



Sorption of Acid Green 16 from Aqueous Solution onto Low-moor Peat and Smectite Clay Co-occurring in Lignite of Belchatow Mine Field

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1. Introduction

The consumption lifestyle and an increased demand on various colored textile, paper, cosmetic and food products contributes to creation of larger and larger amounts of wastewater containing dyes. Presently over 100,000 industry dyes are used and its annual production is estimated to be 7×10^5 Mg. Approximately 10–15% of dyes used in coloring processes seeps into the natural environment becoming a serious threat for surface water, because even minor concentrations of dyes in water suppress oxygen diffusion, which blocks and prevents light from getting to autotrophs. Because of these, designing effective methods of dye containing wastewater treatment becomes an object of wide research. Such treatment, besides being efficient, should enable multiple reuse of treated water in technological processes [5,14,33].

Among the most popular processes of wastewater treatments are: adsorption, coagulation, oxidation, precipitation, ozonation, ultrafiltration, reversed osmosis and biological techniques [6,7,13,24]. Nevertheless, chemical methods of removing dyes from wastewater create sewage sludge, the disposal of which could be problematic.

Among the methods of water and wastewater treatment, adsorption is a highly efficient one, considering its high effectiveness at relatively low costs.

A sorbent commonly used to remove metal and metalloid ions, as well as organic pollutions (e.g. dyes), from water and wastewater is an activated carbon [3,27,30]. Its physical and chemical properties, including specific surface area, porosity and high surface reactivity, make it a popular component of adsorption treatment methods. On the other hand, the high costs of its production and the necessity of its regeneration force a search for new, low cost, though equally effective sorption materials. Due to this fact, mineral and organogenic materials of both natural and waste origin, characterized by high sorption capacity and wide availability, become objects of numerous research studies in the recent years. Among such sorbents are clay and clay minerals (smectites, illites, kaolinites and bentonites clays), zeolites, biolites (peats, lignites), bio-sorbents (composts, biomass) and waste materials (fly ashes) [1,8,15, 18,22,25,29].

Smectites are part of phyllosilicates group of 2:1 ratio, which means that between two tetrahedral sheets there is an octahedral sheet. The tetrahedral sheets, built of T_2O_5 units, normally contain Si, Al or Fe as the central atom. Two types of octahedral sheets occur in smectites: the *dioctahedral* type, where two-thirds of the octahedral sites are occupied mainly by trivalent cations (Al^{3+} or Fe^{3+}), and the *trioctahedral* type, with most of the sites occupied by divalent cations (Mg^{2+}). The negative charge of the layers is balanced by hydrated exchangeable cations in the inter layers (mostly Ca^{2+} , Mg^{2+} , Na^+) [34]. They are an important material for ceramic, rubber, paper, pharmaceutical, chemical and food industries. Sometimes they are used as components of mineral fertilizers and drilling fluids. They are also used as sealing layers, stockpiles, vertical clay barriers, ash stabilizers and rock mass sealers in coal mines [23]. Due to the high surface area and high cation exchange capacity (CEC) they can also be used as sorbents. The main centers of sorption in the smectite minerals are silanol groups ($-Si-OH$) and aluminol groups ($-Al_2-OH$) created by breaking $Si-O-Si$ and $Al-O-Al$ bonds. In contrast, the interlayer cations, weakly bound to the mineral structure, are responsible for the ion-exchange sorption.

Peat is an organogenic sedimentary rock and a product of the earliest stage of plants coalification. It belongs to the rocks widespread in northern Europe (Scotland, Ireland, Sweden, Germany, Denmark, Poland, Finland, Iceland, and Russia), Asia (Siberia, Russia) and North America (Canada, USA). In Poland, about 70% of peatlands are located in the northern part of the country and the overwhelming number, i.e. 95.5%, belong to the low type. Peats are used for fuel, fertilization (horticultural and agricultural), medicine and sanitary purposes. They are used in the chemical and foundry industries as both an extender and insulating material. Due to its characteristics and availability they can also be used as an adsorbent to remove pollutants from water and wastewater [16,21,32]. The main centers of sorption in peats are $-\text{COOH}$ and $-\text{OH}$ fulvic and humic acids in which the H^+ ions may be substituted by alkaline earth metal ions, especially Ca^{2+} .

The aim of this study was to determine the sorption capacity of smectite clay (natural and thermally activated at 250°C) and the low-moor peat co-occurring with lignite of Belchatow mine field (Central Poland) for the cationic acid dye – Acid Green 16 (AG-16), as well as determining the effect of the clay thermal activation on its sorption capacity. In addition, the article presents the results concerning the applicability of three isotherm equations (e.g. Freundlich, Langmuir, and Dubinin-Radushkevich) to describe sorption as well as determine the rate of the sorption process and to estimate parameters in the kinetic equations.

2. Research materials

2.1. Acid Green dye 16 (AG-16)

The dye Acid Green 16 (AG-16), belonging to the acid dyes, was used. It came from Zakład Boruta-Zachem Kolor Sp. z o.o. – the biggest producer of dyes and pigments in Poland.

AG-16 dye is used to color wool and fibers of animal origin, as well as paper and ink.

Figure 1 shows the structural formula of the dye and its characteristics, i.e. Colour Index – CI, CAS number, molecular weight – M, the cation diameter – d_d , as well as the wavelength – λ at which the measurements of the concentration and pH were performed, in the water, 1000 mg/dm^3 dye concentration.

The dye belongs to the arylmethane group of acid dyes. In its structure one can notice a naphthalene ring, two aryl-amino-dimethyl groups, and two sulfonic groups ($-\text{SO}_3\text{H}$). The molecule has a cationic structure and $-\text{SO}_3\text{H}$ groups can act as proton acceptors in a hydrogen bond. However, the dye is characterized by a lack of donor groups. Due to the small size of the dye particle (diameter of the cation dye – 1.51 nm) and its relatively low molecular weight (539 g/mol) it shows a tendency to form bonds and interact with the surface of the adsorbent. Furthermore, it is not affected by steric effects, due to the lack of a branched structure of the molecule.

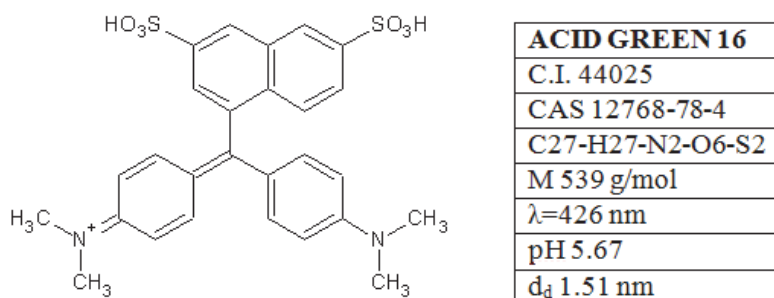


Fig. 1. Characteristic of dye AG–16

Rys. 1. Charakterystyka barwnika AG–16

2.2. Sorbents and their physical and chemical properties

Sorbents applied in these studies were lignite co-occurring rocks from "Belchatow" field mine:

- smectite clay (BC) neogen age,
- low-moor peat (BP) holocen age.

In order to enhance the sorption capacity of smectite clay it was subjected to thermal activation at 250°C for 8 h (BC 250), which led to the removal of water from the structure of the smectite as a result of the dehydration process.

The chemical composition of the studied sorbents and their physicochemical properties, i.e. porosity (n), an average pore diameter (d) and their distribution, total (SSA H_2O) and external (SSA N_2) surface area, pH, and the point of zero charge (pH_{PZC}), defined by pH at which the

charge of the particle is zero, as well as the cation exchange capacity (CEC) are all marked by methods described in other publications [22,35] and are shown in Tables 1–3.

Table 1. Chemical composition of natural and temperature activation smectite clay and low-moor peat, (%)

Tabela 1. Skład chemiczny termicznie iłu smektytowego – naturalnego i aktywowanego termicznie oraz torfu, (%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
BC	55.81	15.25	6.45	2.82	1.74	0.042	0.57
BC 250°C	56.65	16.57	7.65	3.23	2.32	1.11	1.32
BP	8.26	2.32	2.31	4.57	0.33	0.067	0.213

Table 2. Physicochemical properties of natural and temperature activation smectite clays and low-moor peat

Tabela 2. Właściwości fizykochemiczne iłu smektytowego – naturalnego i aktywowanego termicznie oraz torfu

Samples	Porosity, n	Average pore diameter, d (μm)	Surface area (m ² /g)		pH	pH _{PZC}	CEC (cmol ₊ /kg)
			SSA (H ₂ O)	SSA (N ₂)			
BC	0.0682	0.0186	141.8	41.38	7.85	7.40	82.39
BC 250°C	0.1113	0.0322	150.2	70.94	7.83	7.20	80.40
BP	0.5211	2.1503	218.9	11.38	5.62	5.77	125.0

The main clay building mineral was Ca-smectite and apart from this the presence of quartz, calcite and kaolinite was also indicated. Its chemical composition reflected the mineral one. The high content of CaO was an effect of the occurrence of Ca-smectite, described by Kaczynski and Grabowska-Olszewska as Ca-beidellite [19]. Iron was bound in the structure of the smectite, substituting clay in the octahedral layer, or silicon in the tetrahedral layer and approx. 0.091% of it was present in a form of free anamorphic oxides. The low Na₂O content was a result of the lack of feldspars in the examined clay [22].

Thermal activation of clay at 250°C and smectite dehydration did not cause significant changes in its chemical composition [35].

Table 3. Distribution of pores in studied samples**Tabela 3.** Rozkład porów w badanych próbkach

Samples	Distribution of pores(%)		
	Macropores d > 30 μm	Mesopores 30 μm > d > 0,2 μm	Micropores d < 0,2 μm
BC	11.45	12.43	76.12
BC 250°C	12.11	15.23	72.66
BP	35.65	62.37	1.98

Low-moor peat was characterized by a high decomposition degree (70%) and amorphous structure. Ash content was 20.88%. The dominant mineral constituent in a peat sample was SiO₂ (8.26%), coming mainly from the sand deposited by water and wind. CaO content amounted 4.57%, it came from peat-forming plant incineration and was a result of the presence of calcite and gypsum minerals in the samples. MgO content was approximately one order lower (0.33%), similarly to K₂O content (0.213%). Iron occurred mainly in the form of amorphous oxides (1.39%). Main functional groups of humic acids contained in the peat are carboxyl groups (–COOH) and hydroxyl phenols (–OH) respectively in the amount of 90.0 cmol₊/kg and 115.3 cmol₊/kg [22].

The examined smectite clay was characterized by a high total surface area (141.83 m²/g), while the external surface area was 41.38 m²/g (Tab. 2). The porosity was 0.0682 and it was dominated by micropores of a diameter <2 μm (Tab. 3). Cation exchange capacity (CEC) was 82.39 cmol₊/kg; exchangeable cations were dominated by Ca²⁺ (72.5 cmol₊/kg) and Mg²⁺ (8.56 cmol₊/kg).

As a result of clay thermal activated, an approximately 60% increase in porosity to the value of 0.1113, an approximately 70% increase in size of the external surface to 70.94 m²/g and a slight increase in total surface area occurred. Thermal activated did not affect the pore distribution in the clay (Table 3).

On the other hand, the studied peat was characterized by a high total surface area (218.98 m²/g) and a high porosity level of 0.5211, dominated by mesopores and macropores (Table 3). Cation exchange capacity was 125 cmol₊/kg; main exchangeable ions were Ca²⁺ (95.18 cmol₊/kg), H⁺ (21.8 cmol₊/kg) and Mg²⁺ (7.14 cmol₊/kg).

The pH of clay samples in water was weakly alkaline (pH 7.85 and 7.83), while of peat – acidic (pH 5.62).

3. Methods

3.1. Determination of sorbents' sorption capacity

Sorption capacity of the studied sorbents for dye AG-16 as well as the percentage removal of dye in the aqueous solutions was determined in static contact mode of a solid and a solution phases using the "batch" method. The basic dye solution was prepared through dissolution of 1000 mg of dye powder in 1 dm³ of distilled water; then the pH was measured. Next, through appropriate dilutions, the basic solution was turned into working solutions of the dye, which were used in laboratory studies; their concentrations were 1, 10, 25, 50, 100, 150, 250, 500, 750 mg/dm³.

Tests were carried out with a ratio solid phase:solution 1:20 (1 g of sorbent + 20 ml of solution of dye AG-16, having the appropriate concentration in the concentration range 1–1000 mg/dm³) during 24 hours contact. Next the liquid phase was separated from the solid one by centrifugation at 4000 rpm for 20 minutes. Then, using the UV-VIS spectroscopy (Varian Cary 50 Scan UV-VIS) both initial (C_0) and equilibrium (C_{eq}) dye AG-16 concentrations in a solution were indicated. The wavelength at which the absorbance of the dye was measured was 426 nm. Tests were carried out at room temperature of $25 \pm 2^\circ\text{C}$.

In all the equilibrium solutions values of pH was measured and also, using flame photometry (photometer BWB-XP), the concentration of Ca^{2+} ions for dye concentrations C_0 50 and 500 mg/dm³ was indicated and converted to load (mg/g).

An adsorbed amount of dye (q) by the sorbents was calculated from the formula:

$$q = (C_0 - C_{eq}) \frac{V}{m} \quad (\text{mg/g}) \quad (1)$$

and a percentage dye removal (R) from the formula:

$$R = \frac{C_0 - C_{eq}}{C_0} \cdot 100\% \quad (2)$$

where:

q – dye adsorbed per unit mass solid (mg/g),

R – a percentage dye removal (%),

C_0 – initial concentration of a dye in a solution (mg/dm³),

C_{eq} – dye concentration in an equilibrium solution (mg/dm^3),

m – a sorbent mass (g),

V – a solution volume (dm^3).

3.2. The equations of adsorption isotherms.

In order to estimate the theoretical maximum sorption capacity of the sorbent and in order to determine the mechanism of the binding of the dye three 2-parameter isotherm equations were used: Freundlich, Langmuir and Dubinin-Radushkevich [11,20,25]. Constants in the equations were estimated by linear regression. Table 4 shows the formulas used in equations as well as their linear forms.

Table 4. Sorption isotherms and their linear forms

Tabela 4. Równania izoterm sorpcji i ich formy liniowe

Isotherm	Equation	Linear form	Plot	No Eq.
Freundlich	$q = K_F \cdot C_{eq}^{1/n}$	$\log q = \frac{1}{n} \log C_{eq} + \log K_F$	$\log q$ vs. $\log C_{eq}$	3
Langmuir-1	$q = \frac{q_L K_L C_{eq}}{1 + K_L C_{eq}}$	$\frac{C_{eq}}{q} = \frac{C_{eq}}{q_L} + \frac{1}{K_L q_L}$	C_{eq}/q vs. C_{eq}	4.1
Langmuir-2		$\frac{1}{q} = \left(\frac{1}{K_L q_L}\right) \frac{1}{C_{eq}} + \frac{1}{q_L}$	$1/q$ vs. $1/C_{eq}$	4.2
Langmuir-3		$q = q_L - \left(\frac{1}{K_L}\right) \frac{q}{C_{eq}}$	q vs. $1/C_{eq}$	4.3
Langmuir-4		$\frac{q}{C_{eq}} = K_L q_L - K_L q$	q/C_{eq} vs. q	4.4
Dubinin-Radushkevich	$q = q_D \cdot \exp(-\beta \varepsilon^2)$	$\ln q = \ln q_D - \beta \varepsilon^2$	$\ln q$ vs. ε^2	5

where: K_F – Freundlich isotherm constant (dm^3/g) and it is an approximate indicator of adsorption capacity, $1/n$ – a function of the strength of adsorption in the adsorption process, q_L – maximum monolayer coverage capacity (mg/g), K_L – Langmuir isotherm constant related to the affinity of binding sites (dm^3/mg), q_D – the sorption capacity of studied materials (mol/g), β – the constant (mol^2/J^2), ε – the Polanyi potential (J/mol)

which is equal to $\varepsilon = RT \ln(1 + \frac{1}{C_{eq}})$, R – the gas constant (8.314 J/molK), T – absolute temperature (K).

Furthermore, considering the isotherms course, they were classified to an appropriate type using the classification of Brauner and Giles [2,12]. According to Brauner [2] type I isotherm is characterized by monolayer filling of an adsorbent surface and describes a chemical adsorption and, rarely, a physical one; type II describes a physical adsorption with a multi-layer filling of an adsorbent surface, the type III occurs when a heat of adsorption is equal or less than the heat of condensation of a pure component. This describes the case when the interaction of adsorbate and adsorbent particles is much smaller than the intermolecular interactions of adsorbate molecules. Types IV and V correspond to curves II and III and differ from them in the fact that at a certain section they run parallel to the OX axis, because in the adsorbent pores, due to the pore diameter, only a limited number of adsorption layers is formed. Giles [12], on the other hand, distinguished four main groups of adsorption isotherms: S, L, H and C, differing in course in low concentrations, which is connected to the competitive nature of the interaction of both solute and solvent with the surface of an adsorbent. Type S isotherm shows that in low concentrations of an adsorbate, a surface has a low affinity to it, which increases with an increase of its concentration in a solution. To this type belong isotherms, which strongly adsorb a solvent. For the L type (Langmuir) characteristic is a decreasing slope of an isotherm along with increasing concentrations of an adsorbate in a solution. In low concentrations of an adsorbate in a basic solution it indicates a high affinity of an adsorbate and adsorbent sorption centers, which decreases along with an increase in solution concentration. To the H-type belong isotherms for systems with a strong interaction between an adsorbate and an adsorbent. Type C is characteristic for isotherms of linear progress, which indicates a proportional distribution of a substance between a solid phase and a solution [31].

3.3. Kinetics of sorption process

The rate of the sorption process is controlled by a mass transfer in a solution, adsorbate diffusion through a liquid layer surrounding a parti-

cle, a process of adsorption equilibrium and diffusion within pores. Intraparticle diffusion is a process significantly affecting the overall rate of an adsorption [28].

Kinetics studies were carried out at an initial dye concentration in the solution i.e. 250 mg/dm³. Measurements of the dye concentration in the solution were made after 2.5, 5, 15, 30, 60, 120, 300, 720, 1080 and 1440 minutes.

To interpret the results and to determine the relationship between an adsorbed amount of dye and reaction time, as well as to determine the kinetic constants, i.e. the amount of adsorbed dye per q_t and the constant adsorption rate k , the linear forms of kinetic equation of pseudo-first and pseudo-second order were used [26] (Table 5).

Table 5. Kinetic equations of sorption process

Tabela 5. Równań kinetyczne opisujące proces sorpcji

Equation	Formula	Linear form	No eq.
Pseudo-first order sorption	$\frac{dq_t}{dt} = k_1(q_{e1} - q_t)$	$\ln(q_{e1} - q_t) = \ln(q_{e1}) - k_1 t$	7
Pseudo-second order sorption	$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2$	$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	8

where: k_1 – the rate constant of the pseudo-first-order sorption (min⁻¹), q_t – the amount of sorption at time (mg/g), q_e – the amount of sorption at equilibrium (mg/g), k_2 – rate constant of pseudo-second-order sorption (g/mg/min).

On the other hand, to determine the role of diffusion within the particle during the sorption process the Boyle formula was used:

$$q = K \cdot t^{1/2} \quad (6)$$

where:

K – intraparticle diffusion rate constant (mg/kg min).

4. Study results and discussion

4.1. Sorption of AG-16 dye by natural and thermally modified clays and peat

Experimental sorption isotherms of AG-16 dye on natural and temperature activated clays and peat were shown in the Figure 2, the percentage dye removal – in the Figure 3, while the pH in the equilibrium solutions – in the Figure 4.

AG-16 dye was bound to the minerals building smectite clay in an amount from 0.016 to 12.070 mg/g, depending on the initial concentration varying in the range 1–1000 mg/dm³ (Fig. 2). This indicates that the percentage dye removal from the solution was respectively between 88.89 to 61.21% (Fig. 3). It was found that the percentage removal decreased along with increasing the initial concentration of the dye [17].

Sorption proceeded with minor changes of the pH in the range between 8.14–8.23 (Fig. 4). Despite the acidic condition of the dye solution (pH 5.67), after sorption in the equilibrium solutions their pH was similar to the pH of the clay, which proves the good buffer capacity of clay.

As a result of the thermal activation, there occurred an increase in the sorption capacity of the clay in all concentrations to a value within the range of 0.017 to 13.10 mg/g. It means a maximum increase in the sorption capacity of 8%. The percentage dye removal was 90–66.43% (Fig. 3). The dye sorption on the grains of the natural and activated clay proceeded at similar pH (Fig. 4), because the thermal activation did not affect the chemical properties of the clay, including its buffer property.

According to Giles classification, the experimental sorption isotherm of AG-16 dye on the natural clay belong to the S type, which means that in the low initial concentration of 250 mg/dm³ impact of dye molecules on the surface of the sorbent was much weaker than the interaction of water molecules with the surface. The affinity of the dye molecules and the surface increased along with the increase in concentration of the solution. Thermal activation of the clay did not cause an alteration of the type of isotherm.

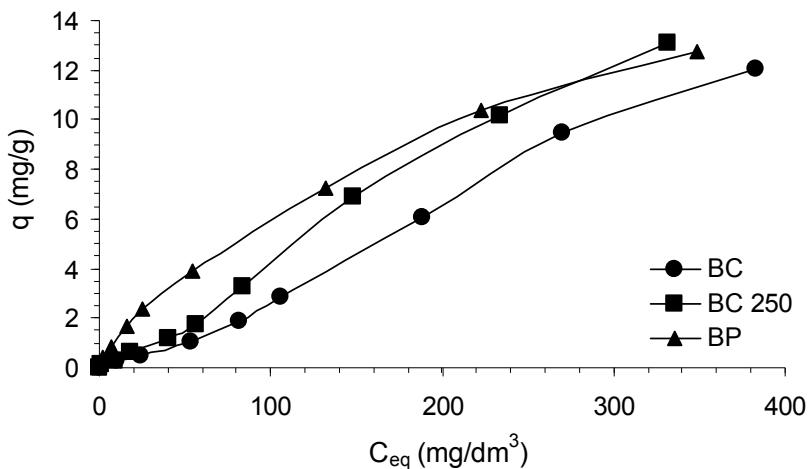


Fig. 2. Experimental sorption isotherms of dye AG-16 onto natural and temperature activation clays and peat

Rys. 2. Doświadczalne izotermy sorpcji barwnika AG-16 przez ił naturalny i aktywowany termicznie oraz torf

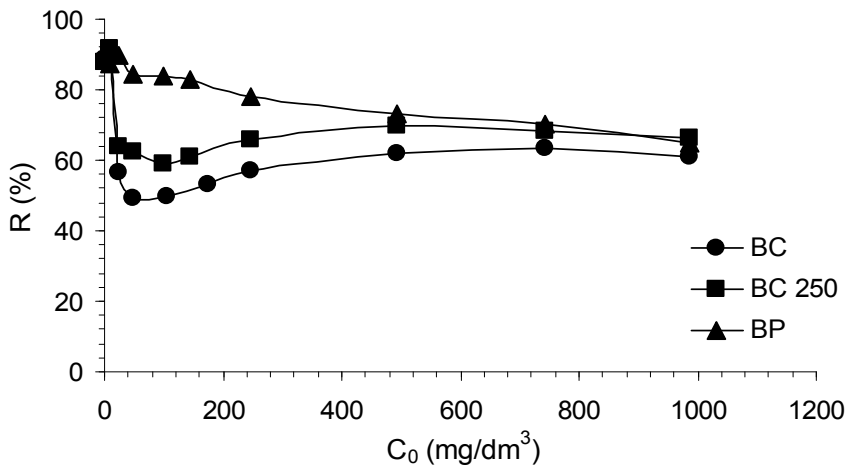


Fig. 3. Percentage removal of AG-16 dye from solutions

Rys. 3. Stopień usunięcia AG-16 z roztworów wodnych

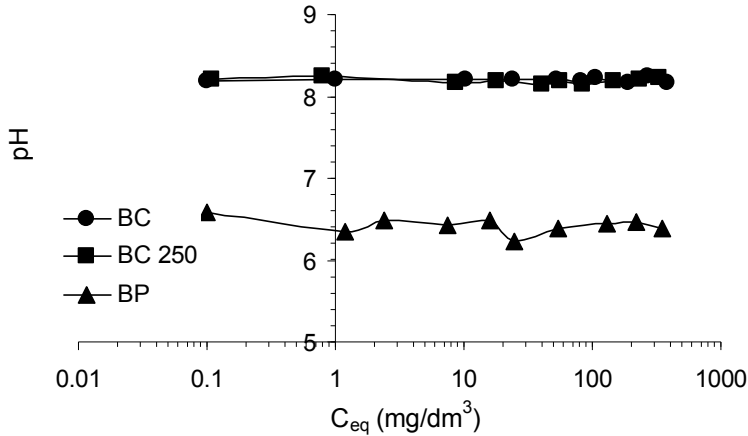


Fig. 4. Values of pH in equilibrium solution after sorption

Rys. 4. pH w roztworach równowagowych po sorpcji

According to Brauner classification, dye sorption isotherm of AG-16 belongs to a V-type. It depicts, on the one hand, stronger interactions between the dye molecules themselves than between them and the surface of the sorbent. On the other hand, it is a result of a domination of micropores in the examined clay, limiting formation of multiple layers. Despite the increase in total porosity at the time of activation of clays, neither the percentage share of micropores in the total porosity nor the isotherm type changed.

In contrast to the peat the AG-16 dye was bound to the amount of 0.018 mg/g at the initial concentration of 1 mg/dm³ to 12.752 mg/g at the concentration of 1000 mg/dm³. The percentage removal of dye from the solution varied between 90 and 64.67%; it decreased along with an increasing concentration of the dye in a solution.

Sorption on the peat also proceeded with minor changes of pH and with higher values than the sorbent pH (between 6.23 and 6.59).

Despite the similar maximum experimental sorption capacity of the peat in comparison to the activated clay, the course of the sorption of the AG-16 dye onto these materials varied significantly, especially at low concentrations.

Considering the shape of the experimental sorption isotherm of the AG-16 dye on the studied peat, it was found that according to the

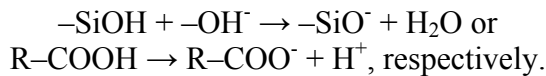
Giles classification it belonged to L type, which indicates that it is much stronger than the impact of the dye molecules on the surface than the one of the water in all concentrations. According to the Brauner classification the isotherm belongs to the I type, characteristic for the monolayer sorption.

Thus, these results show that the clay, which is of an organic nature, having higher surface area and porosity, is an effective sorbent for the removal of cationic dye in the whole initial concentration range. Another very important parameter, except porosity, determining the effectiveness of the sorbent is a high contribution of macro and mesopores in pore distribution.

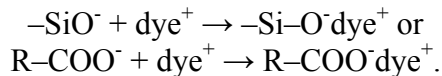
Moreover the surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent for dye ions. As a result, peat was more effective in the adsorption of basic dyes than anionic dyes [32].

Giving the pH in the equilibrium solutions after sorption of the AG-16 dye on the examined sorbents, it was found that in all cases the pH was higher than the pH at which the surface of the colloidal particles of the sorbent is of zero charge (pH_{PZC}), i.e. $\text{pH} > \text{pH}_{\text{PZC}}$.

The surface of clays and peat becomes negatively charged according the mechanisms:



It indicates that in all cases the sorption took place along with the negatively charged surface of the sorbent. It can therefore be concluded that one of the mechanisms binding the AG-16 dye of cationic nature by the natural and modified smectite clay and the peat are electrostatic interactions.



Fill et al [10] indicated that at the sorption of cationic dyes the pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to the final pH. An increasing solution pH increases the number of hydroxyl groups thus, it increases the number of negatively charged sites and enlarges the attraction between cationic dye and adsorbent surface.

The results show that except the pH of the dye solutions, an important parameter for determining the pH of the equilibrium solution is the buffer capacity of the sorbent. In this study, despite the acidic dye AG-16 (pH 5.67), the pH of the equilibrium solutions clay-dye was > 8 (Figure 4) due to the high buffering capacity of the clay.

Another mechanism of dye binding on the tested sorbents could be ion exchange. Determined in equilibrium solutions ion load Ca^{2+} for the clay-dye system were suitable for the concentration of the dye in solution C_0 50 and 500 mg/dm^3 18 and 112 mg/kg which was 0.12 and 0.77% of the exchangeable calcium and it indicates that in the process of sorption of the AG-16 dye on the grains of clay, this type of binding was unimportant.

But for the peat-dye system calcium load indicated in the equilibrium solution were respectively 1550 and 1684 mg/kg which was 6.18 and 8.40% of the exchangeable calcium. It indicates that the dye could be bound by ion exchange with exchangeable Ca^{2+} cations substituting H^+ ions in the fulvic and humic acids of the peat. Moreover, the presence of sulfonic groups in the dye molecule suggests its potential binding with the peat via hydrogen bonding, where in the proton donors were H^+ ions derived from the iron hydroxide $\text{FeO}(\text{OH})$, which pH_{PZC} is set at pH 8.5–8.8 [4].

4.2. Freundlich, Langmuir and Dubinin–Radushkevich isotherm equations

Estimated sorption parameters and corresponding values of the determination R^2 coefficient of the linear forms of Freundlich, Langmuir and Dubinin-Radushkevich equations on natural and modified clay and peat are shown in table 6.

Based on the estimated values of sorption (Tab. 6) and the value of determination coefficient indicating that the theoretical curve fit the experimental data, it was found that the process of sorption of the AG-16 dye onto natural and modified clay may be, with high probability, described by the Freundlich equation. The values of R^2 coefficient were > 0.92 . An even better fitting of the Freundlich isotherm was obtained for the sorption of the AG-16 dye on peat where R^2 was 0.9892. The estimated values of $1/n$ were less than 1, which indicates a favorable sorption process.

Table 6. Isotherm parameters for the sorption of AG–16 dye onto studied sorbents**Tabela 6.** Parametry w równaniach izoterm opisujących sorpcję AG–16 na badanych sorbentach

Isotherm	Sorption parameters	BC	BC 250	BP
Freundlich	K_F (dm ³ /g)	0.08115	0.09519	0.1475
	$1/n$ [-]	0.7518	0.7943	0.8090
	R^2 [-]	0.9299	0.9567	0.9892
Langmuir-1	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	19.23	66.66	16.92
	K_L (dm ³ /mg)	0.000015	0.000688	0.00726
	R^2 [-]	0.0000115	0.02818	0.9418
Langmuir-2	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	1.272	3.086	12.99
	K_L (dm ³ /mg)	0.1268	0.04696	0.0271
	R^2 [-]	0.9972	0.9953	0.9998
Langmuir-3	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	45.67	53.89	12.18
	K_L (dm ³ /mg)	0.0437	0.0400	0.0121
	R^2 [-]	0.0966	0.1133	0.7557
Langmuir-4	q_{max} (mg/g)	12.07	13.10	12.75
	q_L (mg/g)	16.07	18.40	14.77
	K_L (dm ³ /mg)	0.0042	0.0045	0.0092
	R^2 [-]	0.0966	0.1133	0.7557
Dubinin-Radushkevich	β (mol ² ·kJ ⁻²)	0.0102	0.0097	0.0059
	q_D (mmol/g)	0.4779	0.5590	0.224
	R^2 [-]	0.9648	0.9817	0.9978
	E (kJ/mol)	7.14	7.18	9.13

In the case of the Langmuir isotherm, it was observed that coefficient of determination values for all the four linearized form of Langmuir isotherm equations were different (Tab. 6). Similar results were obtained by K. Vasanth Kumar and S. Sivanesan [20] in studies of sorption Bismarck brown onto rice husk particles.

From the Table 6, based on R^2 values, type 2 Langmuir isotherms showed the best fit for AG–16 onto smectite clays and peat. Whereas type 1 of Langmuir isotherm shows a poor fit towards the experimental

data for clays and good – for peat. Types 3 and 4 forms have the same R^2 values and show a poor fit towards the experimental data of the dye onto all studied sorbents.

This indicates that the sorption of the AG–16 dye on natural and modified clay samples can only be thermally described by the type 2 of the Langmuir equation (eq. 4.2). R^2 coefficient at 0.9972 indicates a very good fit of the theoretical curve to the experimental data. However, the estimated value of the q_L constant indicates the maximum sorption capacity approximately one order lower than the maximum experimental sorption. It suggests that it may not be appropriate to use this model in representing the equilibrium uptake of AG–16 onto smectite clay particles.

In contrast, the value of determination R^2 coefficient indicates a very good sorption fitting of the AG–16 dye on peat molecules through type 1 and 2 of Langmuir equation. The estimated at linear 4.1 and 4.2 forms of the Langmuir equation, q_L values were close to the maximum value of experimental sorption (Tab. 6).

Moreover the value of determination coefficient ($R^2=0.9648-0.9978$) indicates that there is a strong positive relationship for the data and that sorption data of the AG–16 onto clays and peat follows the Dubinin–Radushkevich isotherm.

On the basis of the estimated value of the parameter β free energy (E) per molecule of the adsorbate was determined from the formula:

$$E = \frac{1}{(2\beta)^{1/2}} \quad (9)$$

The E value distinguishes physical adsorption ($E < 8$ J/mol) from ion exchange ($8 < E < 16$ J/mol).

The estimated values of the E parameter indicated that the sorption of the examined dye on the natural and modified clay is of a physical nature ($E < 8$ kJ/mol) and the sorption on the peat – of the ion exchange nature ($E > 8$ kJ/mol). These results confirmed the earlier theory of the ion exchange ability to participate in the binding of the dye on peat.

4.3. Sorption kinetics

The curves depicting the amount of dye adsorbed by clay and peat particles during time are shown in the Figure 5. While analyzing the amount of the AG–16 dye sorbed onto the natural clay and after thermal

activation in time it was found that after 5 minutes of contacting the solid phase: solution amount of dye adsorbed was approximately 50% of the amount adsorbed in the equilibrium conditions, and on peat – approximately 40%. After 1 hour the clay sorbed approx. 78%, and the peat approx. 70%, after 5 hours the clay – 90%, the peat 75%.

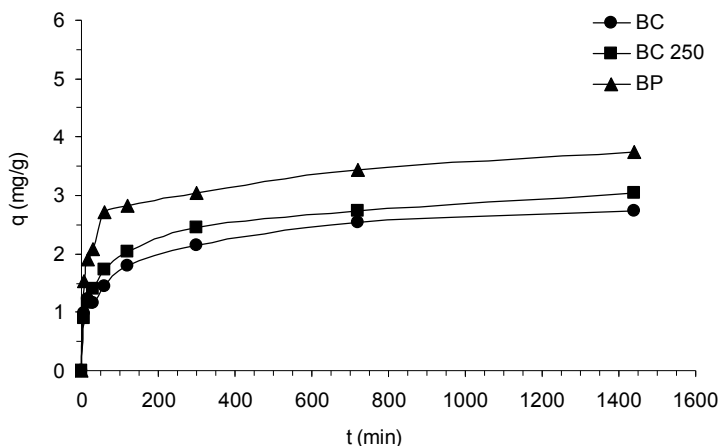


Fig. 5. Amount of dye adsorbed by clay and peat during time

Rys. 5. Adsorpcja barwnika przez ily i torf w czasie

Parameters estimated from the pseudo-first and pseudo-second order equations are shown in Table 7. On the basis of kinetic parameters and coefficients of determination R^2 , it was found that the adsorption process occurred according to the pseudo-second order equation, as proved by the high values of the determination coefficient $R^2 > 0.99$. In addition, the estimated values of the q_{e2} parameter were at the level of the values determined experimentally. Research conducted by Ho and McKay [16] also shows that the process of sorption of the cationic dyes is better described by the pseudo-second order equation.

It was found that the rate constant k_2 of sorption of the AG-16 dye on the activated clay was higher than on the natural one, which indicates that the thermal activated affected not only the increase in the sorption capacity of the clay, but also the rate of the sorption process. This is because increasing the external surface area of the clay particle exposes more active sites to AG-16 ions. Erdem et al [9] found that with the decrease of particle size of diatomite adsorbent from 300 to 60 μm external surface area and the adsorption rate of dye increased.

Table 7. Kinetics parameter for sorption process of AG–16 dye onto studied sorbents**Tabela 7.** Wartości parametrów w równaniach kinetycznych opisujących sorpcję barwnika AG–16

Sorbent		BC	BC 250	BP
Sorption capacity	q (mg/g)	2.826	3.266	3.866
Pseudo-first order sorption	q _{e1} (mg/g)	1.751	1.893	1.845
	k ₁ (1/min)	0.00315	0.00283	0.00209
	R ² [-]	0.9350	0.9026	0.6512
Pseudo-second order sorption	q _{e2} (mg/g)	2.778	3.058	3.704
	k ₂ (g/mg·min)	0.008608	0.009082	0.010049
	R ² [-]	0.9961	0.9962	0.9940
Intraparticle diffusion	K (mg/g·min)	0.0773	0.1025	0.0918
	R ² [-]	0.9719	0.9571	0.7846

Using Boyle model, a significant role of the of intraparticle diffusion in the process of the AG–16 dye sorption on clay, and much less in the dye on peat sorption, was indicated.

The kinetics of the sorption process of AG–16 dye onto peat was found to follow a pseudo-second order rate and equilibrium data agrees well with the Langmuir isotherm. The determination coefficient R² for the pseudo-second order kinetic model are greater than the determination coefficient R² for the intraparticle diffusion coefficients for the sorption of AG–16 onto peat. This strongly suggests an activated sorption mechanism which could occur because of the chemical character of peat [15].

5. Summary

The present study showed that low-moor peat was an effective adsorbent for the removal of AG-16 from water and wastewater in a wide initial concentration and smectite clay – at a high initial concentration. As a result of thermal activation of the clay, the sorption capacity for the dye increased. The process of sorption proceeded with the negatively charged surface of the sorbents and indicated that one of the mechanisms of binding the cationic AG–16 dye were electrostatic interactions. In addition, the dye was also bound by peat as a result of ion exchange with exchangeable Ca²⁺ ions. The results fitted the equilibrium data of Freundlich, Langmuir and Dubinin–Radushkevich isotherms for smectite clay – the dye system has

been best described by the Freundlich and Dubinin–Radushkevich isotherm model and the peat–dye system – by all of the isotherm models. The estimation of the E parameter from the Dubinin–Radushkevich equation indicated that the sorption test of the dye on the natural and modified clay is of a physical nature ($E < 8$ kJ/mol) and the sorption on peat – of the nature of an ion exchange ($E > 8$ kJ/mol). The sorption process of the AG–16 dye sorbents proceeded according to the equation of pseudo-second order and an important role of the intraparticle diffusion in the dye sorption on natural and modified clay molecules was observed.

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Sorpcja barwnika Acid Green 16 z roztworów wodnych na torfach niskich i iłach smektytowych towarzyszących złożom węgla brunatnych w polu Belchatów

Abstrakt

Celem badań było wyznaczenie pojemności sorpcyjnej łu smektytowego i torfu niskiego towarzyszących pokładom złóż węgla brunatnych w stosunku do barwnika Acid Green 16 (AG-16) oraz określenie mechanizmu jego wiązania.

Wyniki wskazały, że badany torf niski był skutecznym sorbentem barwnika AG-16 w całym zakresie stężeń początkowych (1–1000 mg/dm³), natomiast łu smektytowy – jedynie z zakresie stężeń wysokich (> 250 mg/dm³). W wyniku aktywacji termicznej łu nastąpił wzrost jego pojemności sorpcyjnej w stosunku do badanego barwnika. Proces sorpcji barwnika przebiegał przy ujemnie naładowanej powierzchni sorbentów i wskazywał, że jednym z mechanizmów wiązania barwnika AG-16 były oddziaływania elektrostatyczne. Ponadto barwnik ten był wiązany przez torf również w wyniku wymiany jonowej z jonami Ca²⁺ występującymi w jego kompleksie sorpcyjnym. Stwierdzono, że sorpcję barwnika AG-16 na iłach najlepiej opisuje izoterma Freundlicha i Dubinin-Raduszkiewicza, a na torfie – wszystkie 3 izotermy. Sorpcja barwnika na iłach miała charakter fizyczny a na torfie była to chemisorpcja. Proces sorpcji przebiegał według równania pseudo-drugiego rzędu. Istotną rolę dyfuzji wewnątrz cząsteczkowej stwierdzono jedynie dla sorpcji barwnika na cząstkach łu naturalnego i modyfikowanego.

Słowa kluczowe:

sorpcja, barwniki, ły smektytowe, torf, izotermy sorpcji

Keywords:

sorption, dyes, smectite clay, peat, sorption isotherms