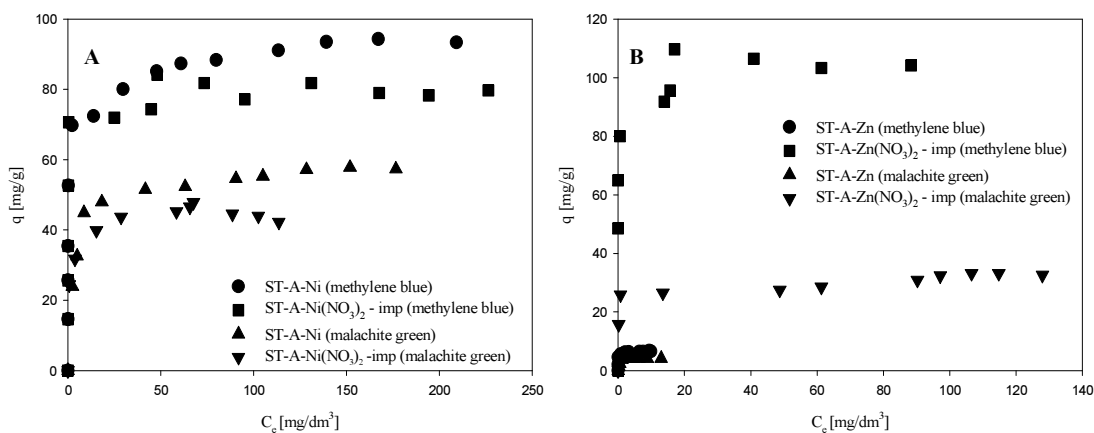

Fig. 4. **Adsorption isotherms of methylene blue and malachite green on mesoporous carbon--metal composites**

Rys. 4. **Izotermy adsorpcji błękitu metylenowego oraz zieleni malachitowej na mezoporowatych kompozytach węglowo-metalicznych**

In order of more precise analysis of obtained isotherms, two commonly adsorption isotherms models were applied: Langmuir isotherm and Freundlich isotherm [28, 34].

Langmuir isotherm can be written in linear form as:

$$\frac{C_e}{q} = \frac{1}{q_m}C_e + \frac{1}{q_m K} \tag{5}$$

where:
C_e - equilibrium concentration of colorant aqueous solution, mg/dm^3;
q - amount of substance adsorbed by elementary mass of adsorbent, mg/g;
q_m - maximum adsorption capacity, mg/g;
K - adsorption equilibrium constant, dm^3/g.

Freundlich isotherm can be written in linear form as:

$$\log q = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where: K_F, n - Freundlich isotherm constants, describing relative intensity and adsorption ability, respectively.

Table 3. **Langmuir and Freundlich equations parameters and correlation coefficients R^2, describing adsorption of methylene blue and malachite green on mesoporous carbon composites**

Tabela 3. **Parametry równań Langmuira i Freundlicha oraz współczynniki korelacji R^2 opisujące adsorpcję błękitu metylenowego oraz zieleni malachitowej na mezoporowatych kompozytach węglowych**

Adsorbent	Adsorbate	Langmuir isotherm			Freundlich isotherm		
		q_m mg/g	K dm^3/g	R^2	1/n	$\log K_F$	R^2
ST-A-Ni	MB	90.91	458	0.999	0.16	1.66	0.828
	MG	58.82	218	0.999	0.17	1.40	0.850
ST-A-Ni(NO$_3$)$_2$-imp	MB	76.92	3250	0.999	0.13	1.65	0.690
	MG	45.46	1100	0.999	0.13	1.43	0.939
ST-A-Zn	MB	6.65	8801	0.999	0.14	0.71	0.844
	MG	4.25	4027	0.999	0.24	2.71	0.788
ST-A-Zn(NO$_3$)$_2$-imp	MB	104.17	2823	0.999	0.07	1.90	0.955
	MG	31.85	547	0.993	0.08	1.33	0.798

Analyzing data showed in Table 3 it can be noticed that adsorption of MB on all studied mesoporous carbon composites proceeded in compliance with Langmuir isotherm model ($R^2 = 0.999$). Similar, the adsorption of MG on all studied composites proceeded in compliance with Langmuir model, $R^2 = 0.999$, in one case only

$R^2 = 0.993$. Calculated, from Langmuir isotherm equation, values of q_m parameter (maximum adsorption capacity), are higher for MB adsorption from solution than for MG. This confirms the higher efficiency of investigated adsorbents in adsorption process of MB from solution.

Knowing adsorption equilibrium constant K from Langmuir isotherm, it is possible to calculate free enthalpy from equation [6]:

$$\Delta G = -RT \ln K \qquad (7)$$

where:
ΔG - free enthalpy;
R   - gas constant, J/mol K;
T   - temperature, K;
K   - constant expressed in dm^3/mol.

Determined values of ΔG for investigated colorants are shown in Table 4.

Table 4. **The free enthalpy values of investigated adsorbates**

Tabela 4. **Wartości entalpii swobodnej badanych adsorbatów**

Adsorbent	Adsorbate	ΔG kJ/mol
ST-A-Ni	MB	−29.46
	MG	−28.06
ST-A-Ni(NO₃)₂-imp	MB	−34.31
	MG	−32.07
ST-A-Zn	MB	−36.78
	MG	−35.05
ST-A-Zn(NO₃)₂-imp	MB	−33.98
	MG	−30.14

Obtained values of free enthalpy changes (ΔG < 0) for investigated colorants have the negative sign. Adsorption process proceeded as the spontaneous process.

Conclusions

In adsorption investigation, mesoporous carbon-nickel and carbon-zinc composites were applied. Carbon composites, obtained by the soft-templating method, have a large surface area S_{BET} from 511 m^2/g (ST-A-Zn) to 674 m^2/g (ST-A-Ni). Obtained adsorbents have also large pore volumes V_t: 0,32 cm^3/g (ST-A-Zn) to 0,65 cm^3/g (ST-A-Ni), mesopores volume participation is from 44 to 78%. Mesopores dimension is approx. 7 nm. SEM photos confirmed the occurrence of ordered, homogeneous mesopores, particularly in materials obtained by impreg-

nation with zinc nitrate(V), and occurrence of nickel and zinc nanoparticles on the surface of investigated adsorbents.

On the basis of performed adsorption studies following conclusions can be draw. Adsorption equilibrium for studied configurations colorant-mesoporous carbon composite settled after 90 minutes (ST-A-Ni(NO$_3$)$_2$-imp-MB and ST-A-Zn(NO$_3$)$_2$-imp-MB), after 120 minutes (ST-A-Ni-MB), after 240 minutes (ST-A-Ni-MG) and after 360 minutes in four remaining cases. The adsorption kinetics for methylene blue and malachite green on studied mesoporous composites can be described by pseudo II-order reaction kinetic equation. The exception is adsorption of malachite green on ST-A-Zn carbon which proceeds in compliance with pseudo I-order reaction equation.

Adsorption process of methylene blue and malachite green on all investigated carbon-metal composites proceeds in compliance with adsorption model described by Langmuir equation. Adsorption ability of investigated mesoporous carbon composites is significantly greater for methylene blue than malachite green. The best adsorbent, in relation to methylene blue, was ST-A-Zn(NO$_3$)$_2$-imp (q_m = 104.17 mg/g), and the worst was ST-A-Zn (q_m = 6.65 mg/g). In case of malachite green, the best adsorbent was ST-A-Ni (q_m = 58.82 mg/g), and the worst was ST-A-Zn (q_m = 4.25 mg/g). On the basis of K constant, determined from Langmuir equation, the value of free enthalpy ΔG was calculated. Obtained values are changing in the range from –28.06 to –36.78 kJ/mol.

Acknowledgements

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Streszczenie

W pracy zbadano adsorpcję błękitu metylenowego i zieleni malachitowej na mezoporowa-
tych kompozytach węglowo-niklowych oraz węglowo-cynkowych (ST-A-Ni, ST-A-Ni(NO$_3$)$_2$-imp
oraz ST-A-Zn, ST-A-Zn(NO$_3$)$_2$-imp). Materiały te otrzymano metodą miękkiego odwzoro-
wania w obecności różnych prekursorów zawierających nikiel lub cynk. Nanocząstek niklu
lub cynku oraz roztworów azotanu(V) niklu lub azotanu(V) cynku użyto jako źródeł niklu
lub cynku.

Dla badanych adsorbentów wyznaczono niskotemperaturowe izotermy adsorpcji azotu,
które posłużyły do obliczenia parametrów struktury porowatej. Otrzymane izotermy można
zaliczyć do IV typu zgodnie z klasyfikacją UPAC. Adsorbenty charakteryzują się dużą po-
wierzchnią właściwą S$_{BET}$: 674 m^2/g (ST-A-Ni), 651 m^2/g (ST-A-Ni(NO$_3$)$_2$-imp) oraz 511 m^2/g
(ST-A-Zn), 654 m^2/g (ST-A-Zn(NO$_3$)$_2$-imp), dużą całkowitą objętością porów V$_t$: 0,65 cm^3/g
(ST-A-Ni), 0,63 cm^3/g (ST-A-Ni(NO$_3$)$_2$-imp) oraz 0,32 cm^3/g (ST-A-Zn), 0,64 cm^3/g
(ST-A-Zn(NO$_3$)$_2$-imp). Udział mezoporowatości w całkowitej porowatości kompozytów
węglowych wynosi od ok. 44% do ok. 78%. Oznacza to, że rzeczywiście badane węgle są
mezoporowate ze znaczną przewagą mezoporowatości nad mikroporowatością, z wyjątkiem
kompozytu ST-A-Zn, który ma nieco bardziej rozwiniętą mikroporowatość. Wymiar mezo-
porów dla maksimum funkcji rozkładu (w przedziale mezoporów) wyznaczono metodą
Kruka-Jarońca-Sayari (KJS). Dla wszystkich badanych adsorbentów wymiar ten wynosił
ok. 7 nm.

Zdjęcia SEM potwierdziły występowanie uporządkowanych mezoporów, szczególnie
w materiałach otrzymanych w wyniku impregnacji azotanem cynku, a także obecność na
powierzchni węgla nanocząstek np. niklu o różnych wymiarach i kształtach (ST-A-Ni).

Stężenia adsorbatów przed i po adsorpcji wyznaczano metodą spektrofotometryczną.
Badania adsorpcyjne prowadzono w temperaturze 25ºC. Równowaga adsorpcyjna dla bada-
nych w pracy układów mezoporowaty kompozyt węglowo-metaliczny - roztwór barw-
nika ustaliła się po 90 minutach (ST-A-Ni(NO$_3$)$_2$-imp-MB i ST-A-Zn(NO$_3$)$_2$-imp-MB),
po 120 minutach (ST-A-Ni-MB), po 240 minutach (ST-A-Ni-MG) oraz dla pozostałych
czterech przypadków po 360 minutach. Badania szybkości procesu adsorpcji wykazały,
że w większości przypadków kinetyka adsorpcji przebiegała zgodnie z modelem reakcji
pseudo II-rzędu, w jednym tylko przypadku zgodnie z modelem pseudo I-rzędu: ST-A-Zn
(zieleń malachitowa). Otrzymane izotermy adsorpcji podstawiono do równania Langmuira
i równania Freundlicha. Proces adsorpcji błękitu metylenowego oraz zieleni malachitowej
na wszystkich badanych kompozytach węglowo-metalicznych zachodzi zgodnie z modelem

adsorpcji opisanym przez równanie Langmuira. Zdolność adsorpcyjna badanych mezo-porowatych materiałów węglowych jest znacznie większa w stosunku do błękitu metyleno-wego niż zieleni malachitowej. Najlepszym adsorbentem w stosunku do błękitu metyleno-wego był węgiel ST-A-Zn(NO$_3$)$_2$-imp (q$_m$ = 104,17 mg/g), a najsłabszym węgiel ST-A-Zn (q$_m$ = 6,65 mg/g). W przypadku zieleni malachitowej najlepszym adsorbentem był węgiel ST-A-Ni (q$_m$ = 58,82 mg/g), a najsłabszym węgiel ST-A-Zn (q$_m$ = 4,25 mg/g). Na podstawie stałej K z równania Langmuira obliczono wartość entalpii swobodnej ΔG. Otrzymane war-tości zmieniają się w granicach od –28,06 do –36,78 kJ/mol. Ujemne wartości ΔG świadczą o tym, że badany proces to proces samorzutny.

Słowa kluczowe: błękit metylenowy, zieleń malachitowa, adsorpcja, mezoporowate kompo-zyty węglowo-niklowe, mezoporowate kompozyty węglowo-cynkowe