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Adsorption of diclofenac sodium from aqueous solutions on commercial activated carbons

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ABSTRACT

The research presented in this paper aimed to evaluate the possibility of using commercial activated carbons currently used in water treatment plants (WG-12, ROW 08 Supra, *F*-300) to remove diclofenac sodium, a drug belonging to the group of non-steroidal anti-inflammatory drugs. The kinetics and statics of diclofenac adsorption from solutions of different pH and temperature were studied. The results were described by kinetics equations: pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion model. The highest correlation coefficients were obtained for Elovich (R^2 0.9937 – 0.9978) and pseudo-second-order models (R^2 0.9885 – 0.9935). The highest adsorption rate was observed for the activated carbon *F*-300 (k_2 = 0.0147 h^{-1}), whereas its lowest values were found for ROW 08 Supra (k_2 = 0.0088 h^{-1}). Adsorption statics was analyzed based on solutions with a concentration of 159–1272 mg/L, pH 6, 8, and 10, and temperatures of 20°C, 30°C, and 40°C. Examinations of isotherms of adsorption on activated carbons WG-12, ROW 08 Supra, and *F*-300 revealed that the lower pH and the higher temperature in the analyzed range, the higher adsorption of the compound tested. The highest adsorption capacities q_m were obtained after adsorption from the solution with pH = 6 and were 107.91 mg/g for *F*-300, 90.41 mg/g for ROW 08, and 88.97 mg/g for WG-12. The adsorption from the solution with pH 10 was much lower: 91.30 mg/g for *F*-300, 70.79 mg/g for ROW 08, and 58.54 mg/g for WG-12. Increasing the solution temperature from 293 K to 313 K caused an increase in the monolayer capacity from 88.97 to 115.29 mg/g for WG-12 carbon, from 90.41 to 145.45 mg/g for ROW 08 and from 107.91 to 147.88 mg/g for *F*-300 coal. Diclofenac sodium was best adsorbed on the activated carbon *F*-300, whereas the poorest adsorption was found for WG-12. The effect of chemical surface structure on the effectiveness of diclofenac sodium adsorption was also observed. The adsorption of sodium diclofenac results from the net force of electrostatic repulsion and attraction forces and hydrogen bonds (H-bonds) and electron donor-acceptor (p–p EDA) interactions. Based on the Langmuir R_L and Freundlich 1/*n* isothermal coefficients, it can be stated that diclofenac sodium adsorption is beneficial for all activated carbons. Among the models used (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich) the study results are best described by Langmuir and Freundlich models.

Keywords: Diclofenac sodium; Activated carbon; Adsorption

1. Introduction

The pharmaceutical sector is one of the areas of industry that are developing most dynamically. The production and consumption of pharmaceuticals and personal care products (PPCP) have been steadily increasing. This leads to environmental pollution by these substances. The most common pollutants in the aquatic environment are drugs from the following groups: non-steroidal anti-inflammatory drugs (NSAIDs) [1,2], antibiotics [3], estrogens [4], beta-blockers

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[5], lipid metabolism regulators [6], and antiepileptic drugs [7]. These drugs are used in medicine, veterinary medicine, animal husbandry, and are therefore transferred from very different sources to the environment [8–11]. Along with wastewater from households, health centers, hospitals, and outpatient clinics, they reach wastewater treatment plants and, with sewage after treatment, to surface water. Due to the use of these substances in livestock farming, they are transported with an example, manure to the ground and next to surface water or groundwater. Another source is fish farming, which causes the introduction of medicines directly into the water.

An important problem is over-the-counter (OTC) drugs used in large quantities. These include NSAIDs such as ibuprofen, naproxen, and diclofenac. Due to the wide use of an anti-inflammatory, analgesic, and antipyretic drugs, their consumption is high. This leads to their presence in surface waters, often in fairly high concentrations: diclofenac (931 ng/L) [12], ibuprofen (261 ng/L) [13], and naproxen (100 ng/L) [14]. Furthermore, despite the lack of regular monitoring of these compounds, the following pharmaceuticals have been also identified in drinking water: diclofenac (35 ng/L) [15], ibuprofen (3 ng/L) [16], and naproxen (13 ng/L) [14]. A study of water in European rivers waters found diclofenac and ibuprofen in 83% and 35% of the samples, respectively [17].

The presence of pharmaceuticals in the surface water is mainly due to their incomplete removal in sewage treatment plants. The degree of removal of pharmaceuticals depends on the structure and properties of each pharmaceutical, its concentration, the processes used in sewage treatment plants, and the way they are conducted. Among NSAIDs, paracetamol is well-removed (100%) [18], whereas ibuprofen removal ranges from 53% [19] to 99% [20]. Diclofenac is removed much less frequently, with studies documenting values from 17% [21] to 75% [22]. Diclofenac has been found in treated wastewater in the European Union at concentrations ranging from 140 to 1,480 ng/L (samples were taken in five EU countries) [23].

Pharmaceuticals belonging to the NSAID group are characterized by relatively low toxicity to humans. It was found that about 75% of used diclofenac is discharged to water or soil [24]. However, a potential risk to the environment from the presence of example, diclofenac has been demonstrated. It is believed that the selective toxicity of diclofenac has led to a decline in the vulture population on the Indian subcontinent [25]. The drug has the highest acute toxicity among NSAIDs for phytoplankton and zooplankton. It exhibits chronic toxicity to phytoplankton and benthos. Long-term exposure of rainbow trout to diclofenac causes renal damage and changes in gills [26–28]. The problem of diclofenac presence in surface waters is related to its accumulation in bottom sediments [29]. Diclofenac was identified in 10 out of 27 samples taken from rivers in Cologne, Germany [30]. It was also found in surface waters of Finland (15 ng/L [31] and 302 ng/L [32]), Italy (13 ng/L [33] and 675 ng/L [34]), (France –35 ng/L [35] and 300 ng/L) [36], Spain (313 ng/L [15] and 650 ng/L [37]), and Czech Republic (841.5 ng/L) [38], Germany (370 ng/L [39] and 2100 ng/L [24]), Greece (1.04 ng/L [40] and 457 ng/L [41]), Hungary (931 ng/L [12]), Portugal (3200 ng/L [42]), and Sweden (209 ng/L [43]). Diclofenac has been identified in drinking water from private households in Germany at a concentration of 10 ng/L [29], but also in water mains samples at a concentration of 35 ng/L [15]. The problem also applies to other countries. Diclofenac was determined in drinking water in Poland (4 ng/L) [44], in the Czech Republic (3.9 ng/L) [45] and Canada (6 mg/L) [16]. It is believed that the presence of PPCPs in waters even at very low concentrations may adversely affect human health [46,47].

The significance of the problem of water pollution by pharmaceuticals is confirmed by the fact that the European Commission added diclofenac to the list of compounds whose concentration in EU waters should be monitored (January 2012; Annex of Directive 2000/60/EC of European Parliament and the Council on priority substances in the field of water policy, Brussels 31 January 2012; 2011). Currently, diclofenac is listed in a watch list of substances for Union-wide monitoring of surface waters specified in the Decision (EU) 2015/495 [48].

The presence of diclofenac in drinking water is a consequence of the pollution of surface water and some groundwater by this compound. Conventional water treatment plants do not fully remove diclofenac. The methods used to remove diclofenac from water or sewage effectively include activated sludge adsorption, biodegradation, photolysis, membrane processes, ozone disinfection (ozonation), and combined O_3/H_2O_2 method, and adsorption [2]. Although effective, advanced ozonation methods can be not only expensive but also hazardous. This method accelerates the formation of most of the unknown intermediate ozonation products, often more toxic than the initial compounds [49]. Adsorption is a very effective and relatively inexpensive method and it does not cause secondary water pollution. Therefore, adsorption is now quite widely analyzed in the context of the removal of pharmaceuticals, including diclofenac [50–53]. Studies have the most frequently analyzed activated carbons differing in porous structure and chemical structure of their surface and the effect of these parameters on the adsorption efficiency [50,54,55]. Another direction is the search for carbon sorbents from waste materials [51,56–59]. Furthermore, studies have evaluated the effect of the conditions of the adsorption process (pH and temperature of the solution, the effect of the dose and process time) [54,59].

The aim of this study was to evaluate the effectiveness of diclofenac sodium adsorption on three types of commercial activated carbon used in water treatment plants, depending on the pH and temperature of the solution and the dose of the adsorbent. The results of the research will be described using different models of adsorption kinetics and statics.

2. Methodology

2.1. Activated carbons

Three granulated activated carbons were used in the study: WG-12 (Gryfskand, Poland), *F*-300 (Chemviron Carbon), and ROW 08 Supra (Norit). These were activated carbons with a large specific surface area and improved adsorption properties compared to the test substances (Table 1). Examinations of the specific surface area were performed based on low-temperature nitrogen adsorption at 77 K using a Micromeritics' ASAP 2010 system, whereas

the surface area was calculated according to the standard BET (Brunauer-Emmett-Teller) [60] method using nitrogen adsorption isotherms at 77 K. The pore size was evaluated by means of the Horvath-Kawazoe method [61]. Total acidic and basic group content was evaluated by means of titration (acidic group—NaOH, basic group—HCl) [62]. Next, 25 cm^3 of 0.1 M HCl or NaOH was poured into a weighed carbon amount of 0.5 g, shaken 48 h, after which the solution from above the carbon (filtrate) was titrated with 0.05 M NaOH or HCl using methylene red. Determination of acid and alkaline functional groups is important in explaining the mechanisms of adsorption and has been performed by many authors dealing with diclofenac adsorption [50,51,55]. Elemental analysis of C, H, and N content was performed in the Vario Macro apparatus (Elementar Analysensysteme GmbH).

The Fourier-transform infrared spectroscopy (FTIR) transmission spectra were determined using the Perkin–Elmer Spectrum 2000 FTIR spectrometer. FTIR spectra measurements have been used to characterize the chemical structure of the surface by many researchers [55–57]. The measurements were performed using pastilles made of a mixture of activated carbon and KBr (1:300). In order to eliminate moisture, the pastilles were dried and desorbed at a pressure of 10–2 Pa. The FTIR examinations were carried out in infrared radiation in the range of 4,000 – 400 cm^{-1} wave numbers at a scanning speed of 0.2 cm/s [63].

2.2. Measurement of diclofenac sodium adsorption

Diclofenac sodium $C_{14}H_{10}Cl_2NNaO_2$ (Sigma Aldrich) was used in the study. Concentrations were determined by means of the spectrophotometric method used by many authors (λ = 267 nm) [51,52,54]. Properties of diclofenac sodium are shown in Table 2.

2.3. Measurements of adsorption kinetics and statics

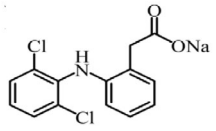
Examinations of adsorption kinetics were conducted from solutions of 318 mg/L (1 mmol/L) and volume of 0.250 L to which 1 g of activated carbon (4 g/L) was added and mixed. The measurements were carried out for 10 h, with the analysis of concentrations performed after 0.5, 1 h, and then every 1 h. The results were described by kinetics equations: pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion model (Weber–Morris) [65]. These equations have been often used to describe the kinetics of adsorption of various pharmaceuticals [51,59,67].

Measurements of the effect of adsorbent dose on the effectiveness of adsorption were conducted for the initial

Table 1
Physical and chemical properties of activated carbons [64]

Parameter	Activated carbons		
	ROW 08	*F*-300	WG-12
Surface area, m^2/g	897 ± 30	847 ± 29	1,034 ± 37
$V_{micr,}$ cm^3/g	0.436	0.476	0.524
$V_{meso,}$ cm^3/g	0.453	0.294	0.066
$V_{total,}$ cm^3/g	1.135	0.987	0.995
Water absorption, cm^3/g (PN-85/C-97555)	0.97	0.72	0.61
pH of water extract (PN-85/C-97555)	6.67	7.15	6.62
Methylene blue number, LM (PN-82/C-97555.03)	34	31	28
Iodine adsorption, LI, mg/g (PN-EN 12902)	1091	1055	1,117
Total acidic group, A, mmol/g	0.672	0.350	0.675
Total basic group, B, mmol/g	0.580	0.660	0.288
Elementary composition,%			
C	80.05	85.25	79.00
H	1.419	0.771	1.252
N	0.932	0.725	0.813

Table 2
Physical and chemical properties of diclofenac sodium [50,52]

Molecular structure	Molecular formulae	Molecular weight, g/mol	Solubility g/L	logK_{ow}	pKa	Surface area, nm^2	Molecular size, nm
	$C_{14}H_{10}Cl_2NNaO_2$	318.1	4.82	0.7	4.15	0.52	0.97 × 0.98

concentration of 318 mg/L. The following doses of adsorbents were analyzed: 1, 2, 4, 6, 8, 10, and 12 g/L.

Adsorption isotherm measurements were performed for solutions with a concentration of 159–1,272 mg/L (0.5–4 mmol/L). All results represent the mean of three measurements. Similar concentrations were used in studies by other authors [54]. Models used to describe the results obtained included: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich. Furthermore, using the constant from the Langmuir equation, separator factor R_L was calculated [66]. The process was conducted for solutions with pH 6, 8, and 10, and at temperatures of 293°K, 303°K, and 313°K. At lower pH levels, diclofenac sodium is poorly soluble and precipitated. The constants of the adsorption kinetics and adsorption isotherm equations were determined from nonlinear forms using the Levenberg-Marquardt algorithm [68]. This algorithm was implemented by the scipy.optimize.curve_fit function, which is part of the SciPy library for the Python programming language.

3. Results

3.1. Kinetics of diclofenac sodium adsorption

In order to determine the time needed to achieve equilibrium, the kinetics of diclofenac sodium adsorption on activated carbons *F*-300, WG-12, and ROW 08 was analyzed. It was assumed that the time to the achievement of the adsorption equilibrium occurs when the change in concentration during 1 h is <0.5% of the initial concentration (Fig. 1). For all activated carbons, the time needed to determine the adsorption equilibrium was 9 h. In further examinations, in order to ensure the equilibrium, the diclofenac sodium solution with activated carbon was mixed for 10 h and then left unmixed for 14 h. Similar contact time of activated carbon with diclofenac sodium solution was used by Bhadra et al. [55].

Adsorption kinetics was described using the four kinetics equations: pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris), Elovich (Table 3). High correlation coefficients, R^2 were obtained for the carbon model of pseudo-second-order kinetics (R^2 0.9885 – 0.9935) and Elovich (R^2 0.9937 – 0.9978). Elovich's model describes chemisorption on a heterogeneous surface. High values of the correlation coefficient, R^2 indicate that the chemisorption process has an effect on the adsorption rate. Equally high correlation coefficients were obtained using the pseudo-second-order equation. This model is the most frequently used by researchers to describe adsorption kinetics, often as the only one [50,54,55]. Significantly lower correlation coefficients were obtained for the pseudo-first-order equation. Similar results have been documented by other authors [51,59,67]. According to many authors, a better fit of the PSO model compared to the PFO indicates that chemical adsorption is an important factor controlling the speed of this process. According to Ahmed et al. [69], this model shows that the adsorption capacity is proportional to the number of active locations. Płaziński and Rudziński [70] argue that drawing conclusions about the nature of adsorption based on PFO (pseudo-first-order equations) and PSO (pseudo-second-order equations) models (2011) is erroneous because these models are empirical [70].

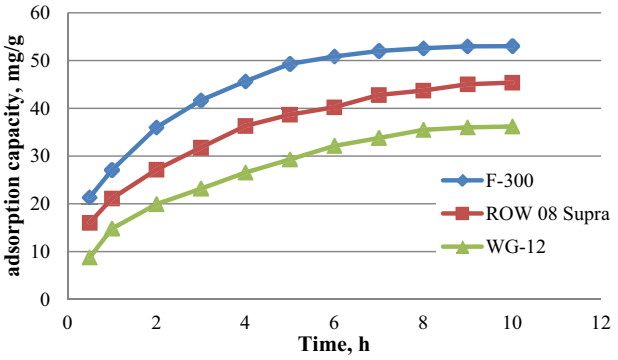


Fig. 1. Kinetics of adsorption of diclofenac sodium on commercial activated carbons: WG-12, ROW 08 Supra and *F*-300.

The evaluation of the fit of the intraparticle diffusion model (Weber–Morris) to the results of the study revealed a non-linear pattern of this process. Lower correlation coefficients compared to other models point to two or three separate process stages (e.g., external and intergranular diffusion). The long time to achieve equilibrium (9 h) indicates that internal diffusion may be the dominant stage [71]. Analysis of the k_2 coefficient (Table 3) that characterizes the adsorption rate leads to the conclusion that diclofenac sodium adsorption occurs the fastest on activated carbon *F*-300 and the slowest on WG-12.

3.2. Isotherms of diclofenac sodium adsorption on commercial activated carbons

The activated carbons used in the study are used in water treatment plants. The aim of adsorption statics studies is to evaluate the opportunities of using activated carbons to remove such specific pollutants as diclofenac sodium. The adsorption of diclofenac sodium from solutions with pH 6, 8, and 10 correspondings to the drinking water range (pH = 6.5 – 9.5) was also analyzed (Fig. 2).

For all carbon sorbents, an increase in pH of the water caused a decrease in the adsorption of the pharmaceutical studied. Diclofenac sodium occurs in a dissociated form (pH = 6, dissociation 99%, pH = 8 dissociation 99.9%). Since it occurs in the form of anions, an increase in pH of the solution leads to the rise in the number of competitive OH^- ions. Furthermore, in alkaline solutions, weak acid groups (COO– and O–) are dissociated on the surface of activated carbons. Therefore, repulsive interactions between the negatively charged surface and the adsorbate anions may become a significant factor. Decreased adsorption efficiency with increased pH was also observed by other researchers [51,55,67,72]. Dissociation of basic weak functional groups on the carbon surface and electrostatic attraction between these groups and diclofenac sodium anions is possible in acid solution (pH = 6). An increase in the pH of the solution reduces the adsorption, but even in a solution with pH = 10, the obtained adsorption capacities are quite high. This proves the presence, besides electrostatic interactions, of other forces responsible for adsorption. These may be hydrogen bonds (H-bonds) between phenol groups on the surface of activated carbon and carboxyl group of diclofenac sodium [55].

Table 3
Constant equations of adsorption kinetics of diclofenac sodium: pseudo first-order, pseudo second-order, Elovich, and intraparticle diffusion model (Weber–Morris)

Nonlinear form	Parameter	*F*-300	ROW 08 Supra	WG-12
Pseudo-first-order				
$\frac{dq_t}{dt} = k_1(q_e - q_t)$	q_{max} (mg/g) is the amount of solute adsorbed et equilibrium and q_t is the amount of solvent adsorbed at time t	51.64	43.50	36.25
	k_1 (h^{-1}) is the rate constant for the pseudo-first-order kinetic model	0.6796	0.5305	0.3822
	R^2 is the correlation coefficient	0.9758	0.9672	0.9823
Pseudo- second- order				
$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	q_{max} (mg/g) is the amount of solute adsorbed at equilibrium and q_t is the amount of solvent adsorbed at time t	59.54	51.51	45.30
	k_2 (h^{-1}) is the rate constant for the pseudo-second-order kinetic model	0.0147	0.0125	0.0088
	R^2 is the correlation coefficient	0.9935	0.9885	0.9926
Elovich				
$\frac{dq_t}{dt} = \alpha e^{-\beta q t}$	α [mg/(g h)] is the initial adsorption rate	117.09	61.64	26.64
	β (g/mg) is reflected the number of sites available for adsorption	0.0826	0.0868	0.0853
	R^2 is the correlation coefficient	0.9937	0.9978	0.9970
Intraparticle diffusion model (Weber–Morris)				
$q_t = k_p t^{0.5} + C$	K_p [mg/(g $h^{0.5}$)] is the slope which refer to intra-particle diffusion rate constant	16.050	13.898	11.820
	C (mg/g) is the intercept which is a constant related to the thickness of the boundary layer	9.211	5.514	1.8427
	R^2 is the correlation coefficient	0.9199	0.9632	0.9839

Electron donor-acceptor (p–p EDA) interactions between the surface of activated carbon (p donor) and the aromatic ring of sodium diclofenac (p acceptor) may also be responsible for adsorption under these conditions [56].

Evaluation of the activated carbons used due to their adsorption capacity with respect to diclofenac sodium, they may be ranked in the following order: *F*-300 > ROW 08 Supra > WG-12. This order does not coincide with the order of compounds due to the specific surface area or pore volume (total, micropores, and mesopores; Table 1). This leads to the conclusion that physical adsorption is not critical for the removal of diclofenac on activated carbon. In order to evaluate the effect of the chemical character of the surface on the adsorption of diclofenac sodium, FTIR spectra were analyzed and the number of oxygen groups was evaluated using the Boehm method (Table 4). It can be concluded that these carbons have similar amounts of acidic (from 0.434 mmol/g for ROW 08 Supra to 0.586 mmol/g for WG-12) and alkaline (from 0.467 mmol/g for WG-12 to 0.592 mmol/g for ROW 08 Supra) groups. The simultaneous presence of acidic and alkaline groups on the surface of activated carbons is characteristic of the sorbents produced by the steam-gas method. It can be noted that activated carbon WG-12, characterized by the lowest sorption properties with regard to diclofenac sodium, has the lowest number of alkaline groups capable of exchanging anions. At the same time, it has the largest number of acid groups, which in the alkaline environment dissociate and give the surface of activated carbon a negative charge. Repulsion occurs mainly between carboxyl groups, which are the most common on the surface of activated carbon WG-12 and diclofenac anions. Furthermore, there are the fewest phenol groups on the surface of this carbon which can form hydrogen bonds with diclofenac sodium. Although activated carbon WG-12 has the largest specific surface area among the adsorbents studied, it represents the weakest diclofenac sodium adsorbent due to the importance of chemical surface structure. However, analysis of the chemical structure of the two remaining activated carbons (*F*-300 and ROW 08 Supra) shows that it is not possible to determine simple connections between adsorption capacity and the number of groups on the surface of activated carbons determined using the Boehm method. Activated carbon ROW 08 Supra has fewer acid groups and more alkaline groups but it adsorbs less diclofenac sodium than *F*-300. However, with such small differences in the chemical structure of the surface of activated carbons, the porous structure and the availability of active locations may also be critical.

The inaccuracies of the Boehm method used should also be emphasized. Therefore, FTIR spectra of the analyzed activated carbons were compared (Fig. 3). Activated carbon *F*-300 adsorbing the largest amounts of diclofenac sodium is characterized by the highest intensity of the

spectra of O–H phenolic groups forming hydrogen bonds (3,200–3,500 cm^{-1}). Lower intensity of spectra of carbonyl groups >C=O (1,740 – 1,500 cm^{-1}) and ester groups C–O–C (1,300 – 1,000 cm^{-1}) was found on *F*-300 coal compared to activated carbon ROW 08 Supra. Only for activated carbon WG-12 a small peak of carboxyl groups (1,732 cm^{-1}) was observed. Therefore, the conclusions of Bhadra et al. [55] that the formation of hydrogen bonds between diclofenac sodium and phenol groups on the surface of activated carbon is essential can be confirmed.

Four models of adsorption isotherms were used to describe the obtained results: Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich (Table 5).

In most cases, the highest value of the correlation coefficient was found during the description of the results obtained with the Langmuir equation ($0.9699 < R^2 < 0.9921$). The value of the partition coefficient R_L for all activated carbons and the tested pH of solutions ranged from 0.02 to 0.36. Since this coefficient was between 0 and 1, it was found that adsorption in the range of concentrations studied was beneficial. This conclusion is confirmed by the calculated *n* coefficient of Freundlich isotherm. The values of this coefficient (Table 4) for all commercial activated carbons are similar and range from 1 to 10, indicating favorable adsorption of diclofenac sodium. The value of 1/*n* indicates the degree of diversity of active locations on the surface of activated carbon. The values of 1/*n* (from 0.2294 to 0.2779) are similar for all activated carbons used in the study. Since they are closer to zero than to unity, it can be concluded that the surface inhomogeneity of the sorbents studied is rather low. K_F coefficient ranges from 26.02 (*F*-300, pH = 6) to 9.17 mg/g (WG-12, pH = 10). The values of the correlation coefficient, R^2 for this isotherm are

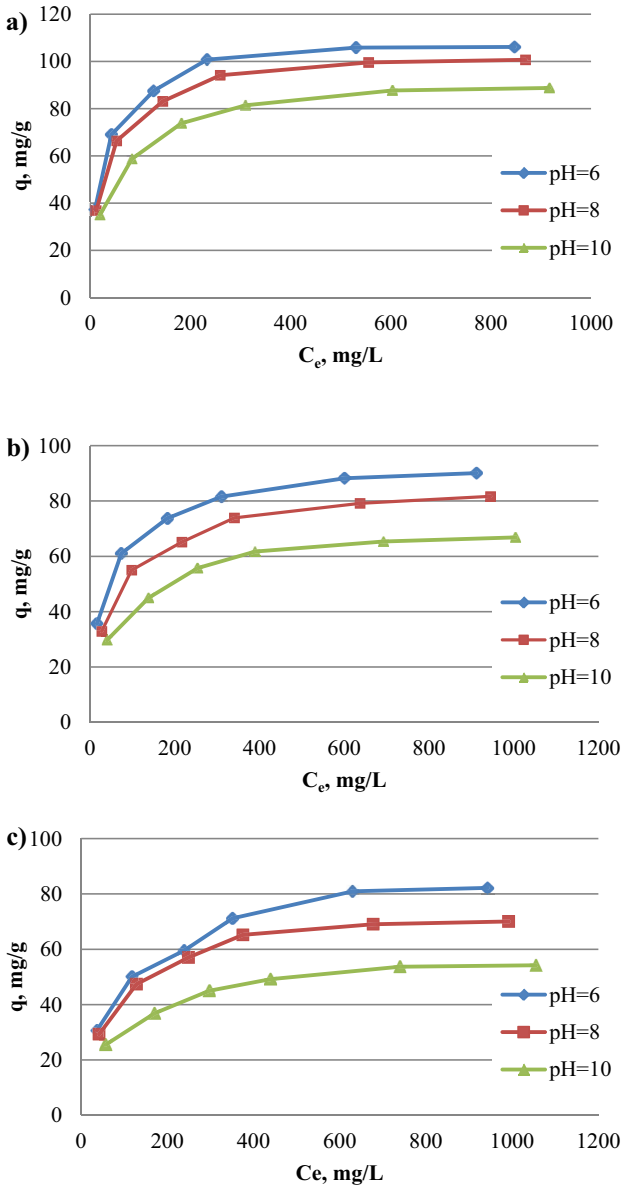


Fig. 2. Diclofenac sodium adsorption isotherms on activated carbon: (a) *F*-300, (b) ROW 08, and (c) WG-12.

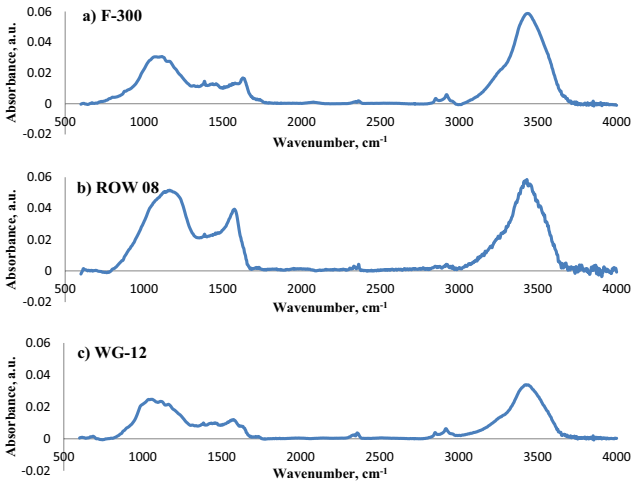


Fig. 3. FTIR spectra for the initial and modified activated carbon: (a) *F*-300, (b) ROW 08 Supra, and (c) WG-12.

Table 4
Number of surface functional groups on initial activated carbons: WG-12, ROW 08 Supra, and *F*-300 determined by the Boehm method

Activated carbon	Surface functional groups, mmol/g					
	Carboxylic groups	Lactonic groups	Phenolic groups	Carbonyl groups	Acidic groups	Basic groups/ sites
WG-12	0.182	0.209	0.110	0.085	0.586	0.467
ROW 08 Supra	0.063	0.120	0.409	0.021	0.434	0.592
F-300	0.138	0.048	0.316	0.060	0.544	0.512

Table 5
Equations and constants for diclofenac sodium adsorption isotherms: Freundlich, Langmuir, Dubinin–Radushkevich adsorption, and Temkin

Nonlinear form	Parameter	pH		*F*-300	ROW 08 Supra	WG-12
Freundlich						
$q = K_F C_e^{\frac{1}{n}}$	$1/n$, adsorption intensity; K_F, mg/g is the Freundlich isotherm constant; C_e, mg/L is the equilibrium concentration; R^2 is the correlation coefficient	6	$1/n$	0.2294	0.2294	0.3114
			K_F	26.015	20.771	10.688
			R^2	0.9047	0.9418	0.9684
		8	$1/n$	0.2319	0.2551	0.2779
			K_F	23.797	15.614	11.484
			R^2	0.916	0.9405	0.9287
		10	$1/n$	0.2441	0.2583	0.2673
			K_F	18.779	12.29	9.1745
			R^2	0.937	0.9454	0.9565
Langmuir						
$q = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_m, mg/g is the solid phase concentration corresponding to the complete monolayer coverage of adsorption sites; K_L, L/mg is the constant related to the free energy of adsorption; R^2 is the correlation coefficient; R_L is the separator factor $R_L = \frac{1}{1 + K_L C_0}$	6	q_m	107.91	90.41	88.97
			K_L	0.0472	0.0329	0.0114
			R^2	0.9836	0.9754	0.9699
			R_L	0.02–0.13	0.02–0.16	0.06–0.36
		8	q_m	102.14	84.19	75.54
			K_L	0.0402	0.0204	0.0141
			R^2	0.9839	0.9854	0.9921
			R_L	0.02–0.16	0.04–0.24	0.05–0.31
		10	q_m	91.30	70.79	58.54
			K_L	0.0265	0.0155	0.0118
			R^2	0.9802	0.9814	0.9830
			R_L	0.03–0.19	0.05–0.29	0.06–0.35
Dubibin-Radushkevich						
$q = q_\varepsilon \exp(-K_D \varepsilon^2)$	q_s, mg/g is a constant in the Dubinin–Radushkevich isotherm model which are related to adsorption capacity; K_D, mol²/kJ² is a constant in related to the mean free energy of adsorption; ε is the Dubibin–Radushkevichishoterm constant, $\varepsilon = RT\ln(1 + 1/C_e)$; R^2 correlation coefficient	6	q_s	95.49	80.08	71.25
			K_D	0.00002	0.00004	0.0002
			R^2	0.7876	0.7875	0.7215
		8	q_s,	90.25	72.68	63.85
			K_D	0.00002	0.0001	0.0003
			R^2	0.7912	0.7984	0.8291
		10	q_s,	79.45	60.46	49.39
			K_D	0.00006	0.0002	0.0004
			R^2	0.7784	0.7856	0.7881
Temkin						
$q = B \ln A_T C$	A, L/mg is the Tempkin isotherm equilibrium binding constant; B is the Tempkin isotherm constant; R^2 is the correlation coefficient	6	A	1.6157	0.9935	0.1719
			B	15.761	13.792	16.697
			R^2	0.9562	0.9832	0.9857
		8	A	1.2859	0.4564	0.2562
			B	15.244	14.000	13.374
			R^2	0.9653	0.9815	0.9665
		10	A	0.6994	0.3268	0.2204
			B	14.483	12.078	10.393
			R^2	0.9745	0.9722	0.9792

high ($0.9047 < R^2 < 0.9684$), However, the interpretation of the obtained Freundlich isothermal constants is consistent with the conclusions resulting from the calculated Langmuir isotherm constants.

High correlation coefficients, R^2 for Langmuir isotherm reflect monolayer adsorption of diclofenac sodium on activated centers. The monolayer capacities calculated from the Langmuir equation are the highest for activated carbon *F*-300 and range from 91.3 (pH = 10) to 107.9 (pH = 6). The lowest q_m values were obtained in the case of the use of activated carbon WG-12 (from 58.54 for pH = 10 to 88.97 mg/g for pH = 6).

The second isotherm in terms of fitting the study results was the Temkin model (R^2 from 0.9562 to 0.9857). It assumes, similar to the two previous isotherms, that the adsorption is of monolayer character. Similarly to Freundlich's isotherm, the second assumption of this isotherm is the heterogeneity of the surface. However, the Langmuir's isotherm describing the diclofenac sodium adsorption also assumes homogeneity of the surface. These results may indicate small differences in the adsorption potential of the surface of the analyzed activated carbons.

The fourth of the analyzed the Dubinin–Radushkevich adsorption isotherm, assuming volumetric filling of micropores, was characterized by low values of the correlation coefficient. This leads to the conclusion that despite the relatively large size of the molecule of diclofenac sodium (about 0.9 nm) compared to the volume of micropores (below 2 nm), the phenomenon of volumetric pore filling was not decisive in the adsorption process.

3.2. Impact of process conditions

The effect of adsorbent dose and solution temperature on all activated carbons used in the study was analyzed (Figs. 4 and 5). The effect of adsorbent dose was analyzed for diclofenac sodium concentration of 318 mg/L and adsorbent doses from 1 to 12 mg/L. Similar doses were used by other researchers: Larous and Meniai [51] – 5 g/L, de Luna et al. [67]—from 5 to 25 g/L, Jodeh et al. [72]—from 2 to 14 g/L. The applied amounts of activated carbon WG-12 allowed for removing diclofenac sodium from 21% (dose 1 g/L) to nearly 90% (dose 12 g/L; Fig. 5). For activated carbon *F*-300, the efficiencies were much higher and ranged from 31 to over 97%. In case of this carbon the dose of 6 g/L allowed for exceeding 90% of adsorption efficiency, and for activated carbon ROW 08 Supra such an effect was obtained for the dose of 8 g/L. For activated carbons, *F*-300 and ROW 08 Supra, increasing the dose from 8 to 12 g/L leads to only a slight increase in adsorption (max. 5%).

The effect of temperature on the results of diclofenac sodium was also analyzed (Fig. 6) and Langmuir isotherms were determined. The examinations were carried out from solutions at temperatures of 293°K, 303°K, and 323°K. For all activated carbons, an increase in temperature led to an increase in the effectiveness of adsorption of this compound. The results obtained were relatively high, whereas maximal capacities of the monolayer ranged from 107.91 to 147.88 mg/g (*F*-300; Table 6). Since physical adsorption is exothermic, better results are obtained at lower temperatures. In this case, the opposite results were obtained: higher adsorption at higher temperatures. Therefore, this confirms

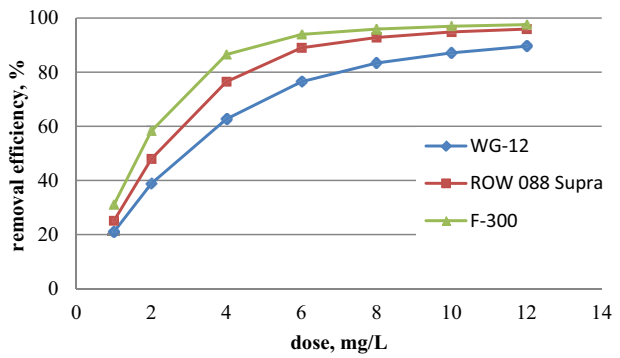


Fig. 4. Effect of the doses of activated carbons on the efficiency of diclofenac sodium adsorption.

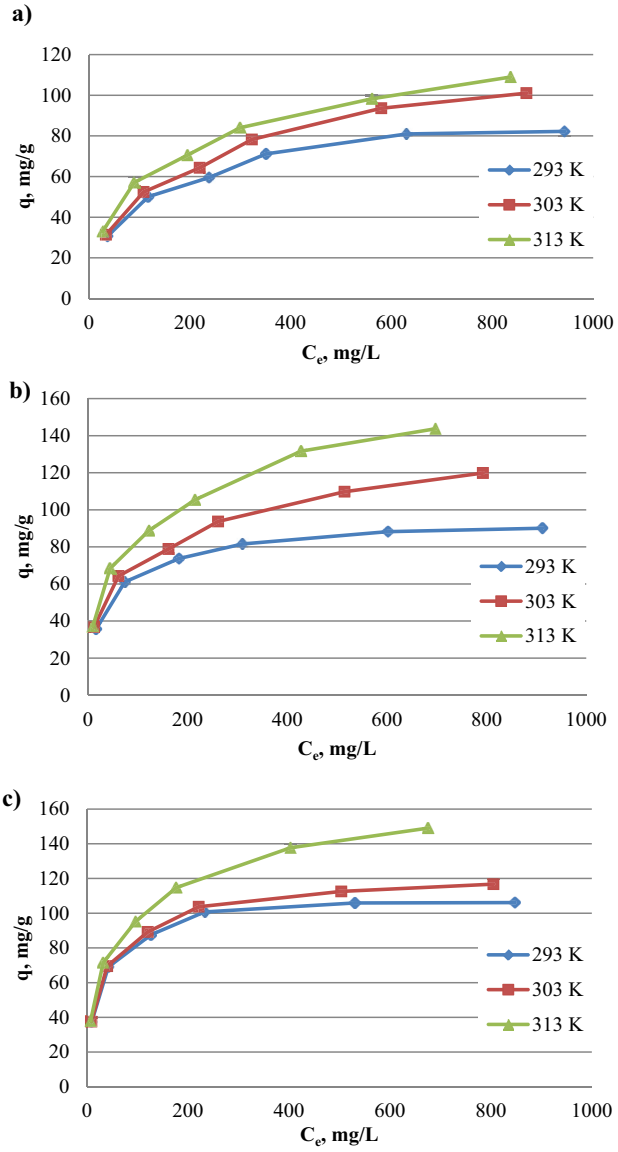


Fig. 5. Effect of temperature on adsorption of sodium diclofenac on activated carbons: (a) WG-12, (b) ROW 08 Supra, and (c) *F*-300.

Table 6
Temperature effect on the efficiency of diclofenac sodium adsorption on commercial activated carbons: (a) WG-12, (b) ROW 08 Supra, and (c) *F*-300

Parameter	WG-12			ROW 08 Supra			*F*-300		
	293 K	303 K	313 K	293 K	303 K	313 K	293 K	303 K	313 K
q_m, mg/g	88.97	112.15	115.29	90.41	117.96	145.48	107.91	115.96	147.88
K_L, L/mg	0.0114	0.0079	0.0104	0.0329	0.01999	0.0178	0.0472	0.0405	0.0268
R^2	0.9698	0.9637	0.9628	0.9752	0.0.914	0.9303	0.9836	0.9729	0.9458

Table 7
Comparison of diclofenac adsorption results based on literature reports

q_m, mg/g	Adsorption isotherms equations tested[a]	The equations of adsorption kinetics studied[a]	Adsorption conditions	Ref.
83	L	PSO	Commercial AC 25–100 mg/L, pH = 5.5, T = 298 K A = 0.212 mmol/g, S_{BET} = 1,016 m^3/g	56
440			Oxidizet AC 25–100 mg/L, pH = 5.5, T = 298 K A = 0.578 mmol/g, S_{BET} = 704 m^3/g	
83	L	PSO	Commercial AC 25–100 mg/L, pH = 5.0, T = 298 K A = 0.21 mmol/g, B = 0.52 mmol/g, S_{BET} = 1,036 m^3/g	51
400			Metal-organic carbon 25–100 mg/L A = 1.16 mmol/g, B = 0.52 mmol/g S_{BET} = 1,855 m^3/g	
11.00	BET L T » F D–R	PSO PFO	AC from olive stones A = 1.6 mmol/g, B = 0.7 mmol/g 25–150 mg/L, T = 295 K S_{BET} = 83.72 m^3/g	52
36.23–46.22	Redlich-Peterson F L	PSO	Commercial AC 10–1,500 mg/L, pH = 5.5 S_{BET} = 462.96 m^2/g T = 298, 308, 318 K	55
0.47	F L T	PSO IPD PFO	AC from cacoa pod husks 10 d, 30 mg/L, T = 298K	68
63.47	Liu L F	General order PSO PFO	AC from cocoa shell 10.00–300.0 mg/L pH = 7–10, T = 298 K	60
22.22	F L	–	AC from Cyclamen persicum T = 298 K, pH = 4	73
79 503	F Sips L	–	AC from metal-azolate pH = 6.5 25–100 mg/L S_{BET} = 1,016 m^2/g S_{BET} = 3,123 m^2/g	74
315	L F	PSO PSF	AC from sugar cane 50–250.0 mg/L pH = 2, T = 298 K S_{BET} = 1,145 m^2/g	57

Table 7
(*Continued*)

q_m, mg/g	Adsorption isotherms equations tested[a]	The equations of adsorption kinetics studied[a]	Adsorption conditions	Ref.
44.6–136	L	PSO	AC from tea waste	58
	F	PSF	10–50 mg/L	
			pH = 6–6.9, T = 303 K	
			S_{BET} = 116.2–895.4 m^2/g	
89–147	L	E	Commercial ACs	This
	T	PSO	159–1,272 mg/L, pH = 6, 8, 10	work
	F	PFO	T = 293 K, 303 K, 313 K	
	D–R	IPD	A = 0.350–0.675 mmol/g	
			B = 0.288–0.660 mmol/g	
			S_{BET} = 847–1,034 m^3/g	

PFO, pseudo-first-order; PSO, pseudo- second-order; IPD, Intra-particle diffusion; E, Elovich; D–R, Dubinin–Radushkevich; T, temperature tested; Co, initial concentration.
[a]The order of equations based on the correlation coefficient R^2.

previous observations that chemical interactions are likely to be critical to diclofenac sodium adsorption. Similar results concerning the effect of temperature on chloramphenicol adsorption were obtained by previous researchers on very different carbon sorbents [54].

The monolayer capacities for commercial and modified activated carbons are at a medium level compared to those obtained by other researchers (Table 7). Very high adsorption capacities (400–503 mg/g) were obtained by researchers after the modification of activated carbons in various ways [50,55,73]. In the case of commercial activated carbons, these capacities were much lower and amounted to 36–83 mg/g [50,54]. Comparison of the results obtained in this study (monolayer capacity 89–147) revealed that all activated carbons used were well matched for sodium diclofenac adsorption. However, similar to this study, other researchers have described the kinetics of diclofenac sodium adsorption using pseudo-second-order kinetics equations with the highest correlation coefficient (Table 7). This equation is often the only one used to describe the results of adsorption kinetics. Therefore, it is difficult to assess based on the literature review the matching of other models to the research results obtained by the researchers. Freundlich and Langmuir isotherms are most commonly used to describe adsorption isotherms. However, it is impossible to unequivocally choose, based on the overview presented in Table 7, a model that would be universal for all the sorbents used in the measurements and would describe the results obtained with the highest correlation coefficient R^2.

4. Conclusions

- Commercial activated carbons (micro- or micro-mesoporous) such as *F*-300, ROW 08 Supra, and WG-12 can be used to remove diclofenac sodium from water since they are characterized by a quite high adsorption capacity, from q_m 58.56 mg/g (WG-12, pH = 10) to 107.91 mg/g (*F*-300, pH = 6). Activated carbons can be ranked according to their adsorption capacity in the following order: *F*-300 > ROW 08 > WG-12.
- Based on the distribution coefficient R_L and adsorption intensity 1/*n*, diclofenac sodium adsorption is beneficial for all the carbons studied.
- A significant effect of pH on adsorption efficiency was also found. In the range of pH from 6 to 10, higher pH values lead to lower diclofenac sodium adsorption on all activated carbon. This confirms the significant effect of the chemical character of the surface on adsorption. The adsorption rate is affected by the formation of hydrogen bonds and electrostatic repulsion between diclofenac anions and the negatively charged surface of activated carbon.
- The adsorption of diclofenac sodium was found to increase with the rise in process temperature from 293°K to 313°K (from 88.97 to115.29 for WG-12 and from 107.91 to 147.88(for *F*-300). This demonstrates that the process is endothermic, confirming the significant effect of chemical adsorption on process effectiveness.
- It was found that among the analyzed isotherms (Freundlich, Langmuir, Dubinin–Radushkevich, and Temkin), the highest correlation coefficients in describing the results were obtained for the Langmuir and Temkin model, whereas the lowest for the Dubinin–Radushkevich.
- The analysis of various adsorption kinetics equations [pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris), Elovich] showed that Elovich and pseudo-second-order models described the results with the highest correlation coefficient R^2. The intraparticle diffusion model (Weber–Morris) described adsorption results to the poorest degree among the models used. This suggests the presence of two or three separate process stages (e.g., external and intergranular diffusion).

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