Adsorption of Naproxen Sodium from Aqueous Solutions on Commercial Activated Carbons

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ABSTRACT

The pollution of surface and drinking water with pharmaceuticals is one of the growing problems. One of the groups used in large quantities involves nonsteroidal anti-inflammatory drugs which can be bought without a prescription. This group includes naproxen, which was identified in wastewater, surface water and even drinking water all over the world. The aim of the study was to assess the opportunities for the removal of naproxen sodium from water using carbon sorbents. The measurements were carried out for three commercial microporous (WG-12 and F-300) and micro-mesoporous (ROW 08 Supra) activated carbons. The kinetics and statics of adsorption were studied. The adsorption from solutions with pH from 6 to 10 and temperature from 20°C to 40°C was analysed. It was found that the higher the pH, the lower the adsorption and the higher the temperature, the greater the adsorption of naproxen sodium. The highest adsorption of naproxen sodium was obtained for the F-300 activated carbon, whereas the lowest – for the ROW 08 Supra activated carbon. It was found that the adsorption results depend on many factors, the most important of which include hydrogen bonds between carboxyl groups of naproxen sodium and phenolic groups on the surface of activated carbons and electrostatic repulsion between the anions of naproxen sodium and negatively charged the surface of the activated carbon. The results of adsorption kinetics were described with the following models: pseudo-first order and pseudo-second order, intraparticle diffusion, and Elovich. The highest values of correlation coefficient R^2 were obtained for the pseudo-second order and Elovich model. The results of adsorption statics were described using the Freundlich, Langmuir, and Temkin models. A good match between isotherms and the obtained results was obtained for the Freundlich and Temkin equations. It was found based on the adsorption intensity $1/n$ and distribution coefficient R_L that this process was beneficial for all the considered activated carbons and the investigated adsorption conditions.

Keywords: naproxen sodium; activated carbon, adsorption

INTRODUCTION

The pollution of the environment by pharmaceuticals and protection against their effects is an increasingly common topic of research. The high consumption of drugs results in their presence in raw and treated wastewater, surface water, groundwater and even drinking water all over the world (Lach et al. 2018; Szymonik et al., 2017). Although this problem has been addressed for many years, no standard has been established to date and there are no legal documents specifying the permissible contents of pharmaceuticals in the raw sewage discharged from wastewater treatment plants, and thus released to ecosystems. The most common pharmaceuticals identified in the aquatic environment are beta-blockers, nonsteroidal anti-inflammatory drugs, antibiotics, female sex hormones, lipid metabolism regulators and antiepileptic drugs (Nikolaou et al., 2007). As early as 2009, de Voogt et al. found that the substances that deserve special attention include atenolol, bezafibrate, ciprofloxacin, diclofenac, erythromycin, gemfibrozil, ibuprofen, carbamazepine, naproxen and sulfamethoxazole, since they are highly toxic to the living organisms, have a high persistence in the environment and are consumed in large quantities. These researchers

postulated that these substances should be monitored first (Voogt et al., 2009). However, in 2012, the European Commission added only diclofenac, ethinylestradiol and estradiol (Annex of Directive 2000/60/EC of European Parliament and the Council on priority substances in the field of water policy, Brussels 31.01.2012;2011) to the list of compounds the concentrations of which in the EU waters should be monitored. The studies devoted to the problem of environmental pollution with pharmaceuticals are constantly being conducted, which is evidenced by the fact that on 11 March 2019, the European Commission issued a communication entitled „European Union Strategic Approach to Pharmaceuticals in the Environment".

Due to their anti-inflammatory, analgesic and antipyretic effects, the nonsteroidal anti-inflammatory drugs (ibuprofen, naproxen, diclofenac, ketoprofen) are often used and commonly detected in the aquatic environment (Bui and Choi, 2010; Onal et al., 2007). These pharmaceuticals are considered to be of high environmental risk, even if they occur in water in trace (ng/L) or low amounts (μg/L) (Hernando et al., 2006; Manzo et al., 2014) . These compounds are often removed in conventional wastewater treatment plants with low efficiency (Feng et al., 2013).

Naproxen is widely used in medicine and veterinary medicine as an analgesic, anti-inflammatory and antipyretic agent. Despite the lack of monitoring of this compound, its presence was found in the surface waters of many countries, e.g. Poland (300 ng/L) (Baranowska and Kowalski, 2012), Czech Republic (180 ng/L) (Baranowska and Kowalski, 2012), Sweden (130 ng/L) (Daneshvar et al., 2010), Hungary (62 ng/L) (Helenkar et al., 2010), China (40 ng/L) (Wang et al., 2010), Italy (10 ng/L) (Patrolecco et al., 2015), France (9 ng/L) (Togola and Budzinski, 2008), Finland (3.3 ng/L) (Lindholm-Lehto et al., 2016), France (1 ng/L) (Minguez et al., 2016). The presence of naproxen in the surface water is a consequence of incomplete removal of this drug in conventional wastewater treatment plants. The presence of naproxen was found in the treated wastewater in e.g. France (3210 ng/L (Santos et al., 2005) and 289 ng/L (Togola and Budzinski, 2008)), Germany (300 ng/L) (Kasprzyk-Hordern et al., 2007), Spain (91 ng/L) (Boleda et al., 2011), and Poland (82 ng/L) (Czerwiński et al., 2015). This medicine was also present in drinking water in Poland (13 ng/L) (Zgoła-Grześkowiak, 2010),

Spain (0.5 ng/L) (Carmona et al., 2014), and France (0.2 ng/L) (Togola and Budzinski, 2008).

The analysis on the usefulness of various methods of removing naproxen revealed that high efficiency was obtained in the cases of using oxidation, membrane and adsorption methodologies (Klavarioti et al., 2009; Monteiro and Boxall, 2010; Tambosi et al., 2010). However, it should be stressed that in many cases, the naproxen oxidation products are more toxic than the parent compound (Stancova et al., 2015). Taking into account the high efficiency of adsorption, the lack of by-products and the ease of the process, this methodology should be considered for the removal of naproxen. To date, the topic of naproxen adsorption has been discussed by few researchers and requires more extensive analysis.

The aim of this paper was to investigate the potential of using commercial carbon sorbents to remove naproxen sodium from water, analyse the kinetics and statics of adsorption and to evaluate the effect of process conditions on the process efficiency.
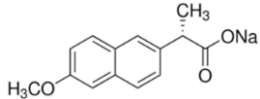
METHODOLOGY

Naproxen sodium adsorption

The naproxen sodium used in the experiment was produced by Sigma Aldrich. The characteristics of naproxen sodium are shown in Table 1. The concentrations were determined with the spectrophotometric method (UV-vis) at λ=230 nm (Attia et al., 2013; Onal et al., 2007). The properties of sodium diclofenac are presented in Table 1.

The kinetics and statics of adsorption

The conditions of conducting the process of adsorption kinetics and statics are presented in Table 2. The experiments were carried out for a 0.25 L solution. The solution with activated carbon was mixed with the rotational speed of 160 rpm. The adsorption kinetics examinations were conducted for 10 h taking samples every 1 h, whereas adsorption statics – for 24 h (10 h of mixing and 14 h of contact without mixing).

The following models were used to describe the kinetics of adsorption: pseudo-first-order, pseudo-second order, Elovich, intraparticle diffusion model (Weber-Morris). The adsorption statics were described using the models developed by

Table 1. Physical and chemical properties of chloramphenicol (Farmakopea Polska, 2008; Naproxen sodium)

Molecular structure	Molecular formule	Molecular weight, g/mol	Solubility, g/L	pKa	The degree of ionization, %**	pH of the solution*
	$C_{14}H_{13}NaO_3$	252.24	30	4.19	98.5 (pH=6) 99.9 (pH=8)	7.2

* This concerns 1 mmol/L solution.
** Calculated using the Henderson and Hasselbach equations.

Table 2. Conditions of the naproxen sodium adsorption

Process	Concentration, mg/L	pH of the solution	Process temperature, K	Dose AC, g/L
Adsorption kinetics	252	7	293	4
Adsorption statics	252; 378; 504; 630; 756; 1008; 1261	6, 8, 10	292, 303, 313	4
Effect of dose AC	252	7	293	1; 2; 3; 4; 5; 6; 7; 8; 9; 10

Langmuir, Freundlich, and Temkin (Dada et al., 2012; Tran et al., 2017; Tran et al., 2017). Furthermore, the R_L separator was calculated based on the Langmuir isothermal constants. The constants of these equations were calculated from non-linear forms using Microsoft Excel Solver.

Activated carbons

Commercial activated coals used in water treatment plants: ROW 08 Supra (Norit, Poland), F-300 (Chemviron Carbon) and WG-12 (Gryfskand), were used in the examinations. These are microporous sorbents, with large specific surfaces and high sorption properties compared to the test substances (Table 3).

An FTIR Spectrum 2000 spectrometer (Perkin-Elmer) was used to determine the FTIR transmission spectra (Lach, 2019).

RESULTS

Naproxen sodium adsorption kinetics

The naproxen sodium adsorption kinetics with the 252 mg/L solution (Fig. 1) was analysed for all activated carbons used in the study. The research was conducted for 10 h, with the samples taken every 1 h. The adsorption equilibrium was established for all activated carbons at that time. The shortest time to determine the adsorption equilibrium was obtained for the F-300 activated carbon (5 h). For other carbon sorbents (ROW 08 Supra and WG-12), this time was 9 h. In this study, it was assumed that the adsorption equilibrium occurs when the change of concentration in the solution within 1 h is less than 1% of the initial concentration.

Table 3. Properties of activated carbons used in tests (Lach, 2019)

| Parameter	Unit	Activated carbons		
		ROW 08	F-300	WG-12
Surface area,	m^2/g	897±30	847±29	1034±37
$V_{micr.}$		0.436	0.476	0.524
$V_{meso.}$	cm^3/g	0.453	0.294	0.066
$V_{total.}$		1.135	0.987	0.995
pH of water extract		6.67	7.15	6.62
Methylene blue number	LM	34	31	28
Iodine adsorption	LI, mg/g	1091	1055	1117
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 H N	,%	80.05 1.419 0.932	85.25 0.771 0.725	79.00 1.252 0.813
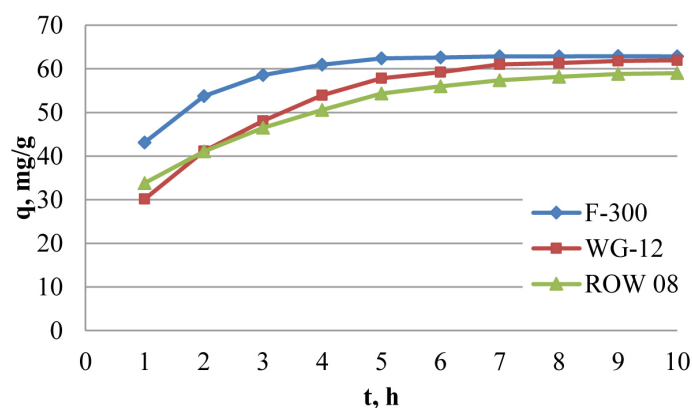
Fig. 1. Adsorption kinetics of naproxen sodium on activated carbons: F-300, ROW 08 Supra, F-300

Four kinetic models were used to describe the results: pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion (Table 1). Among the models used, the best fit for WG-12 and F-300 activated carbons was obtained for the pseudo-second order kinetics equation (R² 0.9794 and 0.9712, respectively), and for ROW 08 Supra-Elovich equation (R² 0.9860). According to Płaziński and Rudziński (2011), the pseudo-first and pseudo-second order models are empirical and do not represent any physical model (Płaziński and Rudziński, 2011). A good match between the results obtained and the Elovich model may indicate a significant effect of chemisorption on the process effects (Tran et al., 2017). Other authors also obtained a good match between the results of naproxen sodium kinetics on activated carbon

and the pseudo-second order equations (Baccar et al., 2012; Onal et al., 2007; Sarici-Ozdemir and Onal, 2010). The analysis of the k_2 coefficient of the pseudo-second order kinetics equation, which characterizes the adsorption rate and the Elovich isothermal coefficient α (initial adsorption rate), activated carbons can be ranked as follows: F-300> ROW08 > WG-12. It should be noted that the rate of adsorption is almost twice as high on F-300 than on the other two.

Naproxen sodium adsorption statics

The studies on the adsorption of naproxen sodium were conducted on three commercial activated carbons from solutions with pH of 6, 8 and 10. In these solutions, naproxen sodium is well

Table 4. Constant equations of adsorption kinetics of naproxen sodium: pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion model (Weber-Morris)

Nonlinear forma	Parameter	ROW 08 Supra	WG-12	F-300
	Pseudo-first-order			
$q_t = q_e(1 - e^{-k_1 t})$	k_1, h⁻¹ - is the rate constant for the pseudo-first-order kinetic model	0.6102	0.5539	1.0629
	R² - correlation coefficient	0.8884	0.8374	0.8036
	Pseudo- second- order			
$q_t = \dfrac{q_e^2 k_2 t}{1 + k_2 q_e t}$	k_2, h⁻¹ - is the rate constant for the pseudo-second-order kinetic model	0.0261	0.0218	0.0509
	R² - correlation coefficient	0.8741	0.9794	0.9712
	Elovich			
$q_t = \dfrac{1}{\beta} \ln(1 + \alpha\beta t)$	α, mg/(g·h) -is the initial adsorption rate	198.68	115.58	567.10
	β, g/mg -is reflected the number of sites available for adsorption	0.0843	0.0670	0.0940
	R²- correlation coefficient	0.9860	0.9656	0.8694
	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	11.74	14.35	7.73
	C, mg/g - is the intercept which is a constant related to the thickness of the boundary layer	25.18	21.39	41.94
	R²	0.9405	0.8954	0.8569

soluble, and at the same time, the pH range is in accordance with the guidelines for drinking water (pH=6.5÷9.5) (Fig. 2). In the analysed solutions, naproxen sodium occurs in a dissociated form (pH=6, dissociation 98.5%, pH=8 – 99.9%). In these solutions, the compound occurs mainly in the form of anions. Regardless of the activated carbon used, an increase in the pH of the solution caused a decrease in the adsorption of naproxen sodium. For all activated carbons, the differences between pH 6 and 8 were small. A very clear decrease in the sorption capacity was observed when the pH of the solutions was increased to 10. The observed decrease in adsorption may be related to the competitiveness of naproxen sodium anions and OH^- ions, with their number greater for the higher pH of the solution. Both basic and

acidic groups are usually present on the surface of activated carbons produced using the steam-gas process. Dissociation of weak basic groups (O^-, COO^-) of the surface of activated carbons is observed in alkaline solutions, leading to the electrostatic repulsion of the sorbed anions. Similar effects of pH were also found by other researchers (Baccar et al., 2012; Cuerda-Correa et al., 2010). In a solution with pH=6, dissociation of weak basic functional groups on the carbon surface and electrostatic attraction between these groups and naproxen sodium anions is likely. Taking into account the obtained adsorption capacities, regardless of the pH of the solution, the best results were obtained on the F-300 activated carbon, whereas the weakest were found for the ROW 08 Supra activated carbon. The F-300 activated carbon has
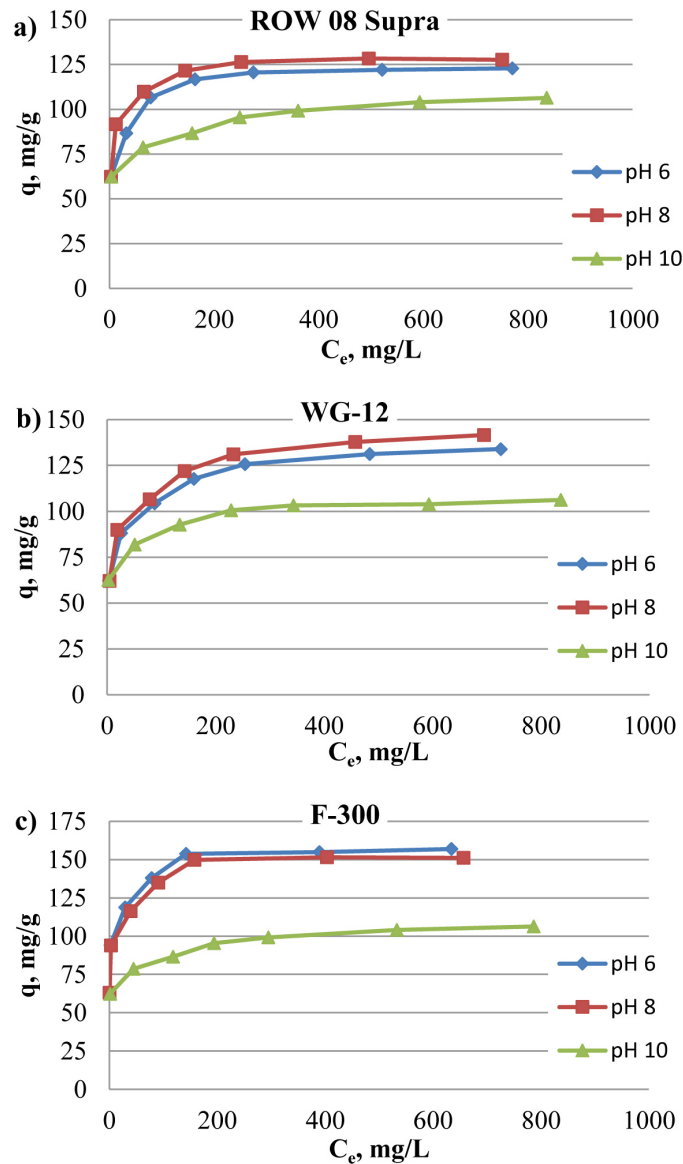

Fig. 2. Effect of pH on adsorption of naproxen sodium on activated carbons: a) ROW 08 Supra, b) WG-12, c) F-300

the highest number of acidic groups and the lowest number of basic groups determined by the Bohem method (Table 3). Other activated carbons were characterized by a similar number of acidic groups. The adsorption of naproxen sodium occurred in the smallest amounts on the ROW 08 activated carbon, despite the fact that this carbon had quite a large number of basic groups. On the basis of the study results, no simple correlations were found between the number of groups on the surface of activated carbons and the effectiveness of naproxen sodium adsorption. The porous structure and availability of active places can also influence the results. However, since adsorption from the solution with pH=10 is quite high (ca. 100 mg/g), electrostatic interactions are not decisive during the adsorption of naproxen sodium. The F-300 activated carbon, which was the most effective in naproxen sodium absorption, is characterized by the smallest specific surface area, the smallest total pore volume and the average volume of micropores among the activated carbons tested. Therefore, physical adsorption is most likely not the decisive mechanism for the adsorption of naproxen sodium. Similarly to other nonsteroidal anti-inflammatory drugs, adsorption may result from hydrogen bonds (H-bond) between phenolic groups on the surface of activated carbon and carboxyl groups of naproxen sodium (Bhadra et al., 2016; Paul et al., 2014). The examinations of FTIR spectra confirmed the highest number of phenolic groups (the highest intensity of the bands of phenolic O-H groups that form the hydrogen bond 3200–3500 cm^{-1}) on the F-300 activated carbon, which was characterized by the highest efficiency of naproxen sodium removal.

The obtained results were described using the Freundlich, Langmuir and Tempkin isothermal models (Table 5). High values of the correlation coefficient were obtained by describing the results with the Freundlich equation ($0.9423<R^2<0.9835$) and Temkin equation ($0.849<R^2<0.9912$). Adsorption on all activated carbons was beneficial because the value of Freundlich isothermal factor $1/n$ ranged from 1 and 10 (except for adsorption on WG-12 carbon from a solution with pH=10 when $1/n=0.0933$). For all activated carbons and for all analysed pH values, the $1/n$ values are similar and range from 0.0983 to 0.1484. This demonstrates the diversity of active places on the surface of activated carbon. If these values are closer to 0 than 1, as is the presented case, a low heterogeneity of the surface of activated carbons

can be concluded. The advantageous nature of the process is confirmed by the value of the division coefficient R_L ranging from 0 to 1 (from 0.001 to 0.026). The K_F coefficient, which characterizes sorption capacity of activated carbons, was the highest for activated carbon F-300 and pH=6 ($K_F=83.534$ mg/g) and the lowest for ROW 08 Supra and pH=10 ($K_F=53.379$ mg/g).

The Temkin equation is an isotherm that is equally well suited to the results. This isotherm, similarly to the Freundlich isotherm, assumes a monolayer adsorption and surface heterogeneity. This proves that the adsorption potential of the surfaces used in the testing of activated carbons is slightly different.

The temperature was another examined parameter that affects the effectiveness of the adsorption processes. The examinations of the adsorption of naproxen sodium on activated carbon were carried out at temperatures of 25, 37 and 50°C (Fig. 3, Table 5). The efficiency of naproxen sodium adsorption increased along with the temperature. The differences are quite large for all activated carbons. The process of adsorption of naproxen sodium on the carbon sorbents studied is therefore endothermic. Since physical adsorption is exothermic, this confirms the previous observations that the chemical interactions are important during the naproxen sodium adsorption. Similar tendencies were also documented by other researchers (Onal et al., 2008; Sarici-Ozdemir and Onal, 2010). An increase in adsorption following a rise in temperature may lead to the increasing mobility of molecules and an increase in affinity of adsorbate molecules to the surface of the adsorbent (Ozdemir and Onal, 2010). However, Baccar et al. found no significant effect of temperature on the process of adsorption of a pharmaceutical (Baccar et al., 2012), whereas Cuerda-Correa et al. observed a decrease in adsorption with an increase in temperature (Cuerda-Correa et al., 2010. Such a different effect of temperature was most likely caused by the differences in the structure of carbon sorbents used in the studies and different dominant mechanisms of adsorption.

The effect of the adsorbent dose on the effectiveness of naproxen sodium adsorption was also analysed (Fig. 5). The effect of the adsorbent dose was evaluated for two initial concentrations: 252 and 1008 mg/L. The adsorbent doses from 1 to 10 g/L were analysed. Similar doses were also used by other researchers during adsorption of various nonsteroidal anti-inflammatory drugs, e.g. Baccar
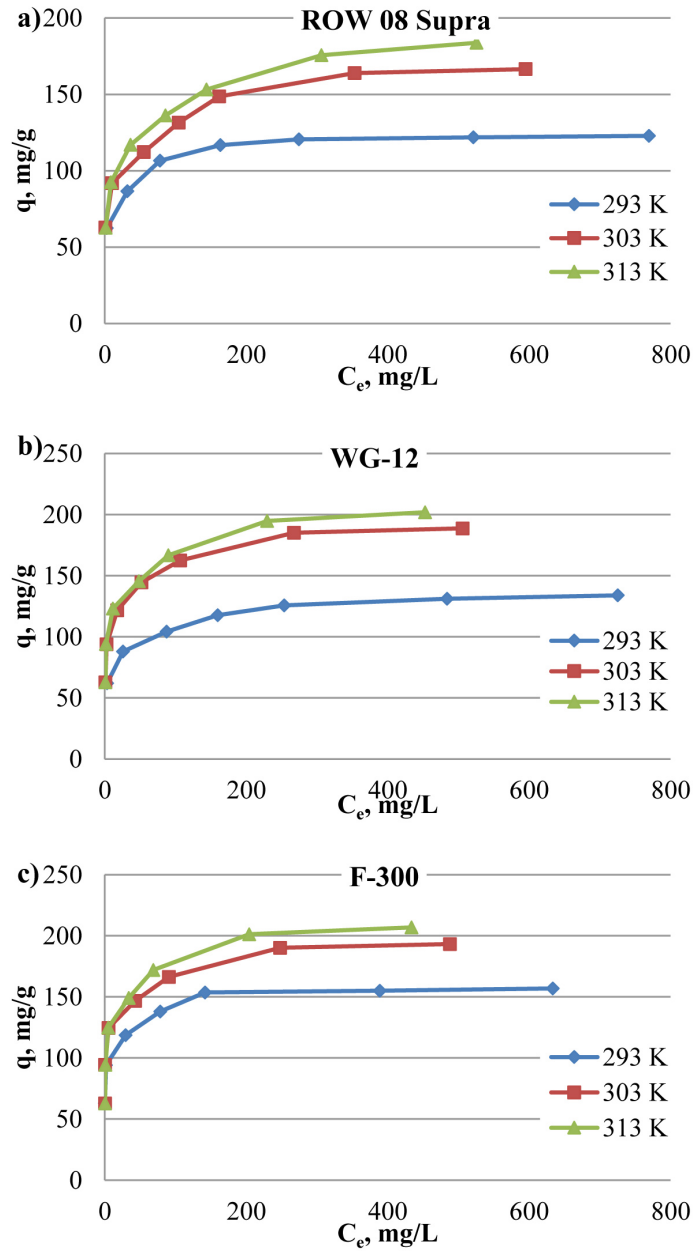
Fig. 3. Effect of temperature on adsorption of naproxen sodium on activated carbons: a) ROW 08 Supra, b) WG-12, c) F-300
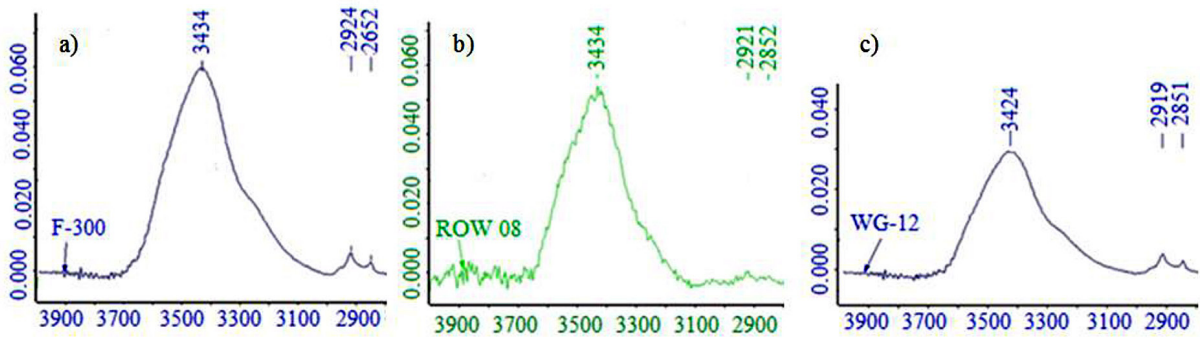

Fig. 4. FTIR spectra for activated carbons: a) F-300, b) ROW 08 Supra, c) WG-12 (part of the spectrum from 2900 to 3900 nm)

Table 5. Isothermal coefficients for naproxen sodium adsorption

| Activated carbon	Parameter	pH 6			pH 8	pH 10
		T=313 K	T=303 K	T=193 K		
Freundlich						
F-300	1/n	0.1450	0.1289	0.1065	0.1103	0.1104
	K_F	89.958	90.877	83.534	78.831	58.779
	R^2	0.9628	0.9513	0.9493	0.9423	0.9815
ROW 08 Supra	1/n	0.1777	0.1581	0.1159	0.1102	0.1026
	KF	62.0178	62.982	60.373	65.891	53.379
	R2	0.9944	0.9819	0.9500	0.9423	0.97913
WG-12	1/n	0.1615	0.1521	0.1393	0.1484	0.0983
	KF	78.417	77.118	55.779	55.900	58.246
	R2	0.9657	0.9745	0.9835	0.9795	0.9733
Langmuir						
F-300	q_m	182.05	171.59	144.10	140.66	108.09
	K_L	0.8595	1.2418	1.6979	1.1067	0.9916
	R^2	0.8519	0.8470	0.8213	0.8297	0.6607
	R_L	0.001-0.005	0.001-0.003	0.001-0.002	0.001-0.004	0.001-0.004
ROW 08 Supra	q_m	162.83	146.42	116.55	124.94	96.20
	K_L	0.1784	0.3160	0.3249	0.2819	0.5484
	R^2	0.7765	0.6943	0.8164	0.9522	0.6751
	R_L	0.004-0.022	0.003-0.012	0.002-0.012	0.003-0.014	0.001-0.007
WG-12	q_m	177.46 0.4550	168.25 0.4608	123.90	132.37	99.28
	K_L			0.2004	0.1479	0.6460
	R^2	0.8376	0.8398	0.8175	0.8798	0.7758
	R_L	0.002-0.009	0.002-0.009	0.004-0.019	0.005-0.026	0.001-0.006
Temkin						
F-300	A	66.70	163.29	677,39	378.21	378.21
	B	20.43	17.38	12.53	12,78	9.49
	R^2	0.9822	0.9680	0.849	0.9690	0.9774
ROW 08 Supra	A	10.74	25.06	83.06	115.12	490.31
	B	20.87	17.23	11.63	11.93	8.08
	R^2	0.9828	0.9650	0.9563	0.9451	0.9555
WG-12	A	23.69	31.33	22.26	12.86	1034.53
	B	21.86	19.88	14.11	15.90	7.87
	R^2	0.9850	0.9949	0.9912	0.9898	0.9774
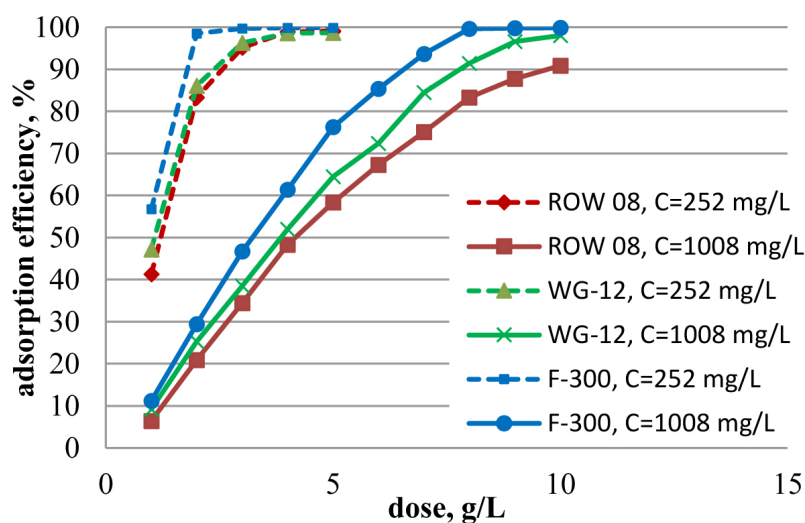
Fig. 5. The effect of adsorbent dose on adsorption efficacy at two initial concentrations of 252 and 1008 mg/L

et al. (from 0.3 to 3.3 g/L for naproxen sodium (Baccar et al., 2012), de Luna et al. 2017 (from 5 to 25 g/L for diclofenac sodium (de Luna et al., 2017), Nourmoradi et. al. (from 0.5 to 10 g/L for ibuprofen (Nourmoradi et al., 2018)). When lower concentrations of naproxen sodium were used (252 mg/L) for all activated carbons, the dose of 3 g/L resulted in a decrease in the concentration by more than 95%. In the case of a higher concentration, the dose of 8 g/L of the F-300 activated carbon allowed for exceeding 95% of the drug removal threshold, whereas for the WG-12 activated carbon, such a dose was 9 g/L. For the ROW 08 Supra activated carbon, the removal of naproxen sodium was not exceeded 95% even for a dose of 10 g/L.

CONCLUSIONS

1. The F-300, ROW 08 Supra, WG-12 commercial activated carbons can be used to remove naproxen sodium from water because they have quite high adsorption capacities ranging from q_m of 96.20 mg/g (ROW 08, pH=10, T=20°C) to 182.05 mg/g (F-300, pH=6, T=40°C). Adsorption of naproxen sodium occurred in the highest amount on the F-300 activated carbon, whereas the lowest amounts were found for ROW 08 Supra over the entire range of solution pH.

2. For all pH values (6, 8, 10), temperatures (20, 30, 40°C) and all activated carbons used, the process of naproxen sodium adsorption was favourable (adsorption intensity 1/n in the range of 1-10, distribution coefficient R_L in the range of 0-1).

3. A significant effect of pH on the magnitude of naproxen sodium adsorption was found for all activated carbons (the higher pH, the lower the adsorption). This leads to the conclusion that that the electrostatic forces and chemical bonds (formation of hydrogen bonds between the carboxyl groups of naproxen sodium and the phenolic groups on the surface of activated carbons as well as the electrostatic repulsion between the anions of naproxen sodium and negatively charged surface of activated carbon) have a significant influence on the adsorption results.

4. It was found for naproxen sodium adsorption at the temperatures of 20, 30 and 40°C that the process is endothermic (the higher the temperature, the most efficient the adsorption). This confirms the significant effect of chemical adsorption on the magnitude of adsorption of the pharmaceuticals.

5. The analysis of the results obtained for the analysed isotherms (Freundlich, Langmuir and Temkin) revealed that the highest correlation coefficients were obtained for the Freundlich and Temkin equations, whereas the lowest – for Langmuir.

6. Adsorption kinetics is well-described by Elovich and pseudo-second order equations. The fastest adsorption occurred on the F-300 activated carbon (value of k_2 about twice as high as for other activated carbons).

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