Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2022.28913

274 (2022) 173–186
October

Adsorption of sulfacetamide on commercial activated carbons: statistics and kinetics of adsorption

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Received 30 March 2022; Accepted 10 September 2022

ABSTRACT

The present study analysed the adsorption of sulfacetamide on six commercial activated carbons. Adsorption on all analyzed sorbents was favourable the tested activated carbons are characterized by average adsorption properties compared to a chemotherapeutic agent (monolayer capacity q_m ranging from 34.58 to 55.54 mg/g). Analysis of the Pearson correlation coefficient revealed a moderate correlation between monolayer capacity and specific surface area, and a very high correlation between monolayer capacity and total pore volume or micropore volume. The specific surface area and pore volume are important but not the only features of activated carbons, determining adsorption capacity of sulfacetamide. Based on the analysis of various models of adsorption kinetics and their matching to the test results, they can be ranked in the following order (taking into account the correlation coefficient R^2): Elovich > intraparticle diffusion > pseudo-first-order > pseudo-second-order. For studies of adsorption statics, the models used in this paper are characterized by a high accuracy of results. Based on the correlation coefficient, they can be ranked as follows: Temkin > Toth > Langmuir > Freundlich > Redlich–Peterson > Jovanovica ≈ Halsey. The effect of pH and solution temperature on the amount of adsorption and that of carbon dose on adsorption efficiency were analyzed. It was found that the highest adsorption was obtained for the solution at pH = 3 (unionised sulfacetamide) and the lowest at pH = 9, in which sulfacetamide is present as an anion. Moreover, it was found that the higher the temperature, the lower the adsorption.

Keywords: Antibiotics; Sulfacetamide; Activated carbon; Adsorption kinetics; Adsorption statics

1. Introduction

Nowadays, one of the challenges is the presence of pharmaceuticals in various areas of the environment. There is a continuous increase in the number of types of drugs and their consumption. For example, around 3,000 drugs are approved for use in the United Kingdom [1]. Pharmaceuticals are organic compounds with specific properties. Most of them are polar and have a molecular weight of less than 500 g/mol. They all induce specific responses in organisms. There is a huge group of compounds that differ, that is, in function, structure, degree of accumulation in organisms, and likelihood of survival in the natural environment in an unchanged form. Some antibiotics can persist in the aquatic environment for a very long time. The half-life of some antibiotics can be as long as tens of days, and they can be carried as far as several hundred km down a typical river from the source of contamination [2,3]. Antibiotics are pharmaceuticals whose presence in various areas of the environment is of concern to many scientists. Their increasingly widespread and frequent use (in human and animal medicine, as animal growth promoters) has resulted in environmental pollution by these compounds. Since 2018, the use of antibiotics to improve the condition and accelerate the growth and development of

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farm animals is prohibited in the EU. In 2022, the European Union prohibits the prophylactic use of antibiotics in entire herds of animals. It was found that approximately 75% of antibiotics are not fully assimilated and are excreted in faeces or urine into the environment [4]. As a result, these drugs are often labelled in surface waters. The presence of antibiotics in the environment, even in low concentrations, can cause various negative effects (e.g., they are toxic to aquatic organisms) that are not fully understood [5,6]. The potential formation of antibiotic-resistant bacteria is very dangerous [8].

One of the groups of chemotherapeutic agents (equivalents of antibiotics but synthetic, with no equivalents in nature) frequently identified in surface waters are sulfonamides, which are one of the most widely used broad-spectrum antibiotics in human and veterinary medicine [8,9]. As sulfonamides are poorly metabolised by humans and animals, a large proportion is continuously released into soil, surface, and groundwater, and subsequently into drinking water. Sulfacetamide and sulfamethoxazole were detected in moderate concentrations in water samples from four rivers flowing through the Hanoi urban area in the Red River delta in northern Vietnam in more than two-thirds of the samples analysed [10]. The presence of antibiotics from this group was determined in many surface waters on different continents and in different countries, for example, sulfamethazine (China: 115 ng/L [11], Hong Kong: 580.9 ng/L [12], Portugal: 123 ng/L [13]), sulfadiazine (Hong Kong: 14.8 ng/L [12], Taiwan: 14.4 ng/L [14], China: 499.5 [14]), sulfamethizole (11.35 ng/L in Bangladesh [15]), and sulfathiazole (Taiwan: 3.0 ng/L [17]). Sulfamethoxazole is most often identified from this group of antibiotics (China: 35.9 ng/L [11], China: 715.3 ng/L [14] and Italy: 68 ng/L [17]). A consequence of the presence of these drugs in surface water, which is often used to supply people with drinking water, is also their presence in this medium, despite multiple methods of its treatment. Sulfamethoxazoles are most often detected from the group of sulfonamides, the presence of which was found, for example, in the USA (0.39–20 ng/L [18]) and China (14 ng/L [19]). Although the concentrations of antibiotics in drinking water are much lower than in therapeutic doses, it is not known how long-term intake of small doses affects human health, for example, the bacterial flora of the gastrointestinal tract. It should be noted that these types of contaminants are not monitored in the environment or drinking water and therefore reports of their presence are rare.

The presence of antibiotics in surface waters, and consequently also those intended for human consumption, is mainly due to their incomplete removal in wastewater treatment plants. The presence of sulfamethoxazole in WWTP in Lede, Belgium, was 245 ng/L in the incoming sewage and 133 ng/L [20] in treated sewage. In WWTP in Dresden, these levels were 321 and 118 ng/L, respectively [21], whereas in India (Udupi), 690 and 420 ng/L, respectively [22]. In some cases (China), no positive effect of sewage treatment on the concentrations of sulfamethoxazole was found [23]. The presence of other sulfonamides has also been reported: sulfoxatine concentration was 563 ng/L in incoming sewage, and 237 in treated sewage in WWTP Gdańsk/Poland [24]; in WWTP Shanghai/China [25], sulfadiazine concentrations were 544.3 and 10.13 ng/L and sulfamethazine concentrations were 10.4 and 5.6 ng/L, in incoming and treated sewage, respectively.

Various methods of removing antibiotics from soil or water are being investigated, including biological treatment [26], electrochemical methods [27], advanced oxidation [28], and adsorption [29]. Of these, adsorption seems to be the best method due to its low cost, simple design, and high efficiency [30]. In addition, adsorption does not generate new products, as may be the case with, for example, biological or chemical oxidation of organic compounds.

One of the antibiotics belonging to the group of sulfonamides is sulfacetamide. It is a synthetic, broad-spectrum antimicrobial agent, but it may cause allergic reactions and be carcinogenic. In more than two-thirds of water samples taken from four rivers in northern Vietnam, sulfacetamide was among those detected in moderate concentrations [10]. Sulfacetamide is active against a variety of Gram-positive and Gram-negative bacteria. It is used in ophthalmology, dermatology, and urology [31].

The problem of antibiotics in wastewater and drinking water has been reported for several years.

It poses risks to the environment and humans, mainly due to the development of antibiotic-resistant bacteria. The search for effective methods to remove antibiotics from municipal wastewater, hospital wastewater, pharmaceutical manufacturing plants, and drinking water, or modification and optimizing existing methods, are topical issues. Studies reported in the scientific literature on removal, including adsorption of sulfacetamide are rare and incomplete.

This study aims to analyze the possibility of sorptive removal of sodium sulfacetamide on commercial activated carbons. These carbons have been used in water and wastewater treatment plants, but differ in their porous structure and chemical structure of the surface. Identification of adsorption mechanisms and evaluation of process conditions and sorbent parameters affecting their effectiveness are important for both scientific and practical reasons.

2. Methodology

2.1. Examinations of sulfacetamide adsorption

Sulfacetamide (Fig. 1) is an antibiotic belonging to the group sulfonamides, which are organosulfonic acid amides [32].

Sodium sulfacetamide ($C_8H_9N_2NaO_3S{\cdot}xH_2O$, with a molar mass of 236.23 g/mol and solubility of 5%, pKa 5.4) purchased from Pol-Aura (Poland) was used for the tests. Examinations of sodium sulfacetamide adsorption were carried out using solutions made of deionized water. The concentrations of

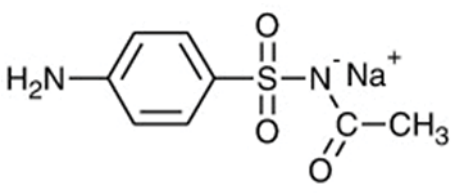

Fig. 1. Structure of sodium sulfacetamide.

sodium sulfacetamide were quantified with the use of a UV-Vis spectrophotometer at a wavelength of λ = 271 nm. The spectrophotometric method presented in the study by Ahmed et al. [33] is accurate and precise and can be used in the determination of this compound in aqueous solutions.

Adsorption kinetics and statics for sulfacetamide were analysed in the solutions with a volume of 0.125 L to which 0.5 g of the appropriate sorbent was added. The whole mixture was stirred at 160 rpm in a mechanical shaker for 10 h. The solutions were then left for 14 h without stirring and the final concentration of sulfacetamide was measured. This time was determined based on studies on adsorption kinetics. The adsorption kinetics was analysed for selected activated carbons in a 100 mg/L sulfacetamide solution with a pH value of 6.5 ± 0.2. To determine adsorption kinetics, the activated carbon solution was stirred for 10 h. During this time, samples were obtained every 1 h. The mixture was then left for 14 h and the final concentration was measured. Each result is the mean of three parallel measurements. Measurements of adsorption isotherms were performed for solutions with pH = 3, 6.5 and 9 ± 0.2, temperature of 293, 303, and 313 K and in sulfacetamide concentrations of 80, 100, 120, 150, 170, and 200 mg/L. The pH was adjusted by adding HCl or NaOH solutions. Examinations of the effect of pH and temperature on adsorption efficiency were conducted on 4 selected activated carbons. A shaking water bath was used to investigate the effect of temperature on the effectiveness of sulfacetamide adsorption (SBW 22N, Manufacturer: LABOPLAY, Polska).

Measurements of the effect of adsorbent dose on adsorption efficiency were made for solutions with a volume of 0.125 L and pH = 6.5 to which 0.125, 0.250, 0.375, 0.5, 0.625, 0.875, 1, 1.125, and 1.25 g were added for the doses of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 g/L, respectively.

Examinations of adsorption kinetics were described using the following kinetic models: pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intraparticle diffusion (IPD) model (Weber–Morris) [34,35]. Two-parameter models were used to describe the adsorption statics: Freundlich, Langmuir, Temkin, Jovanovica, Halsey, and three-parameter models: Redlich–Peterson and Toth [36–38]. The constants of these models were determined by the nonlinear regression method (Solver, Excel add-in).

The number of acid and base groups was determined using the Boehm method [39], and the isoelectric point was determined using the method described by Ferro-García et al. [40].

2.2. Adsorbents used for tests

Six commercial activated carbons were used in the sulfacetamide tests. All of them are used in water treatment plants: granulated activated carbons (WAZ 0.6–2.4; WACC 8X30, Carbon Racibórz, Poland, and Filtrasorb 100, and Filtrasorb 300, Chemviron, Carbon, USA), and granulated moulded activated carbons (ROW 08 Supra, NORIT, Belgium, and WG-12, Gryfskand, Poland) (Table 1).

3. Results

3.1. Adsorption kinetics

Examinations of the kinetics of sulfacetamide adsorption were carried out on four activated carbons: two granulated carbons (F-300 and WACC 8X30) and two formed (ROW 08 Supra and WG-12). Measurements were made for a solution with a concentration of 100 mg/L. The activated carbon solution was stirred for 10 h, and then left unstirred for 14 h, to allow for easier testing. Constants for adsorption kinetics equations were evaluated only for the first 10 h, in which solution mixing with activated carbon was performed. It was assumed that the time to establish the adsorption equilibrium occurs when the concentration change during 1h is below 1% of the initial concentration. The shortest adsorption time was obtained for F-300 and WG-12 (5 h), and the longest – for WACC 8X30 (10 h) (Fig. 2). Leaving the activated carbon solution for 14 h of static contact (without stirring) reduced the concentration of sulfacetamide to a small extent (below 0.5% of the initial concentration) for all tested sorbents.

Four equations of adsorption kinetics were used to describe adsorption kinetics: pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris), and Elovich (Table 2). These are the most commonly used

Table 1
Properties of activated carbons used in research [40]

Activated carbon	Physical properties						Adsorption properties	
	Bulk density, (g/L)	Surface area, (m^2/g)	V_{total} (cm^3/g)	$V_{macr.}$ (cm^3/g)	$V_{mezo.}$ (cm^3/g)	$V_{micr.}$ (cm^3/g)	Iodine adsorption[a] LI, (mg/g)	Methylene blue number[b] LM, (cm^3)
Picabiol	234	1,367	2.103	0.798	0.626	0.679	1,071	30
WG-12	424	1,098	0.99	0.400	0.066	0.524	1,050	30
ROW 08 Supra	381	897	1.135	0.246	0.453	0.436	1,096	30
F-300	542	847	0.987	0,217	0.294	0.476	1,065	28
WACC 8X30	483	839	0.889	0.267	0.214	0.408	1,026	29
WAZ 0.6–2.4	421	820	0.816	0.243	0.177	0.396	1,005	28
F-100	560	674	0.700	0.209	0.159	0.332	850	28

[a]PN-EN 12902;
[b]PN-82/C-97555.03.

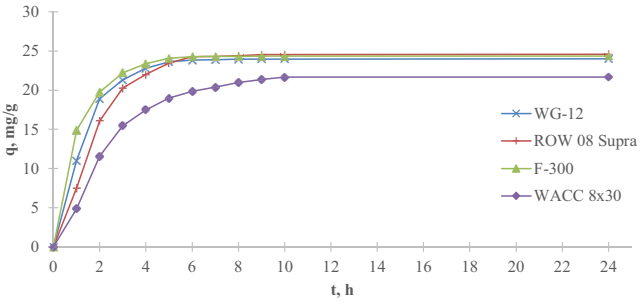

Fig. 2. Sulfacetamide adsorption kinetics.

Table 2
Constants of the sulfacetamide adsorption kinetics equations: pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris) and Elovich

Parameter	F-300	ROW	WG-12	WACC
Pseudo-first-order, $\frac{dq_t}{dt} = k_1(q_e - q_t)$				
q_{max} (mg/g)	24.26	25.23	24.19	22.43
k_1 (1/h)	0.8926	0.4857	0.6911	0.3568
R^2	0.9914	0.9749	0.9874	0.9829
Pseudo-second-order, $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$				
q_{max} (mg/g)	19.6614	14.45	16.09	12.77
k_2 (1/h)	0.1588	0.0751	0.1356	0.0483
R^2	0.9140	0.9139	0.9421	0.9086
Elovich, $\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$				
α (mg/(g·h))	275.86	45.49	76.11	12.68
β (g/mg)	0.2554	0.1756	0.1943	0.1217
R^2	0.9989	0.9955	0.9976	0.9988
Intraparticle diffusion model (Weber–Morris), $q_t = k_p t^{0.5} + C$				
K_p (mg/(g·h$^{0.5}$))	3.74	5.33	4.85	7.10
C (mg/g)	14.20	8.65	10.83	1.30
R^2	0.9977	0.9932	0.9957	0.9977

q_e (mg/g) – is the amount of solute adsorbed et equilibrium; q_t (mg/g) is the amount of solvent adsorbed at time t; k_1/k_2 (1/h) – is the rate constant for the pseudo-first-order/the pseudo-second-order kinetic model; α (mg/(g·h)) – is the initial adsorption rate; β (g/mg) – is reflected the number of sites available for adsorption; K_p (mg/(g·h$^{0.5}$)) – is the slope which refer to intraparticle diffusion rate constant; C (mg/g) – is the intercept which is a constant related to the thickness of the boundary layer.

models of adsorption kinetics. The highest correlation coefficients were obtained by using the Elovich equation (R^2 = 0.9955–0.9989). Only a slightly lower fit to the test results was obtained for the Weber–Morris model (R^2 = 0.9919–0.9977). In the present study, the lowest but also high values of the R^2 coefficient were obtained for the pseudo-second-order kinetic model (from 0.9749 to 0.9914).

The analyzed models were dedicated to different types of adsorption. The Elovich model concerns chemisorption processes on the surface of a solid and assumes no desorption of adsorbed molecules. As the coverage of active sites increases, the adsorption rate decreases. The constant B is believed to express the number of adsorption sites available for the adsorbate [42]. By analyzing this parameter, the activated carbons can be arranged in the following order: F-300 > WG-12 > ROW 08 Supra > WACC 8X30. A similar system of active carbons can be obtained by analyzing the rate constant α of this equation (highest for F-300, lowest for WACC 8X30).

The Weber and Morris model assumes that intramolecular diffusion limits the adsorption kinetics. In view of the long time needed to reach adsorption equilibrium (5–10 h), it can be concluded that it is most likely that internal diffusion is the dominant step in the adsorption kinetics. Basically, adsorption can be controlled by one or two stages [43]. By examining the coefficients of the Weber–Morris equation it is possible to determine whether diffusion in the boundary layer (high values of C) or diffusion inside the particles (C equal to or close to zero) is the dominant stage [43]. In the examinations of the adsorption kinetics of sulfacetamide, quite high C values were obtained, indicating that diffusion in the boundary layer may be the rate-limiting factor in the reaction.

Pseudo-first-order and pseudo-second-order kinetic equations developed by Płaziński and Rudziński [44] do not represent any physical model and are empirical equations from which the rate constants k_1 and k_2 can be determined. However, the type of sorption cannot be determined from these equations. Some researchers, for example, Ahmed et al. [33], however, argue that the pseudo-second-order model presupposes chemisorption. By analyzing the rate constants k_1 and k_2 it can be noticed that the sulfacetamide adsorption process takes place the fastest on the F-300 carbon, and the slowest on WACC 8X30, which is consistent with the conclusions obtained from the analysis of the Elovich equation.

The evaluated models can help understand the adsorption process. The analysis of the studies by other scientists shows that it is not possible to determine the best kinetic equation due to the complexity of the processes occurring during the adsorption of organic compounds on active carbons. The kinetics results are influenced by both the adsorbent and adsorbate structures and process conditions (e.g., pH influences the dissociation of functional groups on the activated carbon surface and the dissociation of adsorbed molecules, temperature, and solute concentration) [45].

3.2. Effect of the type of activated carbon

Examinations of the effect of the type of activated carbon were carried out on six commercial activated carbons for sulfacetamide solutions with a pH = 6.5 ± 0.2 and a temperature of 20°C ± 1°C. All carbon sorbents used in the research were in the form of granules and were intended for water and wastewater treatment. Adsorption isotherms were determined (Fig. 3) to compare adsorption properties. Base on the adsorption capacity, activated carbons can be arranged in the following order: ROW 08 Supra > F-300 > WG-12 > WACC 8X30 > F-100 > WAZ 0.6–

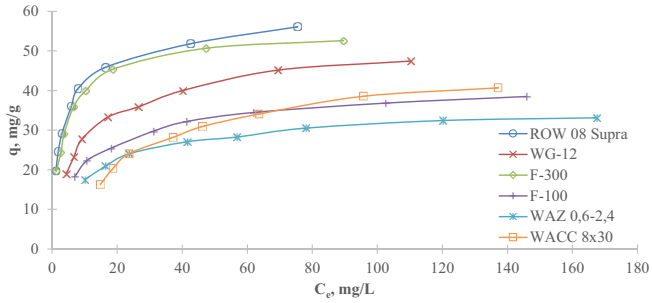

Fig. 3. Sulfacetamide adsorption isotherms on tested activated carbons; pH = 6, 5.

2.4. One of the parameters that can determine the amount of adsorption is the specific surface area. In this case, however, the ranking of activated carbons for sulfacetamide adsorption does not coincide with the ranking of activated carbons for specific surface area: WG-12 > ROW 08 Supra > F-300 > WACC 8X30 > WAZ 0.6–2.4 > F-100. Taking into account iodine adsorption (ROW 08 Supra > F-300 > WG-12 > WACC 8X30 > WAZ 0.6–2.4 > F-100) or the sum of the meso- and micropore volumes (ROW 08 Supra > F-300 > WACC 8X30 > WG-12 > WAZ 0.6–2.4 > F-100) and adsorption of sulfacetamide, great similarities can be noticed between these series.

The curves in the figure are described by several different equations of adsorption isotherms: Freundlich, Langmuir, Temkin, Jovanovica, Halsey, Redlich–Peterson, and Toth (Table 3). In general, it can be seen that regardless of the activated carbon used, the sulfacetamide adsorption process (taking into account the correlation coefficient R^2) is best described by the Temkin equation, and the least by Jovanovica and Halsey. By analyzing the coefficient R^2, these equations can be arranged as follows: Temkin > Toth > Langmuir > Freundlich > Redlich–Peterson > Jovanovica ≈ Halsey. The isotherms that best describe adsorption (Temkin, Toth, Langmuir) have some common assumptions: monolayer adsorption, heterogeneous surface, and generating interactions between adsorbed substances. The Temkin isotherm is related to chemisorption, Langmuir to physisorption and chemisorption, and the Toth isotherm is an empirical modification of the Langmuir isotherm [38,44]. Despite some differences, the above-mentioned isotherms describe, with a very high correlation coefficient, the adsorption of sulfacetamide. It is observed that other scientists also obtained similar results (high R^2 for isotherm models with different assumptions) [47–49]. This is most likely due to the heterogeneity of the surface of activated carbons used in the research and many simultaneous adsorption mechanisms.

The two isotherms that describe the results most poorly (Jovanovica and Halsey) differ significantly from the others. Janovic's isotherm concerns multilayer adsorption and assumes homogeneity of the surface, while Halsey's isotherm concerns only physical adsorption and the formation of a liquid membrane adsorbate on mesoporous adsorbents.

The two isotherms most commonly used to describe adsorption from Langmuir and Freundlich's solution are characterized by high, but not the highest, coefficients R^2. Nevertheless, the Langmuir isotherm, in particular, is often used because it describes the adsorption process well and at the same time determines the maximum monolayer capacity g_{max} which is often used to easily compare sorbents to each other. The obtained monolayer capacities calculated from the Langmuir equation range from 34.58 (WAZ) to 55.54 mg/g (ROW 08 Supra). The maximum adsorption capacity g_{max} is also determined in the case of the Toth isotherm. In this case, the obtained values of sorption capacity are slightly higher and range from 27.52 mg/g (WAZ) to 62.07 mg/g (ROW 08 Supra).

Based on the Langmuir isotherm coefficients, it can be determined whether the adsorption of the test compound is beneficial. The partition coefficient R_L is then determined:

$$R_L = \frac{1}{1 + a_L C_0} \tag{1}$$

$$a_L = \frac{K_L}{q_m} \tag{2}$$

The symbol C_0 indicates the maximum initial concentration of the sorbed substance (mg/L). The value of R_L determines the nature of adsorption: when $R_L > 1$ – adsorption conditions are unfavorable, for $R_L = 1$ adsorption is linear, for $0 < R_L < 1$ adsorption conditions are favorable, and for $R_L = 0$ adsorption is irreversible.

Parameter R_L calculated for all activated carbons ranged roughly from 0 to 1 (from 0.3365 to 0.9584), which means that adsorption of sulfacetamide for the analyzed concentrations and sorbents was favourable.

The constant n in the Freundlich equation for all activated carbons ranged from 1 to 10, which proves the favourable adsorption of sulfacetamide. This confirms the conclusion resulting from the analysis of the Langmuir isotherm. The reciprocal of the coefficient n ($1/n$) indicates the degree of diversity of the active sites of the activated carbon surface. The values of $1/n$ range from 0 to 1. The closer the value of $1/n$ is to 0, the greater the energy inhomogeneity of the adsorption system. For the analyzed activated carbons, the values of $1/n$ (from 0.20 to 0.36) closer to zero than to unity indicate the high inhomogeneity of the surface of the analyzed activated carbons.

Pearson's correlation between q_m/q_{max} determined from the Langmuir and Toth isotherms and the specific surface/total volume of V_{tot}/volume of micropores were analyzed (Table 4). The Pearson coefficient is assumed to determine the strength of the relationship: weak correlation occurs below 0.2, low correlation – for 0.2–0.4, moderate correlation (significant relationship) – for 0.4–0.6, high correlation – for 0.6–0.8, very high correlation – for 0.8–0.9, and virtually complete correlation occurs for 0.9–1.0. Table 4 presents the correlations for activated carbons. A very high correlation was found between the maximum adsorption capacity determined from the Langmuir isotherm equation and the $V_{mic+meso}$ pore/total pore volume. There was also a high correlation between q_m and micropore volume and a moderate correlation between q_m monolayer volume and specific surface area.

Table 3
Constants of sulfacetamide adsorption isotherms on commercial activated carbons

Parameter	F-300	ROW	WG-12	WAZ	F-100	WACC
Langmuir, $q = \frac{q_m K_L C_e}{1 + K_L C_e}$						
q_m (mg/g)	53.01	55.54	48.97	34.58	39.79	48.89
K_L (L/mg)	0.352	0.396	0.133	0.099	0.111	0.037
R^2	0.9794	0.9803	0.9822	0.9833	0.9850	0.9944
Freundlich, $q = \frac{q_m K_L C_e}{1 + K_L C_e}$						
$1/n$ (–)	0.20	0.21	0.25	0.20	0.22	0.35
K_F (mg/g)	23.94	15.30	16.82	12.31	13.39	7.55
R^2	0.9272	0.9640	0.9996	0.9454	0.9614	0.9539
Temkin, $q = B \ln A_T C$						
A (L/mg)	10.25	10.23	2.24	3.01	2.55	0.5
B (–)	8.17	8.73	8.82	5.50	6.68	10.86
R^2	0.9972	0.9977	0.9994	0.999	0.9995	0.9991
Jovanovica, $q = q_\infty \cdot \left(1 - e^{-K_j C_e}\right)$						
K_j (L/mg)	0.255	0.285	0.1068	0.072	0.083	0.036
q_m (mg/g)	48.35	50.64	42.99	30.91	35.36	39.74
R^2	0.8982	0.8938	0.9012	0.9061	0.8897	0.982
Halsey, $q = \left(K_h \cdot C_e\right)^{1/n_h}$						
K_h (mg/g)·(mg/L)$^{1/n}{}_h$	192,276	192,276	192,276	192,276	192,276	192,276
n (–)	4.07	3.99	4.34	4.87	4.65	4.70
R^2	0.8731	0.8919	0.9579	0.9451	0.9608	0.804
Redlich–Peterson, $q = \frac{K_R \cdot C_e}{1 + a_R \cdot C_e^{\beta}}$						
K_R (L/g)	210,341	210,249	210,043	215,746	215,861	214,940
a_R (L/mg)β	9,165	8,782	13,728	17,527	16,121	28,451
β	0.799	0.791	0.749	0.798	0.779	0.647
R^2	0.9166	0.9272	0.964	0.9454	0.9614	0.9539
Toth, $q = q_m \cdot \frac{b \cdot C_e}{\left(1 + \left(b \cdot C_e\right)^v\right)^{1/v}}$						
q_m (mg/g)	58.75	62.07	61.08	27.52	46.68	47.3
b (mg/g)	0.649	0.737	0.295	0.016	0.239	0.036
v (–)	0.659	0.6464	0.550	2.135	0.596	1.09
R^2	0.992	0.9938	0.9957	0.9931	0.9998	0.9946

Table 4
Pearson correlation coefficients

Parameter	Surface area	V_{tot}	$V_{mic+meso}$	V_{mic}
q_m – Langmuir	0.45	0.85	0.80	0.69
q_m – Toth	0.50	0.72	0.58	0.45

3.3. Effect of solution pH

The study analysed the effect of the adsorbent dose, the pH value of the solution, and its temperature on the adsorption of sulfacetamide on four active carbons for which the highest adsorption capacities were obtained (ROW 08 Supra, F-300, WG-12, and WACC 8X30).

First, the effect of pH on the adsorption rate of sulfacetamide, which can be in an ionised form in different solutions, was analyzed (Fig. 4). Examinations of adsorption for solutions with pH values of 3, 6.5, and 9 were carried out. The dissociation of functional groups in the tested solutions was:

pH = 3: sulfanide: 99.7% (non-ionized) and 0.3% (ionized); aromatic amine: 94.1% (non-ionized), 5.9% (ionized),

pH = 6.5: sulfanide: 7.9% (non-ionized) and 92.1% (ionized); aromatic amine: 100% (non-ionized),

pH = 9: sulfanide: 100% (ionized); aromatic amine: 100%, (non-ionized).

Fig. 5 shows the adsorption isotherms of sulfacetamide for solutions with pH 3 and pH 9, whereas the solution with pH 6.5 is presented in Fig. 3. To describe these isotherms, the Langmuir, Temkin, and Toth equations were selected (Table 5) based on the highest values of the coefficient R^2 obtained in the research presented in the previous chapter of the paper. For three of the analyzed adsorbents, sorption occurred best for a solution with a pH of 3, in which sulfacetamide is virtually non-ionized (only the aromatic amine group is ionized in less than 6%). The q_{max} values calculated from the Langmuir isotherm concern activated carbon ROW 08 Supra with 60.4 mg/g for pH 3, 55.54 mg/g for pH 6.5, and 42.32 mg/g for pH 9. Only for WACC, when comparing q max, slightly better sulfacetamide adsorption results were obtained for a solution with pH 6.5 compared to pH 3. This carbon has the highest pH_{PZC} value among those analyzed (Table 4). However, when comparing q_{max} obtained from the Toth isotherm for each activated carbon, the adsorption occurred best for a solution with pH = 3, and the weakest for a solution with pH = 9. This isotherm, both for acidic and alkaline solutions, describes the test results with a slightly higher correlation coefficient than for the Langmuir isotherm. The lowest values of the adsorption capacity were obtained during adsorption for the solution with pH 9, and the =NH group was ionized at 100%. In a solution with a pH of 6.5, this group was also ionized at 92%.

The analysis of the number of acid and base groups using Boehm's method (Table 6) and the isoelectric point of activated carbons was carried out. Since all the analyzed activated carbons were obtained by the steam-gas method, both basic and acid functional groups are present on their surface. Commercial activated carbons were not additionally oxidized and therefore their surface has relatively few acid–base groups. Activated carbon WACC 8X30, which adsorbed the smallest amounts of sulfacetamide regardless of solution pH, had the smallest value of acid groups (0.419 mmol/g) and the largest number of base groups (0.601 mmol/g). For the other activated carbons, no simple correlations were observed between the number of acid/base groups determined by Boehm's method and the

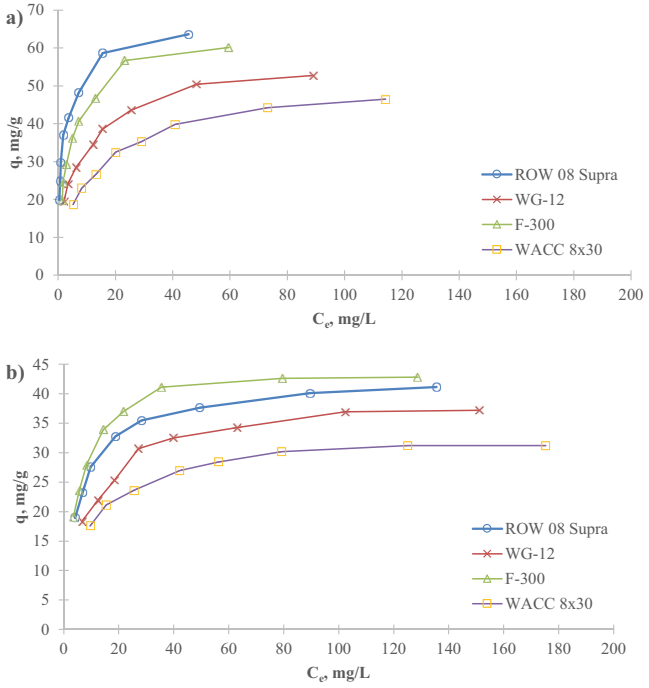

Fig. 5. Isotherms of sulfacetamide adsorption from solutions of different pH values: (a) pH = 3 and (b) pH = 9.

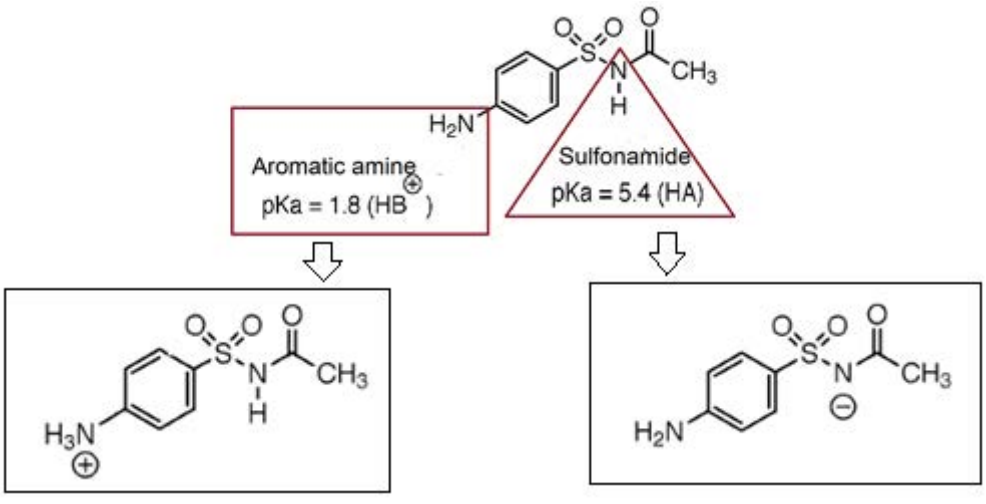

Fig. 4. Molecular structure of sulfacetamide with dissociating groups marked.

Table 5
Constants of sulfacetamide absorption isotherms on selected activated carbons from solutions with pH 3 and 9

Parameter	F-300		ROW		WG-12		WACC	
	pH 3	pH 9	pH 3	pH 9	pH 3	pH 9	pH 3	pH 9
				Langmuir				
q_m (mg/g)	62.09	45.42	60.39	42.32	53.47	39.56	49.09	3289
K_L (L/mg)	0.308	0.200	0.963	0.186	0.202	0.112	0.107	0.117
R^2	0.9708	0.9948	0.9488	0.9973	0.9551	0.9811	0.9860	0.9873
				Temkin				
A (L/mg)	4.95	6.79	23.26	6.57	3.75	2.95	0.35	5.43
B (–)	11.19	6.88	9.48	6.38	9.35	6.45	10.86	4.80
R^2	0.9969	0.9948	0.9984	0.9975	0.9991	0.9977	0.9991	0.9985
				Toth				
q_m (mg/g)	72..02	44.59	78.15	43.23	77.97	41.26	65.34	34.23
b (mg/g)	0.509	0.177	3.568	0.214	0.847	0.141	0.261	0.156
v (–)	0.65	1.11	0.45	0.89	0.41	0.84	0.51	0.82
R^2	0.9828	0.9959	0.9904	0.9982	0.9929	0.9831	0.9933	0.9898

Table 6
Ilość grup o charakterze kwasowym i zasadowym na węglach aktywnych WG-12, F-300, ROW 08 Supra (metoda Bohema)

Activated carbon	WG-12	ROW 08 Supra	F-300	WACC 8X30
Acidic groups (mmol/g)	0.586	0.434	0.544	0.419
Basic groups/sites (mmol/g)	0.467	0.592	0.512	0.601
Punkt izoelektryczny (pH_{PZC})	6.4	6.5	6.6	6.7

adsorption capacity of the activated carbons. With such small differences in the chemical structure of activated carbons, the porous structure and availability of active sites may also be important.

Depending on the pH of the solution, various mechanisms are responsible for the adsorption of sulfonamides, including sulfacetamide: repulsion interactions, π–π EDA interactions (by π+ –π electron donor–acceptor (EDA) which includes the cation –π bonding), H-bond formations, CAHB formations (negative charge-assisted H-bond, (–) CAHB) [33,50]:

Mechanisms of sulfonamides sorption
At very low pH:
Repulsion interactions
AC–OH + sulphonamides = EDA interactions
At a pH of about 4
AC–COOH + sulphonamides ($NHSO_2$–/NH/–NH_2/CH_3) = H-bond formations
At a pH of about 4
Repulsion interactions
Sulfonamides-N^- + H_2O = sulphonamides-NH + $–OH^+$
AC–O…H + $^-$N…Sulfonamides = AC–O^-…H^+…$^-$N… Sulfonamides = CAHB

Similar dependencies for the effect of pH on adsorption of sulfonamides were also obtained by other researchers, for example, for sorption of sulfamethazine by Rajapaksha et al. [51], or sulfamethoxazole and sulfapyridine by Xie et al. [52]. Un-dissociated forms of antibiotics, similarly to the results presented in this paper, were adsorbed to a greater extent than those dissociated but the adsorption of sulfacetamide took place for acidic, neutral, and alkaline solutions.

3.4. Effects of temperature on the adsorption process

One of the parameters affecting the magnitude of adsorption of organic compounds, including sulfonamides, is temperature [53,54]. The effect of temperature on the adsorption of sodium sulfacetamide on four activated carbons was studied. Adsorption was analysed for the solutions with a temperature of 293, 303, and 313 K (Fig. 6, Table 7). The analysis of the adsorption isotherms of sodium sulfacetamide at different temperatures revealed that regardless of the sorbent used, an increase in temperature resulted in a decrease in the adsorption of the organic compound analysed. The differences in maximum adsorption capacity obtained from the Langmuir equation are greatest for ROW 08 Supra activated carbon (41.49 mg/g at 313 K and 55.52 mg/g at 293 K), and the lowest for WG-12 (40.10 mg/g at 313 K and 48.97 mg/g at 293 K). Also, it can be noted that for adsorption at 313 K, the differences between the maximum capacities of activated carbons are lower (from 38.22 mg/g for WACC to 42.39 mg/g for F-300) than at 293 K (from 48.89 – WACC to 55.54 mg/g – ROW 08 Supra).

This effect of temperature suggests that sodium sulfacetamide is dominated by physical adsorption, which is an exothermic process. To confirm this thesis for selected activated carbons, the Gibbs free energy of adsorption (ΔG) was analyzed using the formula $\Delta G° = -RT\ln K_{ad}$ (R – gas constant equal to 8.314 kJ/mol) (Table 8). Since the Langmuir isotherm equation with a high value of the correlation coefficient R^2 describes the obtained test results, it was assumed

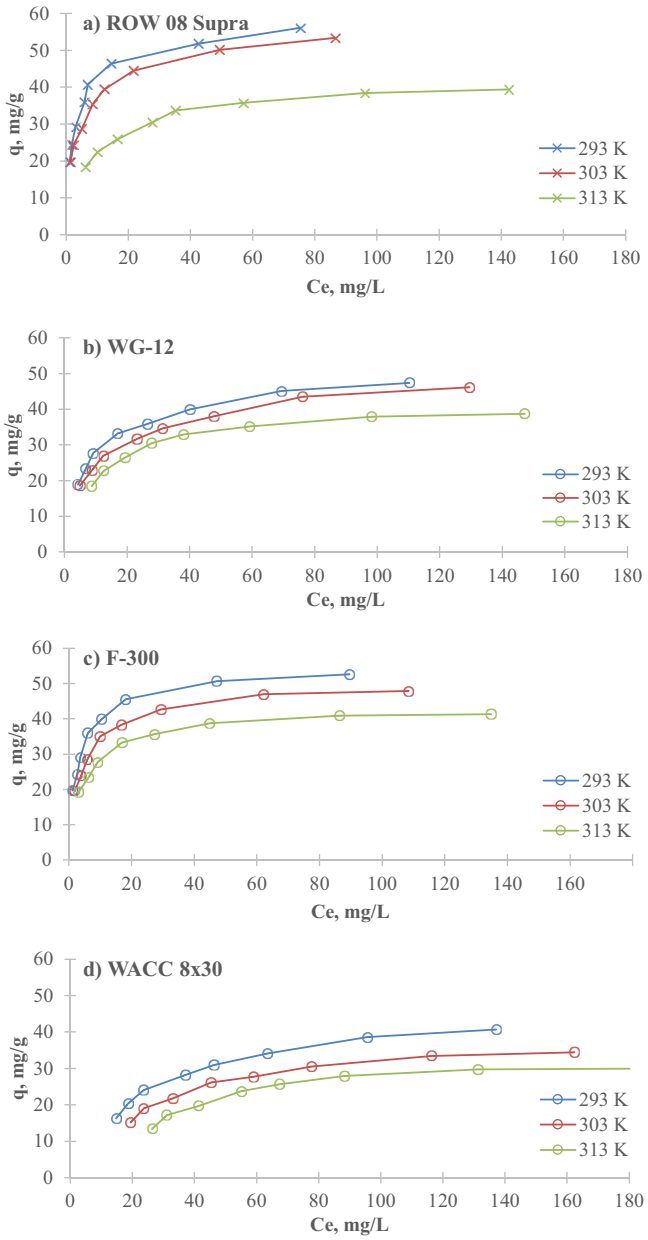

Fig. 6. Sulfacetamide adsorption isotherms in short from the process temperature for activated carbons: (a) ROW 08 Supra, (b) WG-12, (c) F-300, and (d) WACC 8X30.

that $K_{ad} = K_L$. Negative $\Delta G°$ results of –14.6 to –8.5 kJ/mol were obtained for each activated carbon analyzed and each temperature. The negative values show that the adsorption process of sulfacetamide is spontaneous and favourable. This confirms the conclusions obtained based on the values of n from the Freundlich isotherm and R_L from the Langmuir isotherm. It was also found that both ΔH and ΔS are negative, suggesting that the adsorption process is exothermic, spontaneous, and beneficial at lower temperature. Low values of enthalpy ΔH (from –47.2 to –13.4 kJ/mol) indicate the dominance of physical adsorption. Thus, it is likely that ion exchange and van der Waals forces are mainly responsible for the adsorption. Similar results were obtained by, for example, Luo et al. [54] who examined the sorption of sulfamerazine, Yazidi et al. [55], who studied amoxicillin and tetracycline, and for chloramphenicol by Mohd Din et al. [56].

3.5. Effects of adsorbent dose on the adsorption efficiency of sulfacetamide

The effect of the adsorbent dose was assessed for a sulfacetamide concentration of 200 mg/L (Fig. 7). The following doses of activated carbon were used: 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 g/L.

Researchers have used very different doses in their experiments on the adsorption of different antibiotics, for example, Rajapaksha et al. [51] used 1 g/L in the adsorption of sulfamethazine whereas Yazidi et al. [55] used from 0.9 to 14 g/L in the adsorption of amoxycycline and tetracycline. In the range of tested doses of activated carbon ROW 08 Supra, the adsorption efficiency of sulfacetamide was obtained in the range from 27.5% (dose of 1 g/L) to 99.3% (dose of 10 g/L). For F-300, these values ranged from 24.1% to 99.2%, for WG-12 – from 16.6% to 96.7%, and for WACC – from 20.5% to 90.3%. For activated carbons ROW 08 Supra and F-300, a dose of 5 g/L removed sulfacetamide from the initial solution by more than 95%, whereas greater doses improved this effect only slightly. With WG-12, exceeding the 95% efficiency was observed only at the dose of 9 mg/L, while for WACC, this threshold was not reached, even with the dose of 10 g/L (max. 91.9%).

Table 9 presents literature reports on the sorption of sulfonamides. It should be noted that the literature on the sorption of these chemotherapeutics is not extensive. It is important to emphasise that the commercial carbons obtained in the study show average sorption capacities with respect to sulfacetamide (from 33.95 to 55.54 mg/g).

The pseudo-first-order and pseudo-second-order kinetics equations are most commonly used in the literature to describe adsorption kinetics and a better fit in most cases was obtained for the PSO equation. In the studies described in this paper, the Elovich equation of kinetics and intraparticle diffusion model were additionally analyzed, which, describe the test results with a R^2 coefficient higher than the PSO and PFO equations.

Freundlich and Langmuir isotherms are most commonly used to describe adsorption isotherms. No dominance of one of these models was observed based on the analysis of the literature reports. This paper also analyze the models of Temkin, Toth, Redlich–Peterson, and Jovanovica and Halsey. Langmuir, Freundlich, Temkin, Toth and Redlich–Peterson isotherms with a high $R^2 > 0.9$ coefficient described the test results with a high coefficient ($R^2 > 0.9$). Lower correlation coefficients were obtained for the Jovanovica and Halsey models.

By analysing the literature reports on the adsorption of sulfonamides (Table 7), it can be concluded that, irrespective of the adsorbent used and the specific compound belonging to the analysed group, physical adsorption is a very important mechanism, but chemical adsorption can also occur. The literature mainly describes van der Waals forces, π–π EDA interactions, hydrogen bonding, and electrostatic interactions as responsible for sulfonamide adsorption

Table 7
Coefficients of the sulfacetamide adsorption isotherm depending on the process temperature, pH 6, 5

Parameter	F-300			ROW			WG-12			WACC		
	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
						Langmuir						
q_m (mg/g)	53.01	48.59	42.397	55.54	52.48	41.49	48.97	47.57	41.86	48.89	41.58	38.22
K_L (L/mg)	0.352	0.269	0.221	0.396	0.302	0.114	0.133	0.104	0.093	0.037	0.034	0.026
R^2	0.9794	0.9755	0.9840	0.9803	0.9497	0.9891	0.9822	0.9692	0.9980	0.9944	0.9843	0.9547
						Temkin						
A (L/mg)	10.25	8.218	9.049	10.23	7.443	2.601	2.24	1.567	3.717	0.35	0.334	0.236
B (–)	8.17	7.461	6.182	8.73	8.461	6.980	8.82	8.933	6.425	10.86	9.058	8.642
R^2	0.9972	0.9979	0.9976	0.9977	0.9992	0.9986	0.9994	0.9993	0.9989	0.9991	0.9980	0.9956
						Toth						
q_m (mg/g)	58.75	54.95	45.45	62.07	68.97	44.82	61.08	65.64	43.35	47.3	45..56	30.58
b (mg/g)	0.649	0.570	0.363	0.737	1.171	0.166	0.295	0.287	0.206	0.036	0.036	0.018
v (–)	0.659	0.617	0.722	0.6464	0.456	0.748	0.550	0.479	0.732	1.09	0.838	2.612
R^2	0.992	0.9921	0.9922	0.9938	0.9943	0.9942	0.9957	0.9887	0.9976	0.9946	0.9793	0.9934

Table 8
Thermodynamic parameters of the sulfacetamide adsorption onto activated carbons

Activated carbon	T (K)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol)	$\Delta H°$ (kJ/mol)
	293	–14.3		
F-300	303	–14.1	–11.9	–17.8
	313	–14.0		
	293	–14.6		
ROW 08 Supra	303	–14.4	–110.3	–47.2
	313	–12.3		
	293	–8.8		
WACC 8X30	303	–8.9	–15.3	–13.4
	313	–8.5		
	293	–11.9		
WG-12	303	–11.8	–6.28	–13.7
	313	–11.7		

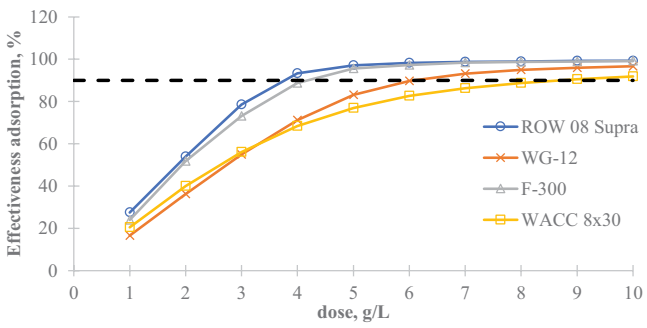

Fig. 7. Effect of activated carbon dose on the adsorption efficiency of sulfacetamide.

depending on the adsorbent used. These mechanisms occur simultaneously, often with one of them predominating depending on the specific sulfonamide sorbed, the pH value of the solution, and the type of sorbent used.

4. Conclusions

(1) The sulfacetamide adsorption process is favorable, spontaneous, and exothermic. The analyzed commercial activated micro- and micro-mesoporous carbons had average adsorption properties (q_m from 33.95 to 55.54 mg/g) and can be used during sulfacetamide adsorption without modification.
(2) When comparing the adsorption capacities of activated carbons with respect to sulfacetamide, they can be ranked in the following order: ROW 08 upra > F-300 > WG-12 > WACC 8X30 > F-100 > WAZ 0.6–2.4. A strong similarity to the series created based on the specific surface area can be observed: WG-12 > ROW 08 Supra > F-300 > WACC 8X30 > WAZ 0.6–2.4.
(3) Pearson correlation coefficients show a moderate correlation between monolayer capacity and specific surface area and a very high correlation between monolayer capacity and total pore volume or $V_{mic+meso}$ volume. The specific surface area and pore volume are important but not the only features of activated carbons that determine the adsorption capacity of sulfacetamide.
(4) The comparison of the adsorption of sulfacetamide in solutions at pH 3, 6.5 and 9 reveals the greatest adsorption for solutions at pH = 3 in which sulfacetamide occurs mainly in the un-ionised form. The lowest adsorption was obtained for solutions with pH = 9, in which sulfacetamide is present as an anion.
(5) As a result of the sulfacetamide adsorption test for solutions with a temperature of 293, 303, and 313 K, sorption capacity was found to decrease

Table 9
Comparison of sulfacetamide adsorption results based on literature reports

Activated carbon	Adsorption conditions	Equations of adsorption kinetics studied[a]	Adsorption isotherms equations tested[a]	q_m (mg/g)	Effect of pH/ temperature	Mechanism of adsorption	References
			Sulfamethazine				
Wheat and corn straw biochar	T = 25°C C_0 = 0.5–50 mg/L D = 50 mg·AC/10 mL pH = 1.5, 6.0 and 9.0	- D-e - PSO - PFO	- F - L	1.39–5.75		- physisorption (partition) - π–π EDA interaction	[57]
Tea waste biochars	T = 25°C C_0 = 0–50 mg/L pH = 3.0–9.0		- F - L	2.7–33.8	pH 3 > 5 > 7 > 9	- π–π EDA interaction - cation-p interaction - cation exchange - H-bonds formations	[51]
Eucalyptus tree biochar	T = 25°C pH = 1.5–10.9 C_0 = 0.250–20.0 mg/L	- PSO - PFO = IPD	- L - F	45.19	pH 4 > 8.5 > 1.5 > 5.5 > 11	- π–π EDA interaction - proton exchange with water by forming CAHB	[33]
AC from shrimp shells	T = 25°C, 35°C, 45°C C_0 = 20–280 mg/L pH = 1.5–10.9	- PSO - PFO	- L - F	699	T 45°C > 35°C > 25°C	- indicating the Van der waals - π–π EDA interaction - H-bonds formations	[58]
			Sulfamethoxazole				
Rice, corn and cotton straw biochar	T = 25°C C_0 = 0.5–64 mg/L					- hydrophobic interactions - π–π EDA interaction - H-bonds formations	[59]
Eucalyptus tree biochar	T = 25°C pH = 1.5–10.9 C_0 = 0.250–20.0 mg/L	- PSO - PFO = IPD	- F - L	20.71	pH 4 > 8.5 > 1.5 > 5.5 > 11	- π–π EDA interaction - proton exchange with water by forming CAHB	[33]
Biochar	C_0 = 5–80 mg/L pH = 1.0–12.0		F = D–A	1.9–173	max pH = 4	- hydrophobic interaction, - π–π EDA interaction - pore-filling	[60]
			Sulfanilamide				
Rice, corn and cotton straw biochar	T = 25°C C_0 = 0.5–64 mg/L pH = 7.1					- hydrophobic interactions - π–π EDA interaction	[59]
			Sulfapyridine				
Graphene oxides	C_0 = 6–100 mg/L pH = 1.0, 5.0, 11			12.6–168	pH 5 > 1 > 10	- hydrophobic interaction - π–π EDA interaction - electrostatic interaction	[53]
			Sulfathiazole				
Graphene oxides	C_0 = 6–100 mg/L pH = 1.0, 5.0, 11			15.7–269	pH 5 > 1 > 10	- hydrophobic interaction, - π–π EDA interaction - electrostatic interaction	[53]

(Continued)

Table 9

Activated carbon	Adsorption conditions	Equations of adsorption kinetics studied[a]	Adsorption isotherms equations tested[a]	q_m (mg/g)	Effect of pH/ temperature	Mechanism of adsorption	References
Eucalyptus tree biochar	T = 25°C pH = 1.5–10.9 C_0 = 0.250–20.0 mg/L	- PSO - PFO = IPD	- L - F	28.29	pH 4 > 8.5 > 1.5 > 5.5 > 11	- H-bonds formations - π–π EDA interaction - proton exchange with water by forming CAHB	[33]
			Sulfamerazine				
Modified biochar KOH	pH = 3, 5, 7, 9, 11 C_0 = 5–50 mg/L D = 0.1 g/10 mL T = 15°C, 25°C, 35°C	- PSO - IPD - PFO	- F - L	0.67	max pH 7 min pH 11	- electrostatic interactions - π–π EDA interaction - H-bonds - cation bridging - surface complexation	[54]

PFO – pseudo-first-order; PSO – pseudo-second-order; IPD – intraparticle diffusion; E – Elovich; D-R – Dubinin–Radushkevich; D-e – double-exponential model; D – dose of activated carbon/volume of the solution; T – temperature tested; C_0—initial concentration;
[a]order of equations.

with increasing solution temperature, indicating a predominance of physical adsorption.

(6) The analysis of different models of adsorption kinetics and their fitting to the test results shows that they can be ranked in the following order taking into account the correlation coefficient R^2: Elovich > intraparticle diffusion > pseudo-first-order > pseudo-second-order. When describing the adsorption statics, the models used in this study describe the experimental results with high accuracy. Based on the correlation coefficient, they can be ranked as follows: Temkin > Toth > Langmuir > Freundli ch > Redlich–Peterson > Jovanovica ≈ Halsey.

Funding

This research was funded by Czestochowa University of Technology, Poland.

Conflicts of interest

The authors declare no conflict of interest.

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