

Article

Adsorption of Chloramphenicol on Commercial and Modified Activated Carbons

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Abstract: The aim of the study was to evaluate the possibility of applying commercial activated carbons currently used in water treatment plants and modified carbon at 400 and 800 °C in the atmosphere of air, water vapour and carbon dioxide to remove chloramphenicol. Adsorption kinetics was examined for solutions with pH of 2–10. Adsorption kinetics were determined for the initial concentration of chloramphenicol of 161 mg/dm³ and the adsorption isotherm was determined for the concentrations of 161 to 1615 mg/dm³. Of the analysed activated carbons (F-300, F-100, WG-12, ROW 08 Supra and Picabiol), the highest adsorption capacity was obtained for the use of Picabiol (214 mg/g), characterized by the highest specific surface area and pore volume. The pH value of the solution has little effect on the adsorption of chloramphenicol (the highest adsorption was found for pH = 10, q_m = 190 mg/g, whereas the lowest—for pH = 6, q_m = 208 mg/g). Modification of activated carbon WG-12 at 800 °C caused an increase in adsorption capacity from 195 mg/g (unmodified carbon) to 343 mg/g. A high correlation coefficient was found between the capacity of activated carbons and the total volume of micropores and mesopores. Among the examined adsorption kinetics equations (pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion), the lowest values of the R^2 correlation coefficient were obtained for the pseudo-first order equation. Other models with high correlation coefficient values described the adsorption kinetics. The adsorption results were modelled by means of the Freundlich, Langmuir, Temkin and Dubinin–Radushkevich adsorption isotherms. For all activated carbons and process conditions, the best match to the test results was obtained using the Langmuir model, whereas the lowest was found for the Dubinin–Radushkevich model.

Keywords: chloramphenicol; activated carbon; adsorption

1. Introduction

Antibiotics represent one of the groups of drugs whose discovery has revolutionized medicine. Since the invention of penicillin in 1928, many different natural and semi-synthetic antibiotics and chemotherapeutic agents (synthetic compounds not present in nature) have been developed. The fact that they are more and more widespread and frequently used (in human and animal medicine, and as animal growth promoters) has caused environmental pollution with these compounds. The sources of antibiotics and their pathways to the environment are diverse. Antibiotics are overused in livestock farming despite the attempts to establish appropriate legislation. In 2018, the use of antibiotics in the European Union (EU) to improve and accelerate the growth and development of farm animals was banned. A law will come into force in the EU in 2022 banning the preventive use of antibiotics in entire herds of animals. Around 75% of the drugs are not digested by animals and excreted in faeces or urine into the environment [1]. In 2012, ca. 3400 tonnes of antibiotics in Europe were sold for medical purposes and 7982 tonnes for breeding animals for slaughter. The average human dose of antibiotic was 116.4 mg/kg, whereas for animals, this was 144.0 mg/kg [2,3].

The consequence of such a wide use of these pharmaceuticals is their presence in various elements of the environment, including surface waters. Antibiotics are considered pollutants to the aquatic environment due to their high biological activity, persistence and susceptibility to bioaccumulation, leading to, among other things, slower biodegradation [4,5]. In this case, an important source of antibiotics is treated wastewater. Conventional wastewater treatment methods are often poorly effective for these pollutants [6,7]. Another problem is the negative effect of antibiotics on the work of the biological part of wastewater treatment [8,9]. Almost all antibiotics used in medicine, veterinary medicine and agriculture are identified in surface waters [10]. Concentrations of antibiotics can reach 2 µg/L and are detected in surface water, groundwater and even groundwater on all continents, in both highly and underdeveloped countries (the USA, the UK, Australia, China, India, Vietnam). The highest antibiotic concentrations are found for sulfamethoxazole (max. 1900 ng/L—USA), ciprofloxacin (max. concentration 1300 ng/L—Australia), norfloxacin—1150 ng/L—Australia), Erythromycin (max. 448 ng/L—Japan), and ofloxacin (306 ng/L—Italy), lincomycin (248 ng/L—Italy) [11–14]. It has been shown that their presence in waters is toxic to aquatic organisms [15,16]. The presence of antibiotics in drinking water was also found, e.g., triclosan—734 ng/L USA [17], ciprofloxacin—679.7 ng/L—China [18], erythromycin—20 ng/L—Germany [19], sulfamethoxazole—20 ng/L—the USA [20].

It was observed that the prolonged presence of low concentration antibiotics in human food also has a negative effect on health by reducing immunity, carcinogenic, teratogenic and mutagenic effects and disturbing physiological functions by acting as hormones [21]. Some antibiotics act as hormones and can interfere with physiological functions [15,21].

Insignificant concentrations of these compounds in the environment and food products cause an increase in the resistance of microorganisms to antibiotics. The presence of antibiotics with low concentrations in the environment results in the development of superbacteria resistant to all known antibiotics [22]. This is one of the most important threats and challenges that medicine faces today [23]. In 2009 report, it was stated that about 25,000 people in European Union countries die every year from hospital-acquired infections caused by bacteria resistant to all groups of antimicrobial drugs [24].

It should be stressed that there is a lack of systematic and comprehensive research into the concentrations of antibiotics in waters. However, their presence has been found in wastewater, groundwater, surface water and even drinking water all over the world, and their negative impact on human health and the environment has been demonstrated. This has inspired research on the effective methods of removing them from wastewater and water. Studies in the world of literature have analysed different ways of removing these specific pollutants from water and sewage. Therefore, a number of antibiotic removal technologies has been developed, including photocatalysis [25], chemical oxidation [26–28], photodegradation [29], membrane processes [30–32], and sorption on activated carbon [33]. Considering the economic and ecological aspects and the absence of by-products, adsorption on activated carbon is an important method for removing antibiotics from wastewater and water [34].

An analysis of the literature reveals that there is a problem with the presence of antibiotics in sewage, surface water and drinking water. Therefore, it is advisable to conduct the research into the methods of removing these compounds from water and sewage. The problems of adsorption of antibiotics, including chloramphenicol, on activated carbons have been explored in few literature reports. They often focus on the production of new adsorbents. However, it is also important to analyse the possibility of using activated carbons manufactured on an industrial scale and already used in wastewater treatment and water treatment or to propose effective methods of modification of these carbons. The main aim of the study is to broaden knowledge on the adsorption of chloramphenicol and, consequently, to optimize the process. Five commercial activated carbons used as chloramphenicol adsorbents were analysed. The partial goals of the study are: 1. Evaluation of the effect of activated carbons properties on the chloramphenicol adsorption efficiency; 2. Matching various chloramphenicol adsorption kinetics equations with the results; 3. Evaluation of the effect of the pH of the solution on adsorption efficiency; 4. Choice of isotherm equations for chloramphenicol

adsorption and determination of the maximum capacity; 5. Evaluation of the effect of high-temperature modification of activated carbons on adsorption efficiency.

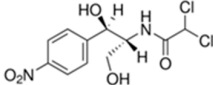
2. Materials and Methods

2.1. Measurement of Chloramphenicol Adsorption

Adsorption examinations were performed for model solutions prepared from deionized water and chloramphenicol produced by Sigma-Aldrich (Table 1). The concentration of chloramphenicol was determined spectrophotometrically at the wavelength of $\lambda = 278$. This wavelength for the spectrophotometric determination of chloramphenicol was also used by other researchers [35–37].

Examinations of kinetics and statics of adsorption of chloramphenicol adsorption were conducted from solutions with a volume of 250 cm³ to which 1 g of activated carbon was added. The solutions were mixed in a mechanical shaker at the speed of 160 rpm. Adsorption kinetics were determined for the initial concentration of chloramphenicol of 161 mg/L (0.5 mmol/L), whereas the adsorption isotherm was determined for the concentrations of 161, 258, 323, 484 and 646 mg/L (0.5 to 2 mmol/L). Adsorption kinetics were examined for solutions with a natural pH of chloramphenicol solution ($\text{pH} = 7 \pm 0.2$) and adsorption isotherms from solutions with pH of 2, 4, 6, 7, 8 and 10. The pH control was performed using an HCl or NaOH solution. Adsorption kinetics were determined based on the samples taken every 0.5 h. Using the results obtained from these measurements, a 10-hour shaking time of solutions with activated carbon was assumed for further measurements of adsorption isotherms. After this time, the samples were left for the next 14 h without shaking, which allowed for the determination of the concentrations on the following day.

Table 1. Physical and chemical properties of chloramphenicol [38,39].

Molecular Structure	Molecular Formula	Molecular Weight, g/mol	logKow	pKa	Molecular Radius, nm
	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₅	323.1	1.10	11.3	0.45

2.2. Models for Adsorption Kinetics and Isotherm

Adsorption kinetics was described by the following equations: pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris), Elovich (Table 2). The chloramphenicol adsorption data correlated with the theoretical models of Freundlich, Langmuir Tempkin and Dubinin–Radushkevich (Table 3).

Table 2. Kinetic models' equations [40,41].

Nonlinear Forma	Parameter
Pseudo-first-order	
$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$	q_e , mg/g—is the amount of solute adsorbed at equilibrium and q_t is the amount of solvent adsorbed at time t k_1 , h^{-1} —is the rate constant for the pseudo-first-order kinetic model
Pseudo-second-order	
$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$	q_e , mg/g—is the amount of solute adsorbed at equilibrium and q_t is the amount of solvent adsorbed at time t k_2 , h^{-1} —is the rate constant for the pseudo-second-order kinetic model
Elovich	
$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (3)$	α , mg/(g·h)—is the initial adsorption rate β , g/mg—is reflected the number of sites available for adsorption
Intraparticle diffusion model (Weber-Morris)	
$q_t = k_p t^{0.5} + C \quad (4)$	k_p , mg/(g·h ^{0.5})—is the slope which refers to the intra-particle diffusion rate constant C , mg/g—is the intercept which is a constant related to the thickness of the boundary layer

Table 3. Equation of isotherms used in research.

Nonlinear Forma	Linear Form	Parameter	Ref.
Freundlich			
$q = K_F C_e^{\frac{1}{n}} \quad (5)$	n —adsorption intensity K_F , mg/g—Freundlich isotherm constant		[41]
Langmuir			
$q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$	q_m , mg/g—solid phase concentration corresponding to the complete monolayer coverage of adsorption sites K_L , L/mg—the constant related to the free energy of adsorption		[41]
Dubinin-Radushkevich			
$q = q_s \exp(-K_D \varepsilon^2) \quad (7)$	q_s , mg/g—is a constant in the Dubinin–Radushkevich isotherm model which are related to adsorption capacity K_D , mol ² /kJ ² —is a constant in related to the mean free energy of adsorption ε —Dubinin–Radushkevich isotherm constant, $\varepsilon = RT \ln(1 + 1/C_e) \quad (8)$		[41]
Temkin			
$q = B \ln A_T C \quad (9)$	A , L/mg—Tempkin isotherm equilibrium binding constant B —Tempkin isotherm constant		[42]

where: C_e —equilibrium concentration of solute in bulk solution (mg/L), R is the gas constant, T is the absolute temperature

The constants of the adsorption kinetics and adsorption isotherm equations were determined from nonlinear forms using the Levenberg–Marquardt algorithm [43]. This algorithm was implemented by the `scipy.optimize.curve_fit` function, which is part of the SciPy library for the Python programming language. Furthermore, using the constant from the Langmuir equation, separator factor R_L (10) [38] was calculated.

$$R_L = \frac{1}{1 + K_L C_{0F}} \quad (10)$$

2.3. Activated Carbons Used in the Study

Chloramphenicol adsorption tests were carried out for five commercial activated carbons used for water treatment. These included granular activated carbons WG-12 (manufactured in Poland by

Gryfskand) and ROW 08 Supra (manufactured by NORIT, Belgium), grain-activated carbons Picabiol (Jacobi Carbons, Sweden), Filtrasorb 300 and Filtrasorb 100 (Chemviron, Carbon, the USA) (Table 4).

Table 4. Physical and chemical properties of activated carbons.

Parameter	Unit	Activated Carbon				
		WG-12	F-100	F-300	Picabiol	ROW 08 Supra
Surface area	m ² /g	1005	730	860	1344	796
Bulk density	g/dm ³	424	560	542	234	381
Iodine adsorption, LI,	mg/g	1050	850	1065	1071	1096
Methylene blue number, LM	cm ³	30	28	28	30	30
V _{micr.}	cm ³ /g	0.524	0.332	0.476	0.679	0.436
V _{meso.}	cm ³ /g	0.066	0.159	0.294	0.626	0.453
V _{total}	cm ³ /g	0.995	0.700	0.987	2.103	1.135

2.4. Modification of the WG-12 Carbon

Activated carbon WG-12 was modified in a rotary kiln at 400 °C in the atmosphere of air, steam or carbon dioxide and at 800 °C in the atmosphere of air, steam or carbon dioxide. The modification was conducted within 1 hour. Modification of carbon with oxygen from the air, carbon dioxide or water vapour leads to the formation of acidic oxygen functional groups on the surface of carbon. Oxidation or activation of activated carbon with water vapour or carbon dioxide at 800 °C leads to the formation of alkaline functional groups. The proposed methods of modification allow for obtaining sorbents of a different chemical character of the surface [44,45]. Before the modification the WG-12 carbons were rinsed a few times with distilled water. Carbon was modified in a rotary kiln for 1 h at a temperature of 400 or 800 °C (Figure 1). Modifying gases, such as air, water vapour and carbon dioxide were initially preheated to the same temperatures. The gas flow rate was 0.5 m³/h for air, 0.5 m³/h for carbon dioxide and 0.3 dm³/h for water vapour produced from water. Gases and activated carbon flowed through the reactor in the counterflow. They were initially heated up to the temperatures at which carbon oxidation was conducted. Initial carbon was further denoted as the WG0 and modified carbons, respectively: WG/400CO₂, where the number 400 denotes modification temperature in °C, H₂O, CO₂ or air are oxidizing gases (water vapour, carbon dioxide and air, respectively) (Figure 1).

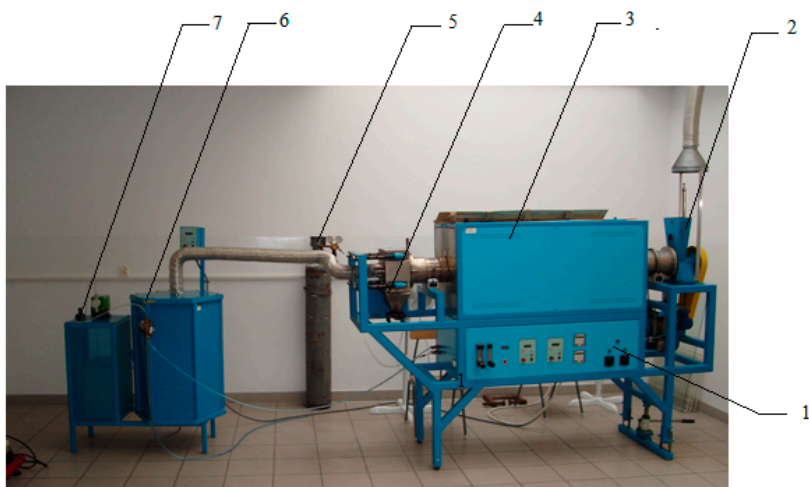


Figure 1. The testing stand of the high temperature modifications of activated carbon: 1. power and control cabinet, 2. activated carbon feeder, 3. insulating casing and rotary reactor, 4. activated carbon receiving chamber, 5. gas cylinder (air or CO₂), 6. superheater steam or gas heater, 7. water tank.

2.5. Research on Activated Carbons

The chemical properties of activated carbons were analysed by means of the Boehm method and Fourier transform infrared (FTIR) spectra.

Alkaline and acidic functional groups were determined using the Boehm method [46]. This method consists in selective neutralization of acid functional groups with bases of different power (NaHCO_3 —0.1 M, Na_2CO_3 —0.05 M, NaOH —0.1 M, $\text{C}_2\text{H}_5\text{ONa}$ —0.1 M) and alkaline groups—with 0.1 M HCl.

The FTIR transmission spectra were determined using the FTIR Spectrum 2000 spectrometer by Perkin-Elmer [47]. The examinations were conducted with the use of pastilles made of a mixture of activated carbon and KBr (1:300), which were first dried and desorbed at a pressure of 10^{-2} Pa in order to eliminate moisture. The tablets were then formed using a hydraulic press. The investigations were carried out in infrared radiation in the range of $4000 \div 400 \text{ cm}^{-1}$ wave numbers at a scanning speed of 0.2 cm/s.

Measurements of the specific surface area and porous structure were performed by means of a Micromeritics' ASAP 2010 system based on isothermal nitrogen adsorption at -196°C (77K) [48]. The size of specific surface area was determined using the BET (S_{BET}) isothermal method. The pore size was determined by means of the Horvath-Kawazoe method [49].

3. Results and Discussion

3.1. Kinetics of Chloramphenicol Adsorption

The kinetics of chloramphenicol adsorption from a 161 mg/L solution on all activated carbons used in the study (F-100, F-300, WG-12, ROW 08, Picabiol) were analysed. It was assumed that the time to the achievement of the adsorption equilibrium occurs when the change in concentration during 2 h is less than 0.5% of the initial concentration. Adsorption studies were conducted for 10 hours, analysing concentrations every 0.5 h (Figure 2). It was found that the adsorption equilibrium was established for all activated carbons used at that time. The shortest time of reaching adsorption equilibrium was obtained for activated carbon Picabiol (6 h), whereas the longest was for activated carbon F-300 (8 h).

The results were described by the following four kinetics equations: pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber-Morris), Elovich (Table 2, Table 5). A good match between the equations and the results was obtained for the model of pseudo-second-order kinetics (R^2 from 0.9542 to 0.9942) and intraparticle diffusion model (R^2 from 0.8866 to 0.9959) and the Elovich model (R^2 from 0.975 to 0.9884). For activated carbons F-100, ROW 08 Supra and Picabiol, higher R^2 values were obtained for the pseudo-second-order kinetics model, but for carbons F-300 and WG-12, this was the case for intraparticle diffusion model. The authors of previous studies on the kinetics of chloramphenicol adsorption on various carbon sorbents received very high R^2 for the pseudo-second-order kinetics model and a slightly lower R^2 for the intraparticle diffusion model [35,37,50]. In the case of the pseudo-second-order kinetics equation, q_e was more similar to the results of the experiment compared to the pseudo-first-order kinetics model. A better match of the pseudo-second order kinetics model indicates that chemical adsorption is an important factor controlling the speed of this process [37,50,51]. According to Ahmed et al. 2017, this indicates that the adsorption capacity is proportional to the number of active locations [51]. However, according to Płaziński and Rudziński (2011), pseudo-first-order and pseudo-second-order models are empirical models and do not represent any physical model [52]. Therefore, it is impossible to draw conclusions about the nature of the process. Taking into account the k_2 factor characterizing the rate of adsorption, the activated carbons can be ranked as follows: Picabiol > ROW08 > F-100 > WG-12 > F-300.

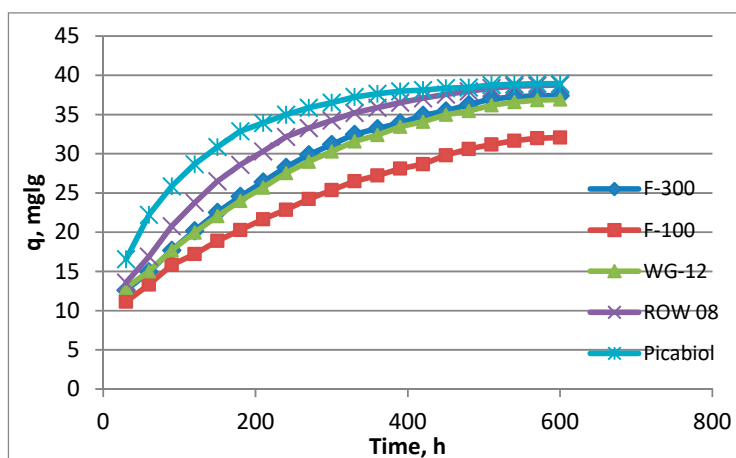


Figure 2. Kinetics of adsorption of chloramphenicol on commercial activated carbons.

Table 5. Constants for the kinetics equations: pseudo first-order, pseudo second-order, intraparticle diffusion model (Weber–Morris) and Elovich.

Parameter	Unit	Activated Carbon				
		F-300	F-100	WG-12	ROW 08 Supra	Picabiol
Pseudo-first-order						
q _e	mg/g	37.45	31.44	36.67	38.19	37.84
k ₁	h ⁻¹	0.3878	0.3807	0.3889	0.5004	0.7816
R ²	-	0.9538	0.9170	0.9405	0.9660	0.9499
Pseudo-second-order						
q _e	mg/g	46.61	38.86	45.45	45.77	43.015
k ₂	h ⁻¹	0.0088	0.0107	0.0092	0.0128	0.0251
R ²	-	0.9753	0.9542	0.9675	0.9883	0.9942
Elovich						
α	mg/(g·h)	30.83	26.79	31.26	50.55	139.6 3
β	g/mg	0.0866	0.1056	0.0898	0.0971	0.1261
R ²		0.9877	0.9819	0.9855	0.9884	0.9750
Intraparticle diffusion model (Weber-Morris)						
K _p	mg/(g·h ^{0.5})	10.8949	9.0064	10.5620	10.3495	8.4923
C	mg/g	5.43	4.80	5.61	9.17	15.75
R ²	-	0.9809	0.9959	0.9861	0.9451	0.8866

3.2. Isotherms of Chloramphenicol Adsorption on Commercial Activated Carbon

In order to compare activated carbons, adsorption isotherms for chloramphenicol adsorption from solutions with room temperature and $pH = 7 \pm 0.2$ were performed. The data presented in Figure 3 reveal large differences between the adsorption of chloramphenicol on different activated carbons. Taking into account the possibility of removing chloramphenicol, these carbons can be ordered as follows: Picabiol > ROW 08 > F-300 > WG-12 > F-100. However, the observed differences between the Picabiol and WG-12 coal are small. The same order of activated carbons is obtained when they are ranked according to the iodine number, total pore volume and total volume of micro- and mesopores (Table 4). This may indicate the significance of the phenomenon of volumetric pore filling. It is a mechanism concerning adsorption of organic compounds of quite large sizes, comparable to pore sizes [53]. The activated carbons tested are sorbents with a high content of micropores (from 32%–52%) and a diameter below 2 nm, while molecular radius of chloramphenicol is 0.45 nm. The ranking of carbons due to the adsorption of chloramphenicol is not in line with the

ranking due to the specific surface area. Picabiol activated carbon had the largest specific surface area and adsorbs chloramphenicol most efficiently. For other activated carbons, there is no simple dependence of surface on adsorption.

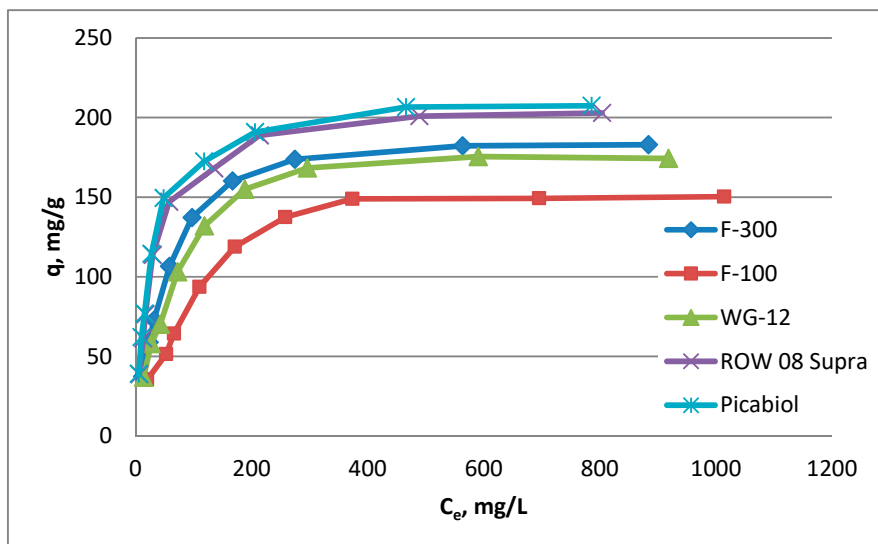


Figure 3. Isotherms of chloramphenicol adsorption on commercial activated carbons.

The obtained results were described by Freundlich, Langmuir Tempkin and Dubinin–Radushkevich equations (Table 3). These models are often used to describe the adsorption of organic compounds, including chloramphenicol on activated carbons [35,54–56]. However, all four forms were analysed in this paper. The determined constants of isotherms are shown in Table 6. The highest value of the correlation coefficient was obtained during the description of the results obtained with the Langmuir equation (Table 6) ($0.9678 < R^2 < 0.9961$). In the case of the Langmuir isotherm, it is beneficial to calculate the distribution coefficient R_L (Table 6). The ranges of the R_L parameter value for all activated carbons ranged from 0.02 to 0.28. Since these values were higher than 0 and lower than 1, adsorption in the examined concentration range had a beneficial pattern. A good fit of the Langmuir isotherm may indicate a monolayer adsorption of chloramphenicol on activated centres. The obtained monolayer capacities calculated from the Langmuir equation range from 174.64 (F-100) to 214.91 mg/g (Picabiol and ROW 08 Supra).

The value of the constant n in the Freundlich equation determines adsorption intensity. Since the values of this coefficient contained in Table 5 for all commercial activated carbons were in the range of $1 < n < 10$, it can be concluded that the adsorption of chloramphenicol is beneficial. The reversal of the coefficient n ($1/n$) ranges from 0 to 1 and indicates the degree of diversity of active places on the activated carbon surface. Obtained values of $1/n$ (from 0.3218 to 0.3891) are similar for the adsorbents tested. K_F coefficient ranges from 12.381 (F-100) to 31.667 mg/g (Picabiol).

Table 6. Constants for isotherms of chloramphenicol adsorption on commercial activated carbons.

Parameter	Unit	Activated Carbon				
		F-300	F-100	WG-12	ROW 08 Supra	Picabiol
Freundlich						
1/n	-	0.3665	0.3981	0.3781	0.3288	0.3218
K _F	mg/g	20.044	12.381	17.447	29.208	31.667
R ²	-	0.8784	0.8928	0.8918	0.8700	0.8698
Langmuir						
q _m	mg/g	200,67	174,68	195.45	212.29	214.91
K _L	L/mg	0.0197	0.0106	0.0161	0.0354	0.0405
R ²	-	0.9931	0.9678	0.9873	0.9953	0.9961
R _L	-	0.03–0.24	0.06–0.37	0.04–0.28	0.02–0.15	0.02–0.13
Dubibin–Radushkevich						
q _s	mg/g	168.21	145.64	162.13	182.87	185.53
K _D	mol ² /kJ ²	0.00014	0.00061	0.00022	0.00004	0.00003
R ²	-	0.8818	0.9032	0.8573	0.8886	0.8634
Temkin						
A	L/mg	0.2690	0.1305	0.2690	0.5766	0.6982
B	-	37.36	34.40	37.07	36.42	36.29
R ²	-	0.9444	0.9206	0.9419	0.9534	0.9541

High values of R² coefficient (from 0.9206 to 0.9541) were also obtained for the Temkin's isotherm. It assumes, similar to the two previous isotherms, that the adsorption is of monolayer character. Similar to Freundlich's isotherm, the second assumption of this isotherm is the heterogeneity of the surface. However, Langmuir's isotherm describing the chloramphenicol adsorption also assumes homogeneity of the surface. These results may indicate small differences in the adsorption potential of the surface of the analysed activated carbons.

The only isotherm for which correlation coefficients were much lower was the Dubinin–Radushkevich model. However, for this model, which describes the volumetric pore filling, the values of R² are high (0.8634–0.9032). Nevertheless, obtaining a better fit to the previously considered models may indicate that the volumetric pre-filling may be of the mechanisms behind chloramphenicol adsorption.

3.3. Impact of Process Conditions

The effect of the adsorbent dose and pH value solution on the level of chloramphenicol adsorption was analysed for WG-12 activated carbon.

The effect of the adsorbent dose was analysed for chloramphenicol concentration of 323 mg/L (1 mmol/L). Similar doses of activated carbon were also used by other researchers, e.g., Fen et al. 2010—8 g/L, Zhu et al. 2018—1 g/L [50,57]. The applied amounts of activated carbon allowed for removing chloramphenicol from 36% (dose 1 g/L) to over 99% (dose 8 g/L) (Figure 4). The differences in the efficiency of chloramphenicol removal between the dose of 6 and 8 g/L are small and amount to about 2%.

The pH value of the solution may have an effect on the adsorption process due to the likelihood of changing the properties of adsorbents and adsorbates. Chloramphenicol is hydrolysed at pH below 2 and above 9 [36,37]. The effect of the pH of the solution on the efficiency of chloramphenicol adsorption was found to be of minor importance for this parameter (Figure 5, Table 7). Slightly better adsorption results were obtained from acidic (pH = 2 and 4) and alkaline (pH = 10) solutions compared to the solutions close to neutral (pH = 6 and 8). Lower adsorption from solutions with pH = 6 and 8 may indicate electrostatic interaction as one of the adsorption mechanisms. The effect of the pH value on the level of adsorption is insignificant, but it may indicate various mechanisms of decisive effect during adsorption from solutions with different pH. Dissolved in water,

chloramphenicol has a positive charge due to dissociation of the hydroxyl group. It can be more strongly attracted to the negatively charged surface of the activated carbon in alkaline solutions. At low pH, the donor-acceptor mechanism (EDA) between the nitro group in the chloramphenicol molecule and the positively charged surface of activated carbon can be decisive. Other mechanisms responsible for the adsorption of chloramphenicol can be the $n-\pi$ interactions between the benzene rings of chloramphenicol (electron acceptor) and carbonyl groups on the surface of activated carbon (electron donors) and the $\pi-\pi$ interactions between π electrons of activated carbons and π electrons in the aromatic ring of chloramphenicol [51,54,58]. Similar trends in the effect of the pH were obtained by other researchers [36,37,53,59].

The chloramphenicol adsorption mechanism is dependent on the pH of the solution [51,55].

- pH about 1,5: $AC-OH^+$ chloramphenicol = EDA interaction
- pH = 4.0–4.25: $AC-COO^- \cdots H^+ \cdots O_2N$ -chloramphenicol = CABH formations with EDA interaction
- pH above 7.0: $AC-OH^+$ chloramphenicol ($H^+/-OH/NO_2/-NH/-Cl$) = H-bond formations repulsions interactions

In this case, the highest R^2 values were obtained for the Langmuir and Temkin isotherm. The small effect of the pH value of the solution on the adsorption process reflects the capacity of the monolayer calculated from the Langmuir isotherm, which ranges from 189.80 to 207.61 mg/g.

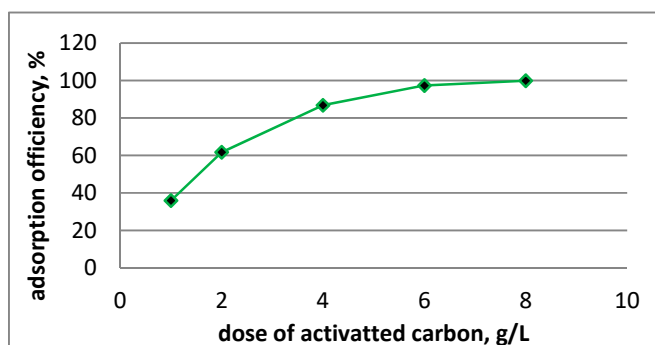


Figure 4. Effect of the doses of activated carbon WG-12 on the efficiency of chloramphenicol adsorption.

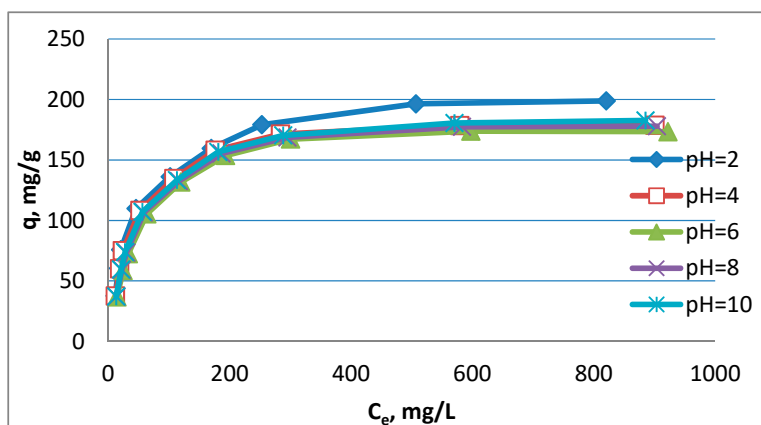


Figure 5. Effect of solution pH on the effectiveness of chloramphenicol adsorption on activated carbon WG-12.

Table 7. Value of coefficients of chloramphenicol adsorption isotherms depending on the pH of the solution (Freundlich, Langmuir (form I) and Temkin).

Parameter	Unit	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
Freundlich						
1/n	-	0.336	0.3557	0.3593	0.3585	0.3566
K _F	mg/g	23.409	20.40	19.45	22.59	20.78
R ²	-	0.871	0.8821	0.8776	0.8961	0.8852
Langmuir						
q _m	mg/g	207.61	190.41	189.80	192.14	195.28
K _L	L/mg	0.0232	0.0251	0.0191	0.0204	0.0209
R ²	-	0.9902	0.9952	0.9951	0.9970	0.9974
Dubinin-Radushkevich						
q _s	mg/g	170.28	160.46	158.34	160.28	162.05
K _D	mol ² /kJ ²	0.00006	0.00006	0.00013	0.00010	0.00009
R ²	-	0.8519	0.8772	0.8765	0.87737	0.8702
Temkin						
A	L/mg	0.3151	0.3739	0.2587	0.2791	0.2841
B	-	38.58	34.13	35.43	35.65	36.39
R ²	-	0.9800	0.9530	0.9497	0.9581	0.9648

3.4. Chloramphenicol Adsorption on Modified Activated Carbons

The modification of activated carbon WG-12 at the temperature of 400 and 800 °C was carried out on a test stand prepared on a fractional-technical scale. In order to characterize modified carbons, the following were determined: specific surface area and porous structure, number of acid and alkaline functional groups (Table 8) (Supplementary Materials—Table S1), FTIR spectra (Supplementary Materials—Figure S1). Modification of WG-12 activated carbon led to the increase in specific surface area, volume of micropores, and the number of acid and alkaline groups determined by the Bohem method. These differences, however, were not large and reached a maximum of several percent. For activated carbons modified at 400 °C, the number of acid groups increased, whereas at 800 °C, this number decreased. Minor changes in the FTIR spectra were also observed. The applied activation procedures led to a gentle oxidation of the carbon surface, causing a relative increase in the intensity of bands of carbonyl groups >C=O (1740 ÷ 1500 cm⁻¹) and C-O-C ester groups (1300 ÷ 1000 cm⁻¹) compared to OH hydroxyl groups (ca. 3450 cm⁻¹). Modification with CO₂ (to a lesser extent with H₂O) caused the appearance of an additional band of acetyl-aldehyde groups -O-CH=O (1385 cm⁻¹). Oxidation with oxygen from the air caused a small peak of -COOH carboxyl groups (ca. 1720 cm⁻¹).

On all modified activated carbons, the chloramphenicol adsorption was higher than on non-modified carbon (Figure 6 Table 9). The highest monolayer capacity (q_m = 343.12 mg/g) was characteristic of carbon modified at 800 °C with carbon dioxide and it was twice as high as for unmodified carbon (q_m = 145.95 mg/g). Modified activated carbons can be ranked according to the capacity of the monolayer in the following order: WG0 < WG400AIR < WG400H₂O < WG400CO₂ < WG800H₂O < WG800CO₂. In order to evaluate the effect of the initial parameter and modified activated carbons (specific surface area, porous structure, number of groups determined by Bohem method), Pearson's correlation coefficients (Table 10) were calculated. Virtually full relationships (0.93) between q_m and the total capacity of micro and mesopores were found, whereas a very high correlation was demonstrated between q_m and micropore volume, specific surface area and the number of alkaline oxides.

Table 8. Characteristic of modified activated carbons.

Parameter	WG-12	WG/400AIR	WG/400H ₂ O	WG/400CO ₂	WG/800H ₂ O	WG/800CO ₂
F _{BET} , m ²	1098	1208	1163	1181	1199	1239
V _{mikro} , cm ³ /g	0.530	0.538	0.542	0.551	0.548	0.553
V _{mezo} , cm ³ /g	0.048	0.044	0.0455	0.0403	0.0468	0.051
V _{makro} , cm ³ /g	0.417	0.413	0.413	0.343	0.321	0.370
B*, mmol/g	0.467	0.535	0.521	0.525	0.546	0.539
A*, mmol/g	0.586	0.629	0.585	0.853	0.562	0.549

* B—basic groups, A—acidic groups.

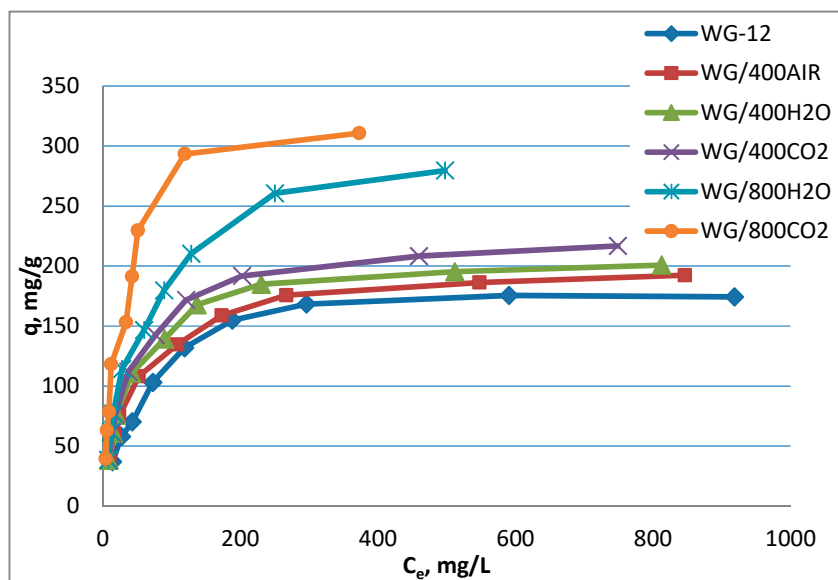
**Figure 6.** Isotherms of chloramphenicol adsorption on modified activated carbons.

Table 9. Isotherms of chloramphenicol adsorption on high-temperature modified activated carbons.

Parameter	WG-12	WG400AIR	WG400H2O	WG400CO2	WG800H2O	WG800CO2
Freundlich						
1/n, -	0.3781	0.3473	0.3503	0.3640	0.4602	0.457
K _F , mg/g	17.45	23.07	24.66	24.92	20.47	29.80
R ²	0.8918	0.9136	0.8924	0.9007	0.9392	0.9021
Langmuir						
q _m , mg/g	195.45	199.81	210.58	225.64	306.54	343.12
K _L , L/mg	0.0160	0.0235	0.0264	0.0264	0.0184	0.0340
R ²	0.9878	0.9950	0.9961	0.9971	0.9881	0.9751
Dubinin–Radushkevich						
q _s mg/g	164.99	174.68	183.46	217.86	246.28	
K _D mol ² /kJ ²	0.00006	0.00005	0.00005	0.00005	0.00005	0.00002
R ²	-	0.8248	0.8497	0.8354	0.7782	0.7885
Temkin						
A, L/mg	0.2690	0.1305	0.2134	0.5766	0.6982	0.8671
B, -	37.069	36.26	38.01	41.31	60.05	65.11
R ²	0.9419	0.9808	0.9673	0.9785	0.9918	0.9606

Table 10. Pearson correlation coefficients.

Parameter	S _{BET}	V _{micro}	V _{micro + meso}	Acidic Groups	Basic Groups
q _m	0.69	0.75	0.93	−0.50	0.63

However, similar to this study, other researchers have described the kinetics of chloramphenicol adsorption with pseudo-second order kinetics equations with the highest correlation coefficient. Freundlich and Langmuir isotherms are most commonly used to describe adsorption isotherms.

The monolayer capacities obtained for commercial and modified activated carbons are at a medium level compared to those obtained by other researchers (Table 11).

However, similar to this study, other researchers have described the kinetics of chloramphenicol adsorption using pseudo-second order kinetics equations with the highest correlation coefficient. Freundlich and Langmuir isotherms are most commonly used to describe adsorption isotherms.

Table 11. Comparison of chloramphenicol adsorption results based on literature reports.

Activated Carbon	Adsorption Conditions	The Equations of Adsorption Kinetics Studied ¹	Adsorption Isotherms Equations Tested ¹	q _m , mg/g	Ref.
AC Picabiol		1. PSO* 2. E* 3. PFO*		214.91	
AC WG-12	T* − 20 °C C ₀ * − 161–646 mg/L D* − 400 mg AC/100 mL pH 2–10	4. IPD* 1. E 2. PSO 3. IPD 4. PFO	1. Langmuir 2. Temkin 3. Freundlich 4. D-R*	195.45	This work
WG-12 modified		-		343.12	
AC from waste	T − 20, 40, 60 °C C ₀ − 300–1000 mg/L D − 50 mg AC/50 mL pH 2–12	1. PSO 2. IPD 3. PFO	1. Langmuir 2. Freundlich	160–893 mg/g	[50]

AC PEG-400	T—30, 40, 50 °C C ₀ —100–400 mg/L D—200 mg AC/200 mL	1. PSO 2. E 3. PFO	1. Temkin 2. Freundlich 3. Langmuir	170– 209 mg/g	[54]
AC from potassium citrate	T—10, 20, 30 °C C ₀ —30–300 mg/L D = 2 mg AC/10 mL pH 3–11	1. PSO 2. PFO	1. Langmuir 2. Freundlich 3. Temkin	329– 506 mg/g	[35]
AC from eucalyptus wood biomass	T—25 °C C ₀ —0.25–20 mg/L D—80 mg AC/1000mL pH 4–4.25	1. PSO 2. PFO 3. IPD	1. Freundlich 2. Langmuir	21 mg/g	[51]
AC from <i>Typha orientalis</i>	T—25 °C C ₀ —32.3–96.9 mg/L D—30 mg AC/50 mL pH 2–8	1. PSO 2. PFO 3. IPD	1. Freundlich 2. Langmuir	137	[39]
F-400				140	
Bamboo charcoal	T—30 °C C ₀ —5–100 mg/L D—20 mg BC/20 mL pH 7	-	1. Freundlich 2.D-R 3. Langmuir	8.1	[56]

* PFO—pseudo-first-order, PSO—pseudo-second-order, IPD—Intra-particle diffusion, E—Elovich, D-R—Dubinin-Radushkevich, D—dose of activated carbon/volume of the solution, T—temperature tested, C₀—initial concentration; ¹ the order of equations based on the correlation coefficient R².

4. Conclusions

1. Commercial activated carbons (micro- or micro-mesoporous) such as F-100, F-300, ROW 08 Supra, WG-12, Picabiol can be used to remove chloramphenicol from water since they are characterized by quite a high adsorption capacity (q_m from 174.68 to 214.91 mg/g). Activated carbons can be ranked according to their adsorption capacity in the following order: Picabiol > ROW 08 > F-300 > WG-12 > F-100.
2. The order of activated carbons according to their adsorption capacity is consistent with their order according to the total volume of pores and the total volume of micro- and mesopores. This indicates the significance of the phenomenon of volumetric pore filling.
3. The analysis of various adsorption kinetics equations (pseudo-first-order, pseudo-second-order, intraparticle diffusion model (Weber–Morris), Elovich) revealed that it is impossible to determine a single equation, which, for all activated carbons, would describe the results of the examinations with the highest correlation coefficient R₂. Among the models used, the adsorption results are described the least efficiently by the pseudo-first order model.
4. The insignificant effect of pH on adsorption efficiency was also found. It was observed that adsorption was better for acidic and alkaline solutions compared to solutions close to neutral. The maximum adsorption was obtained from solutions with pH = 2, but the adsorption capacity obtained was only 9% higher compared to adsorption from solutions with pH = 6.
5. The high-temperature modification of activated carbon WG-12, adsorbents with much higher adsorption capacities were obtained for chloramphenicol. The highest monolayer capacity (q_m = 343.12 mg/g) was obtained for carbon modified at 800 °C in the atmosphere of carbon dioxide and was almost twice as high as in the case of non-modified WG-12. Carbons modified at 800 °C were characterized by an increased specific surface area, volume of micropores and increased number of aerobic groups of alkaline character.
6. It was found that among the analysed isotherms (Freundlich, Langmuir, Dubinin–Radushkevich, Temkin), the highest correlation coefficient in describing the results was obtained for the Langmuir model, whereas the lowest was for the Dubinin–Radushkevich. Temkin's and Freundlich's isotherms described the results well, but slightly worse than Langmuir's isotherm.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: FTIR spectra for the initial and modified activated carbon, Table S1: Number of surface functional groups at the initial WG0 and oxidized activated carbons determined by the Boehm method.

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