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Use of citrus fruit peels (grapefruit, mandarin, orange, and lemon) as sorbents for the removal of Basic Violet 10 and Basic Red 46 from aqueous solutions

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ABSTRACT

Sorptive properties of peels of citrus fruit (grapefruit, mandarin, orange, and lemon) were tested against cationic dyes popular in the industry: BV10 and BR46, and the kinetics of colorant sorption was determined. The experimental data obtained were matched to the pseudo-first/second-order model and to the intramolecular diffusion model. The maximum sorption capacity of citrus fruit peel (Langmuir, Langmuir 2, and Freundlich isotherm) was determined as well. The maximum sorption capacity of BR46, amounting for Q = 57.04 mg/g, was exhibited by orange peel, whereas the best sorbent for BV10 turned out to be lemon peel (Q = 5.66 mg/g).

Keywords: Sorption; Unconventional sorbents; Citrus peels; Cationic dyes

1. Introduction

About 100,000 types of dyes are available on the market and their annual production reaches about 1 million tons [1]. Dyes may be divided in terms of the character of a colored ion produced in an aqueous solution into: direct (non-ionic) dyes, anionic (acid) dyes, and cationic (basic) dyes. The highest dyeing effectiveness, providing a high color intensity at a relatively low dose of the dye, is ensured by cationic dyes. They are used most commonly in the textile industry for dyeing wool, rayon, and polyacrylonitrile fibers, and also in the tanning and paper industries. Because of the imperfections of the currently used material dyeing technologies, about 5% of cationic dyes enter the post-production wastewater [2,3].

Industrial wastewater containing cationic dyes is particularly troublesome. If, alkaline dyes get into the aquatic environment, they cause noticeable changes in water color even at a concentration as low as 1 mg/L (1 ppm). Dyes contained in waters of natural reservoirs curb the access of sunlight to aquatic plants, which inhibits their photosynthesis [4]. A significant proportion of cationic dyes are toxic to aquatic organisms. Products of dyes decomposition, such as aromatic amines, are harmful as well [5]. In the case of the natural environment, it seems advisable to use sewage decolorization technology, which is highly effective especially for cationic dyes.

Sewage decolorization methods can be divided into biological and physicochemical ones. The disadvantage of the biological methods is the low effectiveness of dye biodegradation caused, among others, by their complex chemical structure. Another drawback is that a significant proportion of cationic dyes act as inhibitors of bacterial growth [6].

The physicochemical methods of wastewater decolorization include coagulation, chemical oxidation, photodegradation, and membrane processes. Coagulation is a fast process which does not require complicated installations. It is, however, ineffective with regard to the majority of cationic dyes and contributes to both sewage salinity increase and formation of large amounts of sludge. The chemical oxidation of dyes, for example, by ozonation, is an effective method of decolorization, but causes the formation of toxic substances as a result of the incomplete oxidation of dyes. In turn, the photodegradation of dyes via wastewater

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irradiation is effective only in the case of photosensitive dyes and is currently losing its importance. Finally, membrane processes, such as reverse osmosis, are among the most effective methods of decolorization. Unfortunately, their serious drawbacks include high costs of exploitation, high water losses, and the formation of significant amounts of dense wastewater.

Wastewater decolorization methods include also sorption which is widely recognized as one of the most environmental-friendly methods used to remove dyes from industrial wastewater. During sorption, no toxic intermediates of dye decomposition arise, as is the case with biological methods and in-depth oxidation. In contrast to precipitation methods, no sediments are formed during sorption and sewage salinity does not increase. After completion of sorption, the sorbent can be easily separated from the solution. Whereas, the sorbent saturated with a dye can then be regenerated or used as a fuel in heat and power plants. The effectiveness of sorption and its price depend mainly on the type of sorbent used.

Today, activated carbon is the most commonly used sorbent for dye removal from industrial wastewater. Sorbents based on activated carbons have the ability to bind each type of dye with a satisfactory effectiveness. The disadvantage of activated carbons, however, is their high price, which forces a search for their cheaper alternatives.

For several years, there has been an increasing interest in using waste from the agri-food industry for sewage decolorization. Investigations have been conducted on the use of, among others, sugar cane biomass [7], banana peel [8], rice husk [9], corn leaves [10–12], and mango leaves [13], as sorbents for cationic dyes. The capability of biomass for the sorption of basic dyes is also due to the high contents of lignin and polysaccharides [14].

Due to the high content of polysaccharides (cellulose, hemicellulose, and pectin), citrus peels may also exhibit a high affinity to cationic dyes. Citrus fruits are grown in 141 countries around the world and their global production reaches 100 million tons [15]. Wastes from citrus fruits processing can account for 45%–50% of the fruit weight, most of which are citrus peel (30%–45% of fruit weight) [16]. For this reason, peels of citrus fruits, which are waste products from the agri-food industry, are a widely available and very cheap material. Potentially, they can prove valuable in the production of biosorbents for sewage decolorization and also represent an excellent alternative to the sorbents based on activated carbons.

The study reported in this work explored the possibility of using peelings of such citrus fruits as mandarin, orange, lemon, and grapefruit for the sorption of Basic Violet 10 and Basic Red 46 cationic dyes popular in the textile industry.

2. Materials

2.1. Citrus peels

Peels of citrus fruits: sweet orange (*Citrus sinensis*) – ORN, mandarin (*Citrus reticulata*) – MND, grapefruit (*Citrus paradisi*) – GRP, and lemon (*Citrus limon*) – LMN, were used in the study. All fruits were imported from Spain (harvest period: November 2016) and were peeled "by hand".

Standard contents of polysaccharides and lignins in the dry matter of citrus skins are listed in Table 1 [17,18].

2.2. Dyes

The cationic dyes used in the study, which are Basic Violet 10 (BV10) and Basic Red 46 (BR46), were purchased from the Dyes Factory "Boruta" SA in Zgierz. Their characteristics provided by the manufacturer are summarized in Table 2.

2.3. Chemical reagents

The following chemical reagents were used for analyses: 35%–38% hydrochloric acid (POCH S.A., Poland), 98% sulfuric acid (H_2SO_4) (POCH S.A., Poland), and sodium hydroxide microgranules (POCH S.A., Poland). Purity of all reagents was at the level: pure for analysis or higher.

3. Methodology

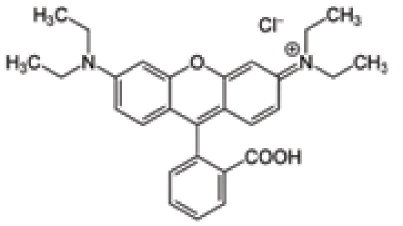
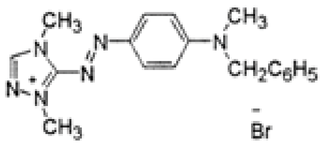
3.1. Sorbent preparation

Peels of citrus fruits were washed, dried at a temperature of 105°C, and then ground in a laboratory mill. After the fragmentation, they were sifted through a laboratory sieve with a mesh diameter of 3 mm. The <3 mm cuticle fraction was then sieved through a sieve with a mesh diameter of 2 mm, which gave a fraction of 2–3 mm. The fraction with a smaller particle diameter (<2 mm) was not used in the study due to the long sedimentation of the sorbent and due to the difficulties with separating the small particles from the solution. The peels (2–3 mm) were immersed in 2 M H_2SO_4 for 24 h (to remove mineral residues). After 24 h, they were washed with distilled water and then immersed in 2 M NaOH for the next 24 h (to remove proteins). In the next step, the rinds were rinsed with distilled water until the pH of the leachate turned neutral. After draining, the peel sorbents were ready for testing and stored in an airtight container

Table 1
Percentage of polysaccharides, lignins and pectins in the dry matter of citrus fruit peels [17,18]

Component	Orange peel (ORN)	Grapefruit peel (GRP)	Mandarin peel (MND)	Lemon peel (LMN)
Cellulose (%)	37.08 ± 3.10	26.57 ± 2.01	30.53 ± 2.35	23.06 ± 2.11
Hemicellulose (%)	11.04 ± 1.05	5.59 ± 0.42	11.04 ± 0.98	8.09 ± 0.81
Lignin (%)	7.52 ± 0.59	11.56 ± 0.98	13.54 ± 1.26	7.56 ± 0.54
Pectin (%)	23.02 ± 2.12	8.53 ± 0.68	2.58 ± 0.22	13.0 ± 1.06

Table 2
Characteristics of Basic Violet 10 and Basic Red 46 dyes

Name of the dye	Basic Violet 10 (BV10)	Basic Red 46 (BR46)
Chemical structure		
Formula	$C_{28}H_{31}ClN_2O_3$	$C_{18}H_{21}BrN_6$
Molar mass	479.0 g/mol	401.3 g/mol
λ_{max}	547.5 (nm)	530.0 (nm)
Dye characteristics	Alkaline (cationic)	Alkaline (cationic)
Usage	For dyeing wool, paper, leather and for printing inks	For dyeing synthetic fibers

at 4°C until used. The sorbent preparation procedure was identical for each type of citrus peel.

3.2. Determination of the effect of solution pH on the effectiveness of dye sorption

Citrus peels (1 g d.m.) were weighed into a series of conical flasks (250 mL). Next, dye solutions (100 mL) with concentrations of 100 mg BR46/L or 10 mg BV10/L and pH 2–11 (pH correction with HCl or NaOH) were added to the flasks that were placed on a shaker (150 rpm). After 2 h of the sorption process, samples of solutions (10 mL) were taken from the flasks to determine the concentration of the remaining dye in the solution. The pH value at which the amount of the adsorbed dye was the highest was found to be optimal. The pH value of the dye solution after sorption was measured as well.

3.3. Determination of dye sorption kinetics

Citrus peels (5 g d.m.) were weighed into a series of beakers (600 mL). Then, dye solutions (500 mL): 25/100/300 mg BR46/L or 10/25/100 mg BV10/L with the optimal pH determined according to the method described in section 3.2, were added to the beakers after which the beakers were placed on a magnetic stirrer (150 rpm). At specific time intervals (5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, and 360 min), samples (5 mL) were taken from the solutions to determine the concentration of dye remaining in the solution.

Various concentrations of dyes used in the study result from different sorption efficiencies of these dyes, which were determined in preliminary studies. To enable the comparison of sorption kinetics of BR46 and BV10, two of the three initial concentrations: 25 and 100 mg/L, are common for both dyes.

3.4. Determination of the maximum sorption capacity

The sorbent (1 g d.m.) was weighed into conical flasks (250 mL). Dye solutions with the optimal pH value (point 3.2) and concentrations of 10–100 mg/L for BV10 and 10–500 mg/L for BR46 were added to the flasks which were then placed on a shaker (150 rpm) for the time specified in 4.2. After completion of sorption, samples (10 mL) were taken from the solutions to determine the concentration of dye remaining in the solution.

3.5. Determination of dye concentration

The concentrations of dyes were determined by the spectrophotometric method using a UV/VIS spectrophotometer (UV-3100PC, VWR, China). Analyses were carried out in a quartz cuvette (10 mm) at the wavelengths of: λ_{max} = 548 nm for BV10 (calibration curve up to 10 mg/L) and λ_{max} = 554 nm for BR46 (calibration curve up to 50 mg/L). At higher dye concentrations (outside the calibration curve scale), the solutions were diluted with distilled water.

3.6. Calculation methods

The amount of pigmented dye was calculated according to:

$$Q_S = \frac{\left(C_0 - C_E\right) \times V}{m} \tag{1}$$

Q_S – mass of the sorbed dye (mg/g d.m.); C_0 – initial dye concentration (mg/L); C_E – concentration of dye left in the solution (mg/L); m – sorbent mass (g d.m.); V – volume of the solution (L).

The kinetics of dyes sorption on the tested sorbents was described using the pseudo-first (Eq. (2)) and pseudo-second (Eq. (3)) models, and a simplified model of intraparticle diffusion (Eq. (4)):

$$\frac{dq}{dt} = k_1 \times \left(q_e - q\right) \tag{2}$$

$$\frac{dq}{dt} = k_2 \times \left(q_e - q\right)^2 \tag{3}$$

q – momentary quantity of the sorbed dye; q_e – equilibrium quantity of the sorbed dye (mg/g); t – sorption time (min); k_1 – constant in pseudo-first-order equation (1/min); k_2 – constant in pseudo-second-order equation (g/(mg*min)).

Phases of dyes sorption onto chitosan sorbents were described with a simplified model of intraparticle diffusion (Eq. (4)):

$$q_t = k_d \times t^{0,5} \tag{4}$$

q_t – momentary quantity of the sorbed dye (mg/g); k_d – intraparticle constant of diffusion rate (mg/g*min$^{-0.5}$); t – sorption time (min).

Experimental data derived from analyses of the maximum sorption capacity were described by three popular sorption isotherms:

Langmuir isotherm (Eq. (5)):

$$Q = \frac{\left(Q_{\max} \times K_C \times C_E\right)}{\left(1 + K_C \times C_E\right)} \tag{5}$$

Q – equilibrium amount of the sorbed dye (mg/g d.m.); $Q_{\max}$ – maximum sorption capacity (Langmuir) (mg/g d.m.); K_C – constant in Langmuir equation (L/mg); C_E – concentration of dye remaining in the solution (mg/L).

Langmuir II isotherm (double Langmuir isotherm) (Eq. (6)):

$$Q = \frac{\left(b_1 \times K_1 \times C_E\right)}{\left(1 + K_1 \times C_E\right)} + \frac{\left(b_2 \times K_2 \times C_E\right)}{\left(1 + K_2 \times C_E\right)} \tag{6}$$

Q – equilibrium amount of the sorbed dye (mg/g d.m.); b_1 – maximum sorption capacity of sorbent (active sites of type I) (mg/g d.m.); b_2 – maximum sorption capacity of sorbent (active sites of type II) (mg/g d.m.); K_1 and K_2 – constants in Langmuir equation (L/mg); C_E – concentration of dye remaining in the solution (mg/L).

Freundlich isotherm (Eq. (7)):

$$Q = K \times C_E^{1/n} \tag{7}$$

Q – equilibrium amount of the sorbed dye (mg/g d.m.); K – equilibrium constant in the Freundlich model; C – concentration of dye remaining in the solution (mg/L); n – heterogeneity parameter.

4. Results and discussion

4.1. Influence of solution pH on the effectiveness of dye sorption

The effectiveness of BR46 sorption on citrus peels increased with an increase of the initial pH up to pH 6, but decreased with a further increase in solution pH (Fig. 1a). The observed trend was similar for each tested sorbent based on citrus peels. As shown in the preliminary studies, BR46 is a dye susceptible to alkaline environment; its solution becomes discolored at pH > 8. For this reason, the sorptive effectiveness of BR46 at pH 9–11 is not included in Fig. 1a.

The highest effectiveness of BR46 sorption at pH 6 was also confirmed in the research on the purification of colored sewage using pine needles [19]. The high effectiveness of BR46 sorption at a similar pH value (pH 7.0/7.5) has also been confirmed in studies on the removal of dyes using beet pulp [20] and *Pleurotus mutilus* biomass [21].

The BV10 binding effectiveness on the sorbents tested was the highest at pH 2 and decreased with pH increasing up to pH 11 (Fig. 1b). However, this decrease was not uniform throughout the entire pH range studied. At the initial pH 4–9, the binding effectiveness of BV10 on sorbents varied only slightly.

The positive effect of low pH on the sorption effectiveness of BV10 was also noted in studies on the decolorization

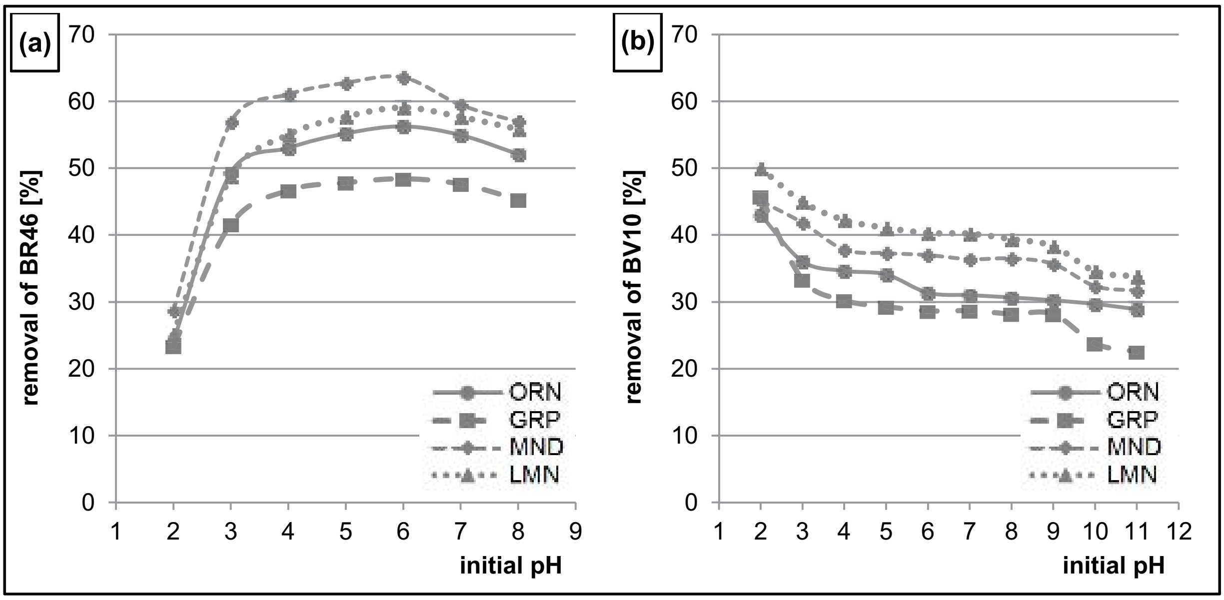


Fig. 1. Effect of pH on the effectiveness of BR46 (a) and BV10 (b) sorption onto citrus peels.

of aqueous solutions using zeolites, sawdust, ashes [22] as well as algae and seaweed biomass [23].

Despite the similar nature of BV10 and BR46, the effect of solution pH on the sorption effectiveness of BV10 on the sorbents tested was different than in the case of BR46, which could be due to their different chemical structure. During sorption at low pH, some of the functional groups of polysaccharides present in the peel of citrus fruits (mainly –OH groups) were protonated, thanks to which the sorbent gained a positive charge. The positively charged surface of the sorbent repelled the cationic BR46 electrostatically, which significantly limited its sorption. Electrostatic repulsion was getting stronger along with the decreasing initial pH of the solution. For this reason, the sorption effectiveness of BR46 on the sorbents tested was the lowest at pH 2 (Fig. 1a). In turn, despite its basic character, BV10 has an acid carboxylic group. Sorbent's surface, which had a positive charge at low pH, attracted electrostatically the carboxyl functional group ($-COO^-$) of BV10 (at pH 2–3, more than 50% of carboxylic groups have a deprotonated form). For this reason, low pH promoted the sorption of BV10 on citrus peels (Fig. 1b).

At high pH, both the sorbent and the dyes could gain a negative charge and repel electrostatically. This caused less intense BV10 sorption at higher pH (10–11) (Fig. 1).

Sorbents in the form of citrus peels affected the pH of the solution in which the sorption took place (Figs. 2a and b). The pH of the solution containing the sorbent always tended to obtain the pH_{ZPC} value (pH of the neutral charge point) (Figs. 2c and d). The pH_{ZPC} value was 7.89 for MND, 8.21 for ORN, 8.20 for LMN, and 8.09 for GRP. There was no clear correlation between the pH_{ZPC} value and sorption effectiveness of dyes on the sorbents tested.

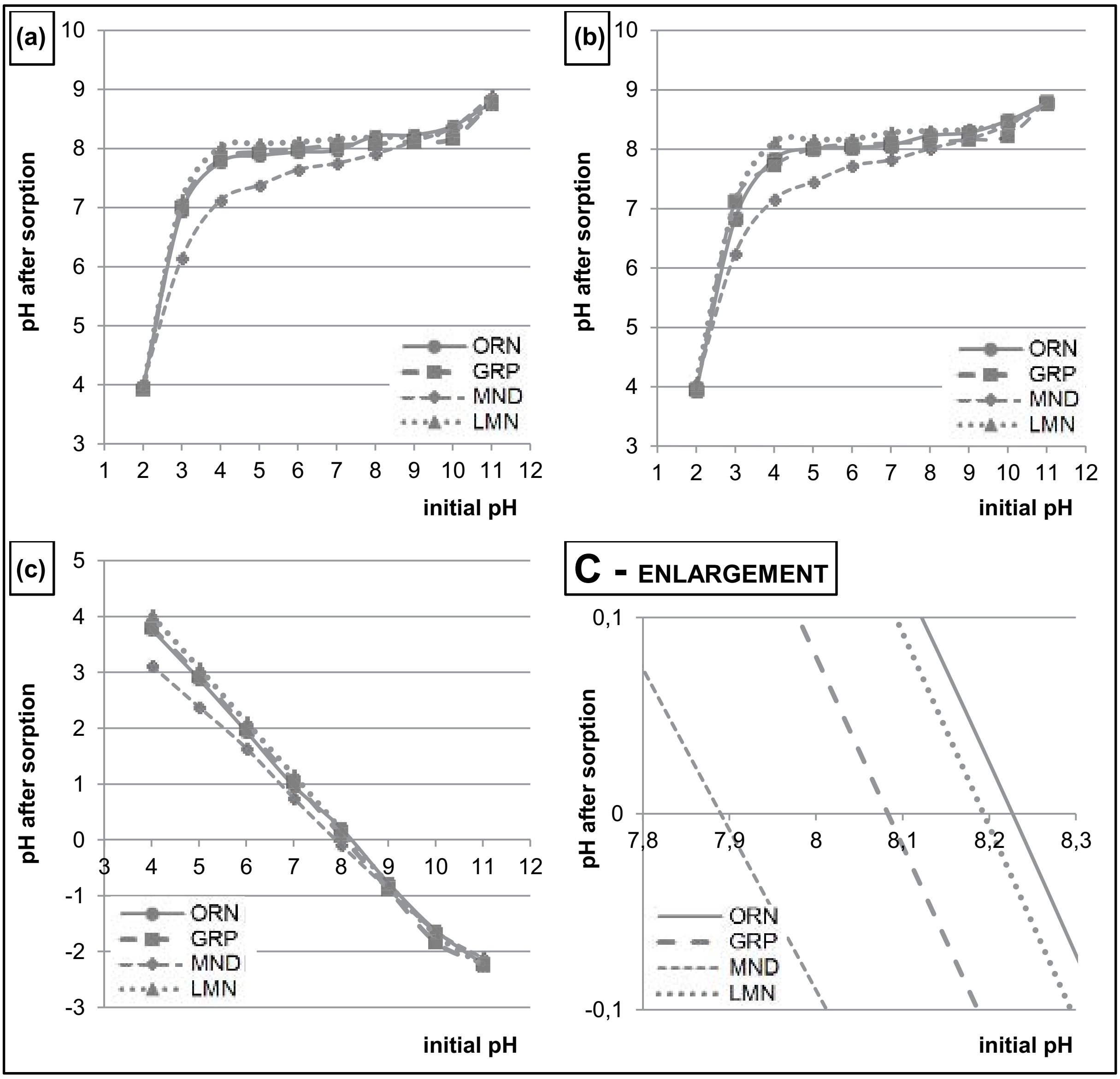


Fig. 2. Effect of citrus peels on changes pH in solution: BR46 (a), BV10 (b), and determination of pH_{ZPC} of the tested sorbents with titration method (c, d). Temperature 22°C.

4.2. Kinetics of dyes sorption

Fig. 3 shows the percentage changes in the concentration of dyes in BR46 solutions during sorption using peels of different citrus fruits. The time needed to reach sorption equilibrium of the dyes on the sorbents tested ranged from 180 min to 240 min. Longer time was usually needed to achieve the sorption equilibrium of the dyes on citrus peels at low initial concentrations of the dye. This is probably due to the lower probability of the collision of sorbate molecules with sorption centers considering their lower number in the solution.

The relatively long time of sorption of cationic dyes on citrus peels could be due to the specific sorbent structure. In contrast to most of the typical lignocellulose sorbents, the citrus peel has a loose structure that allows dyes to pervade into the sorptive centers located in the deeper layers of the sorbent. Due to the interaction of dyes with polysaccharide chains, the process of dyes penetration inside the sorbent is quite slow, which elongates the time needed to reach the sorption equilibrium.

The effectiveness of dye binding on sorbents was the highest in the initial minutes of the sorption process. In relation to the amount of dye removed from the solution after the equilibrium time, 60% to 75% BV10 and 85% to 95% BR46 were bound to the sorbent already in the first 20 min of the sorption process. The percentage of dye removal effectiveness decreased with an increasing initial concentration of the dye (Fig. 3).

In the case of BR46, shorter sorption equilibrium times were obtained in the decolorization studies with sawdust aqueous solutions (40 min) [24], pine needles (90 min) [19], and oyster mushroom biomass (90 min) [21]. Faster achievement of the equilibrium time was also noted in studies on BV10 sorption on mango leaves (50 min) [12], jute stick powder (60 min) [25], and coconut fiber (90 min) [26].

In each research series of the sorption of cationic dyes on sorbents based on citrus peels, the largest fit to the experimental data was shown for the pseudo-second-order model (Fig. 4; Table 3). With an increase in the initial concentration of the dye in the solution, the sorption intensity of BR46 and BV10 increased, whereas the value of sorption rate constant K_2 decreased. This can be explained by the higher probability of sorbates colliding with active centers, in the solution containing a higher number of dye molecules. A similar trend was observed during the sorption of dyes on carbonated peel of pomegranate [27], carbonated beans (*Squamosa*) [28], as well as on chitosan [29].

The effectiveness of the sorbents tested against dyes was similar. The lower effectiveness of BV10 sorption on citrus peels in comparison with BR46 might result from its higher molar mass that hindered its penetration into the sorbent's structure and also from the presence of the –COOH group, whose electrostatic interactions with polysaccharide sorbent chains could impede reaching the sorption centers located in the deeper layers of citrus skins.

The model of intramolecular diffusion adapted to experimental data indicates that, in most cases, the sorption of BR46 and BV10 on citrus peels proceeded in three stages (Table 4; Fig. 5).

The first stage, most intense sorption stage, was simultaneously the shortest one and lasted from 10 to 30 min, depending on the type of dye and its initial concentration. Presumably, at this stage the cationic dyes diffused through the solution to the surface of the sorbent and joined the most available active centers of the sorbent. At the second stage of sorption, dyes filled the last free sorption centers on the surface and also joined active sites located in shallower layers of the sorbent. Due to difficulties in sorbent penetration by dyes during intramolecular diffusion, the second stage of sorption was less intense than the first one and longer (from 20 to 70 min). The third, longest sorption stage lasting from 90 to 160 min was at the same time the least intense and preceded the achievement of the sorption equilibrium. At this stage, the sorption effectiveness of dyes was the lowest due to the low number of the remaining free sorption centers and their location in the deepest, most difficult to reach layers of the sorbent.

In the case of low initial concentration of BR46 (25 mg/L), the intramolecular diffusion model indicated only two stages of the sorption process (Table 4). Presumably, after the first stage, at which most of the BR46 molecules joined the active sorbent centers, the pre-equilibrium stage followed immediately. This was not observed for BV10, probably due its lower affinity to sorbents based on citrus peels.

The k_{d1}, k_{d2}, k_{d3} constants determined from the intramolecular diffusion model, indicating the intensity of sorption in time, increased with the initial concentrations of the dye. As mentioned earlier, this is due to the increasing probability of sorbates colliding with the sorption centers. A similar tendency was observed in the studies on dyes sorption on chitosan [30].

4.3. Maximum sorption capacity

The calculated values of determination coefficient R^2 demonstrate that the Langmuir model and the Langmuir 2 model showed a greater fit to the experimental data than the Freundlich model did (Table 5). It should be noted that values of the constants determined from the Langmuir and Langmuir 2 models, that is, $Q_{\max}$, $K_C/K_1/K_2$, and R^2, were the same in individual series. A similar result was obtained in studies on the sorption of BV10 on maize silage [31]. In both cases, this may suggest the presence of only one type of sorption center in the sorbent tested. Hydroxyl groups of polysaccharides of the citrus skins are probably the discussed type of active site. For this reason, further description of results will be based on the fixed values determined from the Langmuir model.

The maximum sorption capacity of BR46 was similar for the tested sorbents and – reached 54.16 mg/g for MND, 57.04 mg/g for ORN, 53.99 mg/g for LMN, and 54.47 mg/g for GRP (Table 5).

Although orange peels exhibited the highest sorption capacity in the model, they were characterized by the lowest degree of affinity to the dye (K_C = 0.017) (Table 5). A low degree of affinity may suggest that the sorbent can achieve the sorption capacity calculated from the model only at a very high concentration of the sorbate, which usually does not occur under real conditions. Therefore, low K_C values can help predict a low sorption effectiveness at low concentrations of the dye (<1,000 mg/L). The above statement is supported by the results from points 4.1 to 4.2, in which the

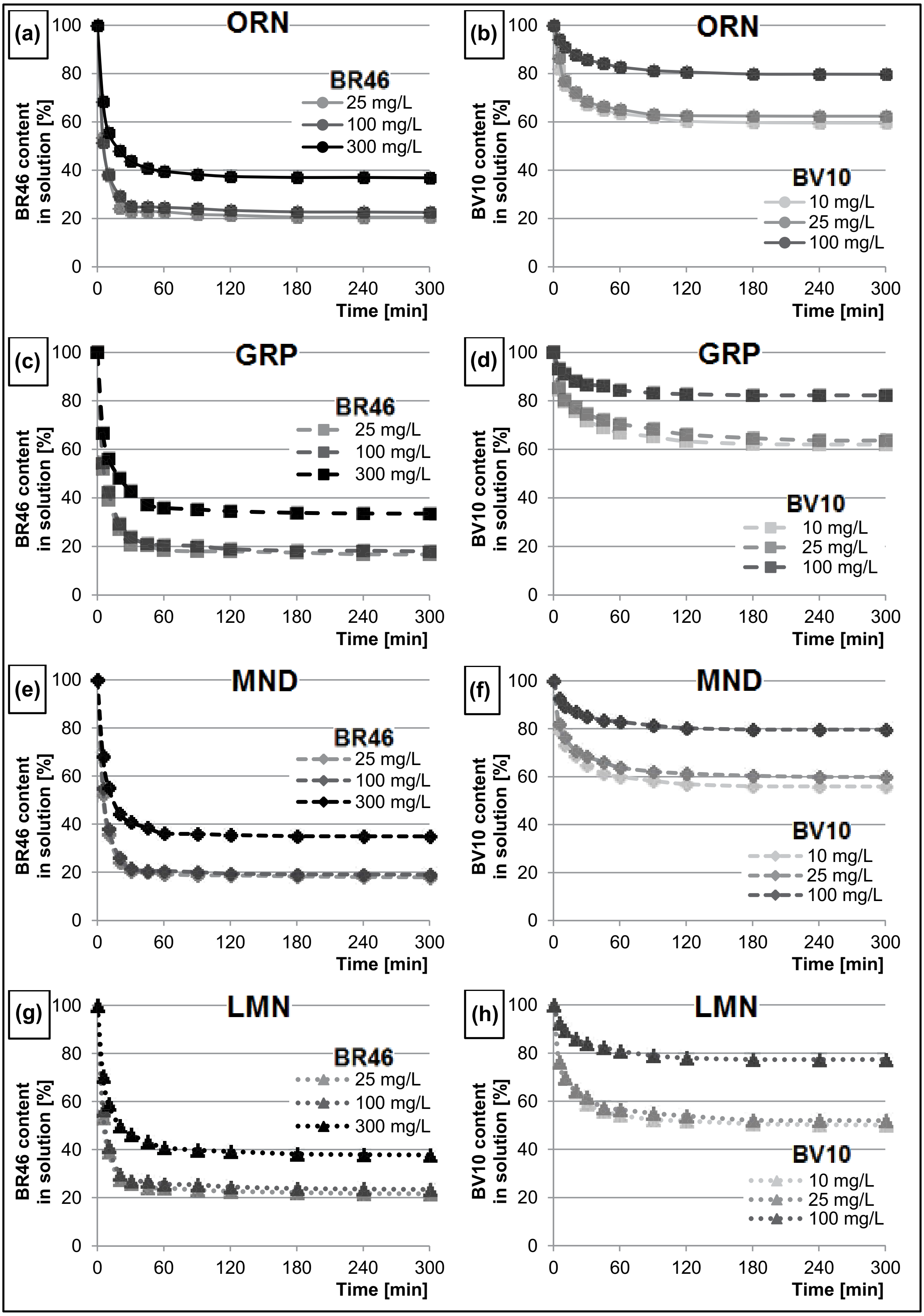


Fig. 3. Changes in concentrations of dyes in the solution during sorption: BR46 onto ORN (a), BV10 onto ORN (b), BR46 onto GRP (c), BV10 onto GRP (d), BR46 onto MND (e), BV10 onto MND (f), BR46 onto LMN (g), BV10 onto LMN (h). Temperature 22°C.

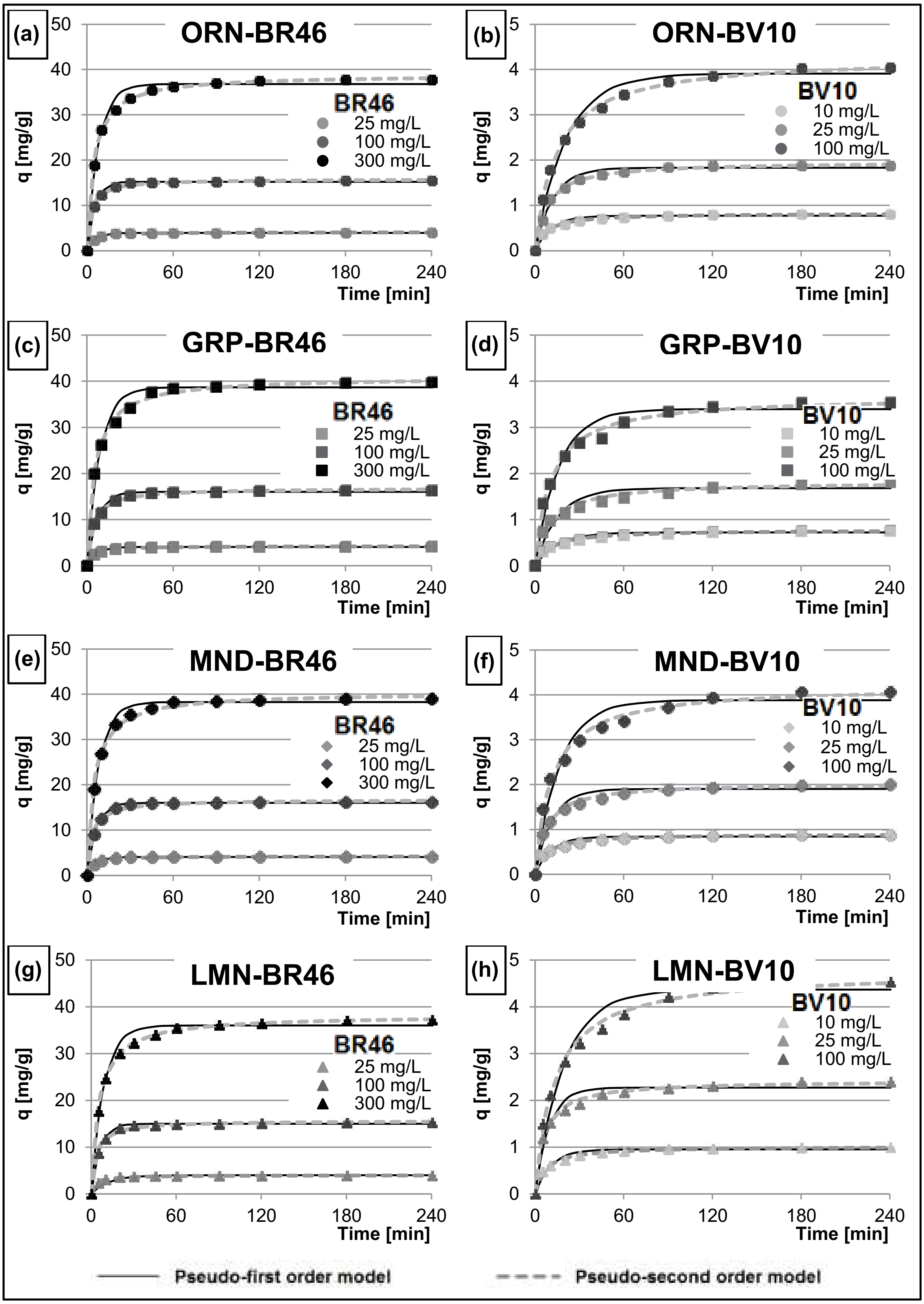


Fig. 4. Sorption kinetics of dyes: BR46 onto ORN (a), BV10 onto ORN (b), BR46 onto GRP (c), BV10 onto GRP (d), BR46 onto MND (e), BV10 onto MND (f), BR46 onto LMN (g), BV10 onto LMN (h). Pseudo-first-order model, pseudo-second-order model. Temperature 22°C.

Table 3
Kinetic parameters of dyes sorption on citrus peels, determined from pseudo-first and pseudo-second-order models

Sorbent	Dye	Sorption pH	Pseudo-first-order model			Pseudo-second-order model			Experimental data
			K_1	q_e	R^2	K_2	q_e	R^2	$q_{e,\exp}$
			(1/min)	(mg/g)	–	(g/mg*min)	(mg/g)	–	(mg/g)
ORN	BR46	25*	0.169	3.92	0.989	0.078	4.08	0.990	3.97
		100**	0.184	15.20	0.994	0.022	15.79	0.997	15.51
		300	0.124	36.79	0.985	0.005	38.86	0.999	37.88
	BV10	10	0.091	0.77	0.960	0.170	0.83	0.997	0.81
		25*	0.082	1.83	0.984	0.063	1.96	0.996	1.88
		100**	0.048	3.91	0.978	0.016	4.28	0.999	4.05
GRP	BR46	25*	0.151	4.08	0.990	0.063	4.26	0.997	4.17
		100**	0.139	16.03	0.988	0.014	16.82	0.997	16.45
		300	0.111	38.68	0.976	0.004	40.96	0.998	39.88
	BV10	10	0.066	0.72	0.948	0.130	0.78	0.991	0.76
		25*	0.064	1.68	0.920	0.053	1.83	0.981	1.82
		100**	0.062	3.39	0.958	0.026	3.67	0.993	3.55
MND	BR46	25*	0.166	4.05	0.993	0.073	4.22	0.997	4.11
		100**	0.155	16.01	0.992	0.017	16.71	0.998	16.24
		300	0.122	38.27	0.992	0.005	40.37	0.996	40.37
	BV10	10	0.092	0.84	0.951	0.161	0.90	0.993	0.89
		25*	0.087	1.90	0.956	0.066	2.04	0.996	2.02
		100**	0.059	3.88	0.954	0.021	4.21	0.993	4.07
LMN	BR46	25*	0.171	3.84	0.995	0.079	4.00	0.995	3.93
		100**	0.161	15.00	0.995	0.019	15.66	0.995	15.32
		300	0.112	36.03	0.982	0.005	38.22	0.999	37.37
	BV10	10	0.094	0.95	0.962	0.147	1.02	0.997	1.00
		25*	0.105	2.27	0.953	0.067	2.43	0.995	2.41
		100**	0.051	4.37	0.965	0.016	4.75	0.996	4.54

*/** – The same initial concentrations of dyes.

ORN, with a concentration of 25–300 mg/L, proved to be a relatively ineffective sorbent.

The highest affinity to BR46 was exhibited by MND ($K_C = 0.026$), which proved to be the most effective sorbent in points 4.1 and 4.2.

The sorption capacity of citrus peels against BV10 was about 10 times lower than against BR46 and reached: 5.03 mg/g for MND, 5.48 mg/g for ORN, 5.66 mg/g for LMN, and 4.63 mg/g for GRP. LMN besides the largest sorption capacity within the sorbents tested, was also characterized by the highest affinity to BV10 ($K_C = 0.046$). As in the case of BR46, the lowest affinity to BV10 was shown for ORN ($K_C = 0.031$) (Table 5).

Different sorptive capacities of citrus peels against BV10 and BR46 may result from different molecular weights of the dyes, from different sorption pHs, and also from different functional groups of these dyes, as explained in section 5.2. The lower sorption capacity of citrus skins against BV10, compared with BR46, may be due to a higher molecular weight of BV10, hindering penetration of the dye into active sites located in the deeper layers of the sorbent. The lower effectiveness of BV10 sorption may also result from the fact that is possesses an acidic group –COOH. The negative carboxyl group generating local charge may have impeded dye attachment to a sorbent having a general acidic character.

Table 6 shows the sorption capacities of various sorbents against Basic Red 46 and Basic Violet 10. The table presents the results of own research as well as literature data.

Citrus peel has a greater sorption capacity than such waste products from the agri-food industry as mango leaves, charred coconut fibers or used coffee beans (Table 6). In the case of BR46, the sorption capacity of citrus peel is higher than that of fir and beech sawdust (Table 6). Poorer sorptive properties of sawdust, despite the higher content of polysaccharides may result from the smaller surface area of sawdust and their compact structure.

The tested peel of citrus fruits exhibited a similar sorption capacity with respect to BR46 as sorbents based on activated carbons [32,34]. Exceptionally high sorptive abilities of citrus peels against BR46 may result from its loose structure that allowed the dye to penetrate into the sorption centers located in the deeper layers of the sorbent.

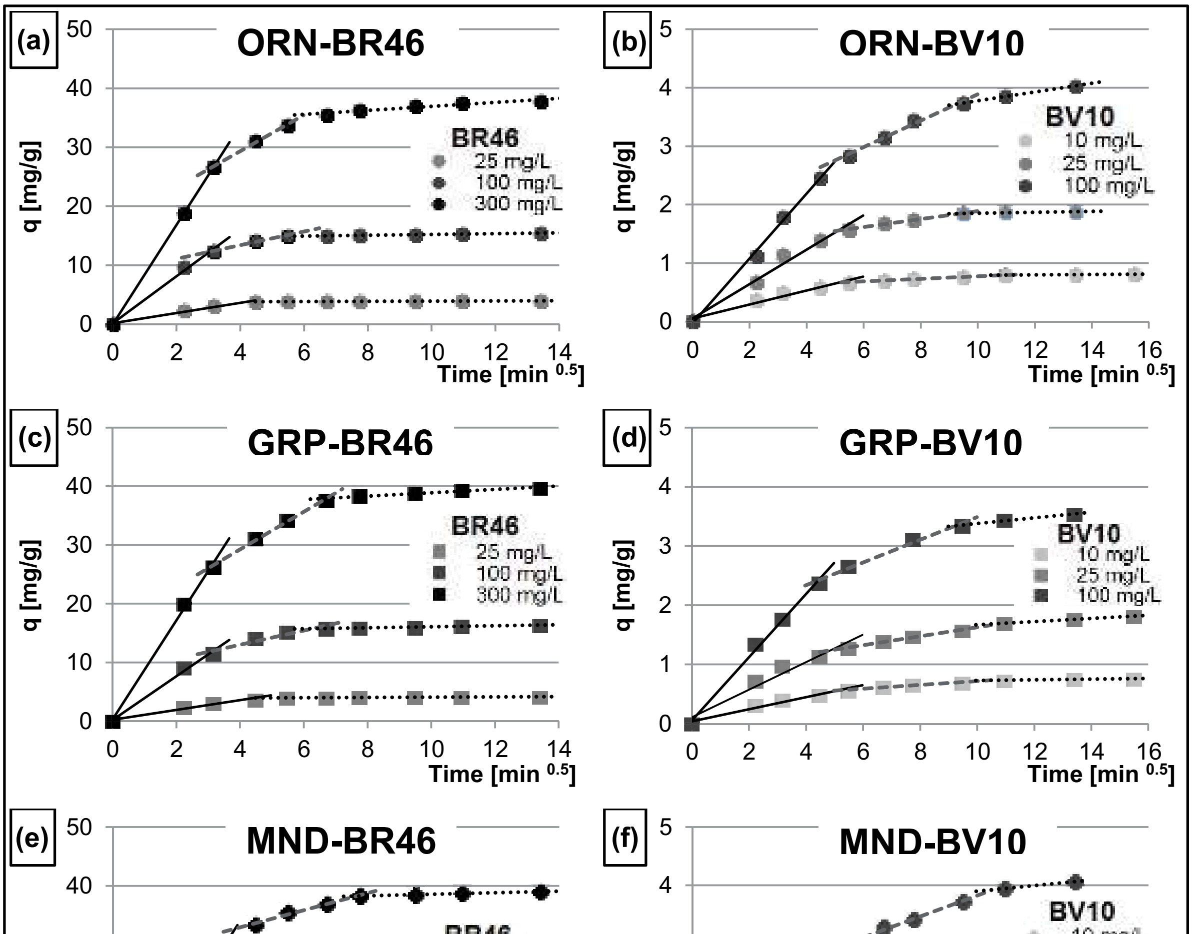


Fig. 5. Intraparticle diffusion model for the sorption of dyes: BR46 onto ORN (a), BV10 onto ORN (b), BR46 onto GRP (c), BV10 onto GRP (d), BR46 onto MND (e), BV10 onto MND (f), BR46 onto LMN (g), BV10 onto LMN (h). Temperature 22°C.

Table 4
Constants of dyes diffusion rate determined from a simplified model of intraparticle diffusion. Units – k_{d1}, k_{d2}, k_{d3} (mg*g^{-1}*min$^{-0,5}$), phase duration (min)

Sorbent	Dye	Concentration (mg/L)	First phase of sorption			Second phase of sorption			Third phase of sorption		
			k_{d1}	Duration (min)	R^2	k_{d2}	Duration (min)	R^2	k_{d3}	Duration (min)	R^2
ORN	BR46	25*	0.865	~20	0.978	–	–	–	0.016	~160	0.957
		100**	3.977	~10	0.993	1.156	~20	0.983	0.066	~150	0.989
		300	8.427	~10	0.999	3.065	~20	0.995	0.340	~150	0.902
	BV10	10	0.120	~30	0.958	0.021	~60	0.997	0.003	~150	0.925
		25*	0.295	~30	0.975	0.067	~60	0.991	0.007	~90	0.845
		100**	0.555	~20	0.997	0.226	~70	0.984	0.075	~90	0.997
GRP	BR46	25*	0.833	~20	0.964	–	–	–	0.021	~160	0.798
		100**	3.717	~10	0.992	1.201	~35	0.908	0.089	~135	0.963
		300	8.419	~10	0.997	3.206	~35	0.995	0.288	~135	0.921
	BV10	10	0.102	~30	0.966	0.033	~60	0.951	0.006	~150	0.891
		25*	0.232	~30	0.949	0.076	~60	0.981	0.027	~150	0.993
		100**	0.534	~20	0.994	0.192	~70	0.983	0.048	~90	0.973
MND	BR46	25*	0.872	~20	0.969	–	–	–	0.014	~160	0.884
		100**	3.945	~10	0.999	1.432	~20	0.966	0.047	~150	0.951
		300	8.505	~10	0.999	1.453	~40	0.981	0.130	~130	0.993
	BV10	10	0.127	~30	0.943	0.031	~60	0.921	0.007	~90	0.999
		25*	0.331	~20	0.979	0.079	~60	0.968	0.020	~100	0.999
		100**	0.588	~20	0.981	0.180	~60	0.987	0.048	~100	0.999
LMN	BR46	25*	0.829	~20	0.966	–	–	–	0.022	~160	0.871
		100**	3.746	~10	0.999	1.257	~20	0.935	0.084	~150	0.936
		300	7.818	~10	0.999	1.621	~40	0.988	0.283	~130	0.985
	BV10	10	0.148	~30	0.957	0.032	~50	0.963	0.009	~100	0.997
		25*	0.409	~20	0.959	0.077	~60	0.851	0.036	~100	0.999
		100**	0.637	~20	0.998	0.250	~60	0.996	0.053	~100	0.999

*/** – The same initial concentrations of dyes.

Table 5
Constants determined from Langmuir, Langmuir II, and Freundlich isotherms

Model	Constants	Basic Red 46				Basic Violet 10			
		ORN	GRP	MND	LMN	ORN	GRP	MND	LMN
Langmuir isotherm	$Q_{\max}$ (mg/g)	57.04	54.47	54.16	53.99	5.48	4.63	5.03	5.66
	K_C (L/g)	0.017	0.025	0.026	0.018	0.031	0.032	0.042	0.046
	R^2	0.9943	0.9826	0.9864	0.9895	0.9979	0.9969	0.9942	0.9967
Double Langmuir isotherm	$Q_{\max}$ ($b1 + b2$) (mg/g)	57.04	54.46	54.16	53.99	5.48	4.63	5.03	5.66
	b_1 (mg/g)	31.03	27.43	28.70	30.34	2.69	2.33	2.57	3.19
	b_2 (mg/g)	26.01	27.03	25.46	23.65	2.79	2.31	2.46	2.47
	k_1 (L/mg)	0.017	0.025	0.026	0.018	0.031	0.032	0.042	0.046
	k_2 (L/mg)	0.017	0.025	0.026	0.018	0.031	0.032	0.042	0.046
	R^2	0.9943	0.9826	0.9864	0.9895	0.9979	0.9969	0.9948	0.9967
Freundlich isotherm	N (L/g)	0.6008	0.5496	0.5564	0.5915	0.5906	0.5764	0.5422	0.5321
	K	2.3326	3.3398	3.1167	2.3093	0.3195	0.2907	0.3989	0.4844
	R^2	0.9703	0.9469	0.9466	0.9619	0.9707	0.9700	0.9650	0.9539

Table 6
Comparison of the BR46 and BV10 sorption results for different sorbents

Dye	Sorbent type	Capacity (mg/g)	pH	Sorption time (h)	Source
BR46	Active carbon from the *Cerbera* biomass	65.71	7	1.5	[32]
	Orange peel	57.04	6	4.0	This work
	Grapefruit peel	54.47	6	4.0	This work
	Mandarin peel	54.16	6	4.0	This work
	Lemon peel	53.99	6	4.0	This work
	Rape seed husks	49.00	8	0.5	[33]
	ROW 08 active carbon	45.00	8	1.0	[34]
	Ceramic clay	28.05	6	2.0	[35]
	Bone meal	24.56	6	1.5	[36]
	Fir sawdust	20.47	N.A.	2.0	[37]
	Beech sawdust	19.24	N.A.	2.0	[37]
BV10	Active carbon from the palm bark	30.00	3	N.A.	[38]
	Lemon peel	5.66	3	4.0	This work
	Orange peel	5.48	3	4.0	This work
	Mandarin peel	5.03	3	4.0	This work
	Grapefruit peel	4.63	3	4.0	This work
	Cedar cones	4.60	N.A.	6.0	[39]
	Mango leaves (powder)	3.30	N.A.	0.8	[12]
	Orange peel	3.20	4	N.A.	[40]
	Coal-fired coconut fiber	2.60	6.5	2.5	[41]
	Coffee powder	2.50	2	3.0	[42]
	Fly ash (from combined heat and power plant)	1.90	N.A.	72.0	[43]

5. Summary

Properly prepared citrus peels can be an effective sorbent for cationic dyes, representing an alternative to sorbents based on activated carbon. A prerequisite for a satisfactory effectiveness of sorption of pigments on citrus peels is the optimal pH value of the sorption procesess, which should be determined individually for each dye.

Sorption of dyes on citrus peels proceeds in three main stages, varying in intensity and duration. At the first most intense stage of the sorption process, lasting from 10 to 30 min, the amount of sorbed dye can range from 60% to 95% in relation to the weight of the dye after the equilibrium time (180–240 min).

The sorption capacity of the tested citrus peels against the tested dyes was similar. For example, the highest sorption capacity was obtained using orange peels (Q = 57.04 mg BR46/g) and was by only 5.6% higher than the lowest sorption capacity obtained on lemon peels (Q = 53.99 mg BR46/g). This is a promising finding for potential users of the technology involving the use of citrus peels as a sorbent. As the filling of the adsorber, it will be possible to use the cheapest or the most available raw material on the market, without fear of a major decrease in the effectiveness of sewage decolorization process.

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