

REMOVAL OF DIRECT DYES FROM WASTEWATER BY SORPTION
ONTO SMECTITE-CLAY³JOANNA KYZIOŁ-KOMOSIŃSKA^{1*}, CZESŁAWA ROSIK-DULEWSKA¹,
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Abstract: Dyes and pigments are important organic pollutants of the water environment. Dyes may be removed from wastewater by using one of the most efficient methods for wastewater treatment-adsorption onto porous (natural and waste) minerals or organogenic substances. Feasibility of using smectite-clay, co-occurring in brown coal deposits, for removal of direct dyes was investigated. The Freundlich linear regression model was better in modeling of sorption direct dyes onto smectite-clay; it yielded better fit of the theoretical isotherm to the experimental data. The electrostatic interactions and hydrogen bonds were shown to play the most important role in adsorption of direct dyes onto smectite-clay.

INTRODUCTION

Surface and ground waters are subject to the European Union legislation mainly due to their role as a source of high quality drinking water. Restrictive regulations concerning contamination of the aquatic environment in the EU Directives as well as increasing demands for high quality water require more efficient and environmentally sound methods for water and wastewater treatment.

Dyes and pigments are an important class of organic pollutants.

Synthetic dyes are used and released with wastewater by several industries e.g. textile and leather dyeing, cosmetics and paper production. Even low concentration of a dye causes coloring of a large body of water. In water, dyes adversely affect the aquatic ecosystem by reducing availability of sunlight to aquatic plants. Dyes exhibit considerable structural diversity and are classified in several ways. By their water-solubility, they may be divided into soluble (acid, mordant, metal complex, direct, basic and reactive dyes) and insoluble (azoic, sulphur, vat and disperse dyes). Direct dyes play an important role in the textile industry. They are water-soluble and have good color persistence. They are



used for dyeing of cellulosic fibers (cotton, viscose, linen), natural silk and polyamide. In water, molecules of these dyes dissociate into cations or anions giving colorful solutions. Moreover, direct dyes contain azo groups.

Dye-containing wastewater may be treated by means of adsorption, oxidation, coagulation and flocculation, membrane processes and biological methods [3]. Adsorption onto porous (natural or waste) minerals and organogenic substances is one of the most efficient methods of wastewater treatment. The most often used minerals are bentonite, clay, zeolites, sepiolite, diatomite, fuller's earth, and peat [3, 4, 10]. They are very efficient, low cost, and may be an alternative to activated carbon. The rich in smectites clays have high specific surface and porosity and negative surface layer charge. Moreover, they are plentiful and occur in coal deposits. Minerals of smectite family (montmorillonite and beidelite) are 2:1 clay minerals, with both interlayer and ionisable hydroxyl sites on the external surface; they have permanent negative charge in their structural framework. The negative surface layer charge, resulting from the isomorphous substitution of Mg^{2+} or Fe^{2+} for octahedral Al^{3+} or Fe^{3+} and Al^{3+} for tetrahedral Si^{4+} , causes binding of exchangeable cations to the interlayer sites. The cation exchange capacity (CEC) of these minerals is due to the substitution within the structure (pH independent) and to the charges at the edge of the sheets (pH dependent). The point of the zero charge (pH_{pzc} – the pH value at which a solid submerged in an electrolyte has zero net electrical charge on the surface) lies about 2.5.

The principal method for describing the sorption process is an equation that expresses the relation between the concentration in water and the corresponding concentration in solid phase at equilibrium conditions, i.e. the sorption isotherm. The sorption parameters can be determined by using mathematical models, laboratory experiments or *in situ*. Data from experiments are interpreted by using linear or non-linear isotherms. The isotherm is selected by fitting a theoretical curve to empirical data; the coefficient of determination (R^2) is a measure of goodness of the fit [6, 14].

The paper presents application of the batch method in investigations of adsorption of direct yellow 142, direct red 81, and direct blue 74 from a single-dye solution onto smectite-clays from brown coal deposit. Isotherms and kinetics of sorption of the dyes were also studied.

MATERIALS AND METHODS'

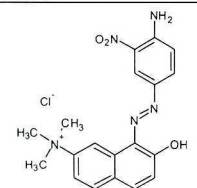
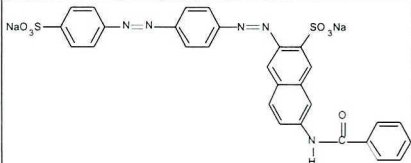
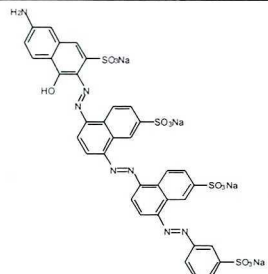
Three direct dyes were examined: direct yellow 142 (DY 142), direct red 81 (DR 81) and direct blue 74 (DB 74). They are produced by Boruta Zachem-Kolor sp. z o.o. (Poland), the leading Polish producer of synthetic organic dyes. Main functional groups of these dyes are azo, nitro, amine, sulfo, carbonyl and hydroxyl groups.

The key features of the used dyes are given in Table 1. The CAS registry numbers of the dyes from the ChemIDplus Lite database are also provided. They help to identify such chemical compounds as dyes that may have different common names.





Table 1. Characteristics of the investigated direct dyes

Dye	CAS	Systematic name	Molecular formula	Molecular weight	Structural formula	pH of 1 g/dm ³ water solution
Direct yellow 142	71902-08-4	[8-(4-amino-3-nitrophenyl)azo-7-hydroxy-2-naphthyl]-trimethylammonium chloride	C ₁₉ H ₂₀ N ₅ O ₃ Cl	401.5		6.95
Direct red 81	2610-11-9	2-naphthalenesulfonic acid, 7-(benzoylamino)-4-hydroxy-3-((4-(4-sulfophenyl)azo)phenyl)azo)-, disodium salt	C ₂₉ H ₁₉ N ₅ O ₈ S ₂ Na	677.6		8.22
Direct blue 74	33540-94-2	2-naphthalenesulfonic acid, 5(or 8)-(2-(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl) diazenyl)-8(or 5)-(2-(6(or 7)-sulfo-4-(2-(3-sulfophenyl) diazenyl)-1-naphthalenyl) diazenyl)-, sodium salt (1:4)	C ₃₆ H ₂₅ N ₇ O ₁₃ S ₄ Na	983.8		8.03

The smectite-containing neogene clay from the brown coal deposit in Bełchatów (Bełchatów Brown Coal Mine, Central Poland) was used as an adsorbent. It is mainly composed of smectite, and it also contains quartz, calcite kaolinite and iron(III) oxide-hydroxide (FeOOH) (Fig. 1a). Bands of H-O-H, Si-O, Al₂-O-H, Al-Fe-O-H, Al-O-Si and Si-O-Si are characteristic of this clay, therefore O-H, Si-O, Al₂-O-H, Al-Fe-O-H groups are the main sorption centers of reaction in it (Fig. 1b). The hydroxyl groups on the surface can, depending on pH, gain or lose a proton. At low pH, the surface sites are protonated and the surface becomes positively charged:



at high pH, the surface minerals lose their protons and surface becomes anionic:

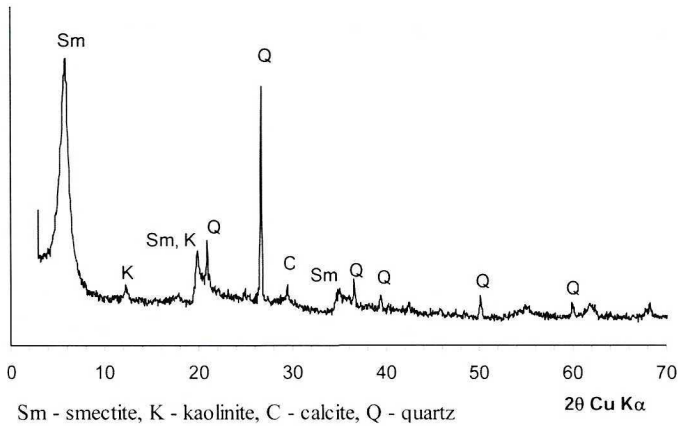


Fig. 1a. X-ray diffractogram of the smectite-clay

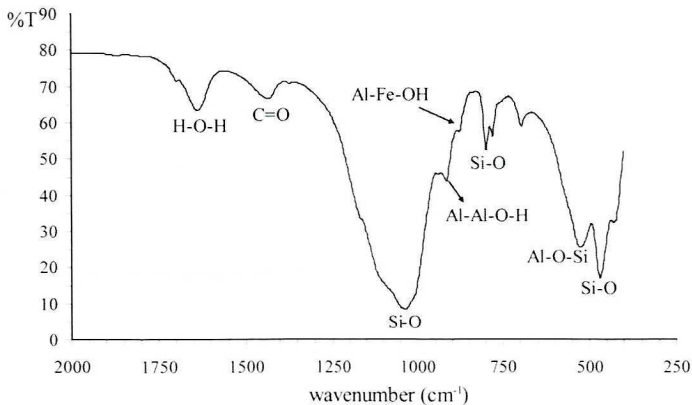


Fig. 1b. FTIR spectra of smectite-clay

The air-dried and homogenized samples of the clay were sieved through a 0.5 mm sieve. The physicochemical properties of the samples are shown in Table 2 [8, 9].

Table 2. Physical and chemical properties of smectite-clay

Bulk density	Specific gravity	Porosity n_o	Specific surface area (SSA)		CEC	pH
			external	total		
[kg/m ³]	[kg/m ³]	[%]	[m ² /g]	[m ² /g]	[cmol(+)/kg]	
1943	2557	6.82	41.38	141.83	82.42	7.96
chemical composition [%]						
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
64.70	13.65	4.37	0.99	1.373	0.109	1.499

The sorption capacity was determined in static conditions by using the batch method. The initial concentrations (C_o) of the dye solutions were within the range 1–1000 mg/dm³, the ratio solid phase (m)/solution (V) was 1:20 and shaking time was 24 h. The clay suspensions were centrifuged at 4000 rpm for 20 min. C_o and equilibrium metal concentrations (C_{eq}) in solutions were determined by means of UV/VIS spectrometry (Varian Cary 50 Scan spectrophotometer, 1 cm long cell). The wavelengths (λ_{max}) used were: 392 nm for direct yellow 142, 510 nm for direct red 81, and 582 nm for direct blue 74. The amount of adsorbed dyes (S) was calculated from:

$$S = (C_o - C_{eq}) \cdot V/m \text{ [mg/kg]}. \quad (3)$$

Additionally, pH was determined in the equilibrium solutions.

To determine whether growth of the concentration causes polymerization of the dye molecules in the solution, the absorbance spectra of dye solution at concentrations 1, 5, 10, 25 mg/dm³ were recorded every one nanometer in the range of 400–700 nm. Sorption parameters were estimated by using linear forms of the Freundlich and the Langmuir equations [13, 14]. Moreover, non-linear regression (STATISTICA ver. 8.0) was used to estimate the constants in these equations. For each system, R^2 expressed goodness of the fit of a theoretical curve to experimental data. In addition, the Lagergren's pseudo-first order rate equation and the pseudo-second order rate equation were used to describe the mechanism of dye sorption onto the smectite-clays. The initial concentration of dyes in the kinetic experiments was 250 mg/dm³. The clay suspensions with dyes were shaken from 5 to 1440 min. For each shaking time, after centrifugation, the concentrations of dyes in the solutions were measured.

RESULTS AND DISCUSSION

Sorption of the direct dyes onto smectite-clay

The dye sorption isotherms were determined by using smectite-clay samples in $S = f(C_{eq})$ system (Fig. 2a).

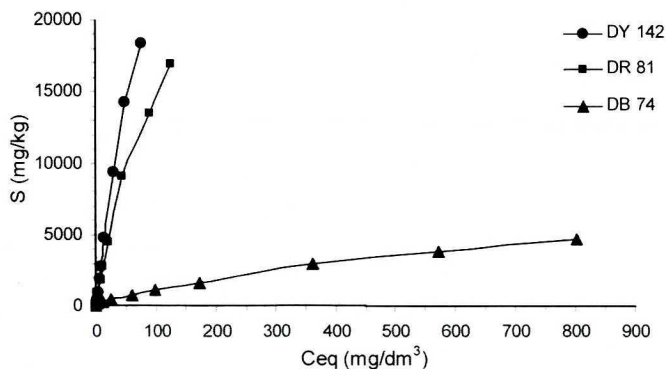


Fig. 2a. Sorption isotherms of direct dyes onto smectite-clay

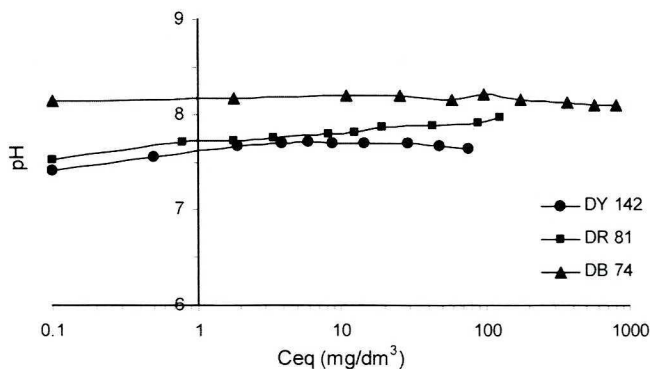


Fig. 2b. Pattern of pH changes in equilibrium solution

According to the Gilles classification [2], direct yellow 142 and direct red 81 had the H-type sorption isotherms what means their very high affinity for smectite-clay. The maximum sorption capacities of smectite-clay for DY 142 and DR 81 were 18378 mg/kg and 16932 mg/kg, respectively. The high affinity of direct yellow 142 for the clay may be explained by the dye cationic structure (Tab. 1). The clay contained mainly smectite (diffractogram in Fig. 1), which was beidellite [7]. Therefore, the clay had high internal and external surfaces, porosity and permanent negative charge, and also high affinity for cationic dyes. High affinity of cation dyes for sorption centers in fuller's earth (rich in Ca-montmorillonite) and the H-type adsorption isotherms were also observed by Atum *et al.* [1]. In the spectrum of DR 81 solution, at the concentrations 10 and 25 mg/dm³, beside the maximum at $\lambda = 510$ nm, a peak at $\lambda = 380$ nm appeared (Fig. 3). It means that, at higher concentrations, DR 81 occurred in dimmer forms and in such forms it was bound. Instead, for all initial concentrations, direct blue 74 was bound by the clay in smaller than other dyes amounts. It had the L-type sorption isotherm and maximum sorption capacity of smectite-clay for this dye was 4700 mg/kg. The slighter than for other dyes slope of the DB 81 isotherm means its weaker affinity for the sorption centers of the clay. This dye

has an anionic character and has high affinity for positively charged surfaces. In equilibrium solution at pH between 8.0 and 8.4, smectite surface is negatively charged and has low ability to bind anionic dyes. The only positively charged component of the clays at pH lower than 9.0 is Fe(III) oxide-hydroxides (FeOOH). Their point of zero charge (pH_{pzc}) is 8.5. However, the iron present in smectite-clay is mainly bound in the smectite structure (96.04% of Fe_i), and only 634.5 mg/kg (1.41 of Fe_i) occurs in nonevly stalline forms [8]. Dyes uptake depends on the dye structure and different dyes have different molecular structures. Sorption capacity of smectite-clay for the studied direct dyes increased in the order: DY142 > DR81 > DB74. Similar order of maximum sorption capacities of montmorillonite for direct dyes was reported by Yavuz and Aydin [15].

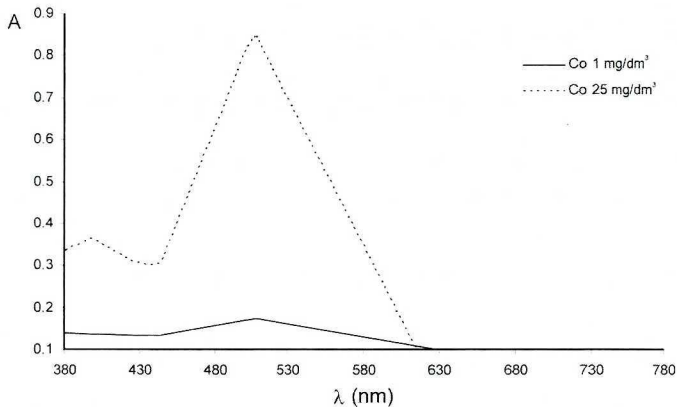


Fig. 3. Visible spectra of direct red 81 in aqueous solution at concentration 1 and 25 mg/dm³

The pH values of the equilibrium solutions are presented in Figure 2b, where a semi-logarithmic scale is used to make the charts more understandable. The sorption of dyes by smectite-clay occurred practically at constant pH due to high buffering capacity of the equilibrium solutions. It demonstrates high efficiency of cationic dye removal and rather low sorption capacity for anionic dyes that increases with decreasing pH of the dye solution [11].

The surface functional groups and chemical properties of the direct dyes were the cause of electrostatic (coulombic) attraction between DY^+ and negative charge on surface of smectite, and between DB^- and positive charge on surface of oxide-hydroxide (FeOOH) at high pH (6–8). Moreover, there occurred surface hydrogen bonds between the Si-O⁻, FeAl-O⁻ and Al-O⁻ surface groups of smectite, and the -NH, -NH₂ and -OH dye groups.

Adsorption isotherms

Linear adsorption isotherms

Two isotherm equations non-linearly model adsorption equilibrium in solution:

$$S = K_F C_{eq}^n \quad - \text{Freundlich equation}, \quad (4)$$

$$S = \frac{K_L Q C_{eq}}{1 + K_L C_{eq}} \quad - \text{Langmuir equation}, \quad (5)$$

where:

S – amount of dye adsorbed per unit mass of clay [mg/kg],

C_{eq} – equilibrium concentration of dye [mg/dm³],

n – Freundlich constant related to surface affinity for the solute,

K_F – constant,

Q – maximum sorption capacity of clay for dye [mg/kg],

K_L – adsorption equilibrium constant [dm³/kg].

In this paper, to estimate the sorption parameters, the linear forms of them were used:

$$\log S = \log K_F + n \log C_{eq}, \quad (6)$$

$$\frac{C_{eq}}{S} = \frac{C_{eq}}{Q} + \frac{1}{K_L Q}. \quad (7)$$

The experimental linear relationship was obtained between $\log S$ and $\log C_{eq}$ (Freundlich) and C_{eq}/S and C_{eq} (Langmuir) (Fig. 4a, b). The values of constants were calculated, and are presented in Table 3.

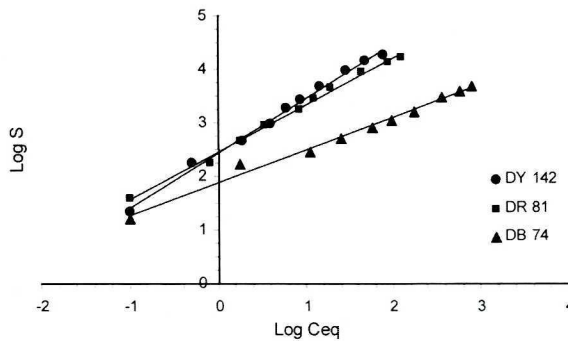


Fig. 4a. Freundlich plots corresponding to the sorption of studied direct dyes onto the smectite-clay

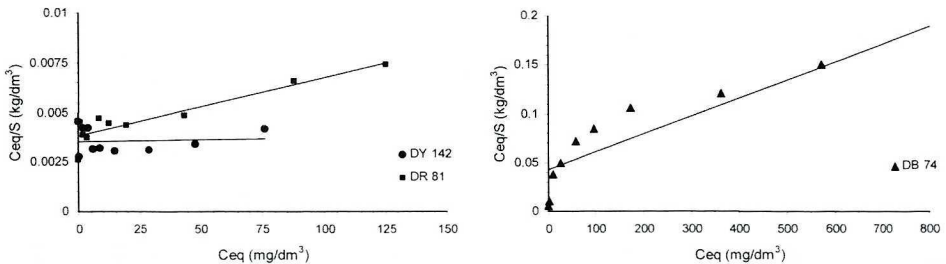


Fig. 4b. Langmuir plots corresponding to the sorption of studied direct dyes onto the smectite-clay

The sorption parameters calculated from (6) fitted the experimental data best; the determination coefficient (R^2) for Freundlich isotherms was close to 1.0. The Langmuir equation (7) was not applied to the results for direct yellow 142. The best performance of

Table 3. Isotherm parameters obtained from the linear regression

Dye	Freundlich isotherm			Langmuir isotherm			
	K_F	n	R^2	S_{max} [mg/kg]	Q [mg/kg]	K_L [dm ³ /kg]	R^2
DY142	274.22	1.0204	0.9936	18378	500000	0.00056	0.000459
DR 81	277.78	0.8857	0.9954	16932	34482.8	0.00762	0.8566
DB 74	75.87	0.6096	0.9904	4700	5464.5	0.00431	0.8276

the Freundlich model in the case of adsorption of the direct dyes indicates the heterogeneous surface binding (Tab. 3).

Non-linear adsorption isotherms

Application of linear regression is burdened with an error since, depending on the selected isotherm, the determined regression line does not minimize the total of:

$$\sum_i [S_i - K_F C_{eq}^n]^2 \quad \text{or} \quad \sum_i \left[S_i - \frac{Q K_L C_{eq}}{1 + K_L C_{eq}} \right]^2 \quad (8)$$

The best-fitting isotherm parameters for the data were received by using the non-linear regression based on the classical least-squares method. The sorption parameters and R^2 values are given in Table 4. Higher R^2 values indicate that application of non-linear regression provided better fit of the curves to the experimental data. Both the Freundlich and the Langmuir isotherms satisfactorily fitted the experimental data (Tab. 4). However, for all dyes, the Langmuir isotherms were better. Shen *et al.* [12] report similar findings in their studies on sorption of anionic dyes onto bentonite.

Table 4. Isotherm parameters obtained from the non-linear regression

Dyes	Freundlich isotherm			Langmuir isotherm			
	K_F	n	R^2	S_{max} [mg/kg]	Q [mg/kg]	K_L [dm ³ /kg]	R^2
DY142	541.7	0.8236	0.9905	18378	52471	0.00729	0.9985
DR 81	506.3	0.7309	0.9937	16932	33889	0.00782	0.9974
DB 74	5.84	0.6573	0.9976	4700	8357	0.001536	0.9944

Adsorption kinetics

Two models were used to describe the mechanism of dye sorption onto smectite-clay. In order to investigate the mechanism of sorption, characteristic constants of sorption were estimated by using the pseudo-first order Lagergren equation and the pseudo-second order equation based on the solid phase sorption. The kinetic parameters for studied dyes were determined for the initial concentration 250 mg/dm³.

The pseudo-first order rate kinetic equation is of the form:

$$\frac{dq_t}{dt} = k_1(q_{eq} - q_t). \quad (9)$$

Equation (9) may be transformed for linear data plotting into:

$$\ln(q_{e1} - q_t) = \ln(q_{e1}) - k_1 t, \quad (10)$$

where:

k_1 – rate constant of first order sorption [1/min],

q_c – amount of dye sorbed at equilibrium [mg/kg],

q_t – amount of dyes sorbed onto clay at time t [mg/kg].

A linearity of $\ln(q_{e1} - q_t)$ versus t confirms the applicability of this kinetic model. From the slopes and intercepts, the rate constant (k_1) and q_{c1} value were determined. The pseudo-second order rate equation can be written as:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2, \quad (11)$$

and after transformation, integrating for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, it gives the following linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2(q_{e2})^2} + \frac{t}{q_{e2}}, \quad (12)$$

where:

k_2 – rate constant of sorption [kg/(mg•min)],

q_{e2} – amount of dye sorbed at equilibrium [mg/kg],

q_t – amount of dye sorbed onto clay at time t [mg/kg].

If the experimental data fits the plot of t/q_t versus t , the pseudo-second order kinetic model is valid [4, 5]. The calculated values of the rate constant k and q_c , experimental S at equilibrium sorption capacity, and the determination coefficient R^2 are presented in Table 5. Figures 5a and 5b illustrate the correlation of $\ln(q_c - q_t)$ versus t and t/q_c versus t , respectively.

Table 5. The pseudo-first and pseudo-second order rates

Dyes	S [mg/kg]	Pseudo-first order model			Pseudo-second order model		
		q_{c1} [mg/kg]	k_1 [1/min]	R^2	q_{e2} [mg/kg]	k_2 [kg/(mg•min)]	R^2
DY142	4762	6.33	0.00196	0.2704	4975	0.000940	1.0000
DR81	4482	173.2	0.0057	0.4983	4566	0.000440	0.9999
DB74	2632	1569	0.0028	0.8154	2762	0.000012	0.9945

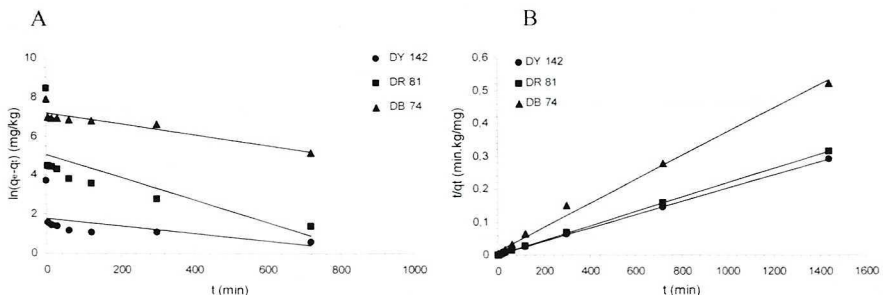


Fig. 5. Pseudo-first order (A) and pseudo-second order (B) sorption kinetic of direct dyes onto smectite-clay

The correlation coefficients in the pseudo-first order model for adsorption of dyes from a single-dye solution changed in the range of 0.2704–0.8154 for the direct dyes. The experimental data did not agree with the pseudo-first order kinetic model. The correlation coefficients in pseudo-second order model were greater than 0.9945. Confrontation of the computed time dependencies with the experimental data assures that the pseudo-second order kinetic equation describes the dye adsorption processes more accurately, especially for the longer period [12]. A similar observation was made for the adsorption of different acid dyes onto bentonite and sepiolite [10].

The kinetic data were fitted very well by the pseudo-second order kinetic model that assumes the chemical sorption or chemisorption, involving valency forces through sharing or exchange of electrons between sorbent and sorbate, as the rate-limiting step [5]. Moreover, the theoretical q_e values from this model were almost equal to the experimental value of S_{\max} .

CONCLUSION

The raw smectite-clay was effective in removal of direct dyes from aqueous solution in the range of the investigated concentrations. Being plentiful and inexpensive, smectite-clay may serve as an adsorbent in removal of direct dyes from textile wastewater.

High affinity of smectite-clay for direct yellow 142 and direct red 81 is confirmed by the H-type isotherm curves, whereas the L-type curve indicate that direct blue 74 adsorption on smectite-clay is not so good.

Within the studied concentration range of investigated direct dyes, the Freundlich adsorption isotherm model fitted equilibrium data much better than the Langmuir one.

The pseudo-second order kinetic model fitted the kinetic data very well, much better than the pseudo-first kinetic model.

Concluding, the smectite-clay from overburden of a brown coal deposit can be used as a cost effective sorbent in removal of dyes from wastewater produced by textile industries.

Acknowledgments

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USUWANIE BARWNIKÓW BEZPOŚREDNICH ZE ŚCIEKÓW METODĄ SORPCJI NA IŁACH SMEKTYTOWYCH

Barwniki i pigmenty stanowią ważną grupę zanieczyszczeń organicznych środowiska wodnego. Jedną ze skutecznych metod usuwania barwników z wód i ścieków jest ich adsorpcja na porowatych substancjach zarówno naturalnych, jak i odpadowych. Przeprowadzono badania nad możliwością wykorzystania iłów smektytowych towarzyszących pokładom złóż węgla brunatnych do usuwania barwników bezpośrednich. Przy oszacowywaniu parametrów sorpcji tych barwników na cząstkach iłu smektytowego lepsze dopasowanie izotermy teoretycznej do danych doświadczalnych uzyskano wykorzystując model regresji liniowej Freundlicha. Uzyskane wyniki badań pokazują, że największą rolę w wiązaniu barwników bezpośrednich przez ił smektytowy odgrywały oddziaływania elektrostatyczne oraz wiązania wodorowe.