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Adsorption capacity assessment for selected adsorbents in the removal of over the counter (OTC) analgesics from water

Daniela Lukášová*, Renata Biela, Světlana Moravčíková

Department of Municipal Water Management, Faculty of Civil Engineering, Brno University of Technology, Žižkova 17, Brno, 602 00, Czech Republic, emails: siblova.d@fce.vutbr.cz (D. Lukášová), biela.r@fce.vutbr.cz (R. Biela), moravcikova.s@fce.vutbr.cz (S. Moravčíková)

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ABSTRACT

Pharmaceutical drugs can get into drinking water sources by different ways and subsequently affect not only the environment but also water quality. As the presence of drugs in water has recently become a hot topic, certain water management processes have already been developed for their removal from water, including adsorption on charcoal. In the context of specific research at the Department of Municipal Water Management, Faculty of Civil Engineering, BUT in Brno, laboratory measurements were implemented to determine the adsorption capacity of selected sorbents, especially the charcoal brands Filtrasorb F100 and F400 as well as Bayoxide E33 and GEH. The removed pharmaceutical group was represented by non-steroidal anti-inflammatory drugs including four types, namely ibuprofen, diclofenac, naproxen and paracetamol. The laboratory removal resulted in a comparison of these sorbents in terms of their adsorption capacity in the removal of the selected drugs from water.

Keywords: Water treatment; Over the counter (OTC) analgesics; Adsorption; Activated carbon; Adsorption capacity

1. Introduction

1.1. Occurrence of drugs in water

The occurrence of drugs in drinking water sources and their removal is a hot topic in the field of water management. Thanks to their presence in water and their bioaccumulation and degradation properties, these pollutants can affect the water biota as well as the performance of water treatment plants and the costs of drinking water production. The quality of drinking water sources is deteriorating due to population growth, leading to more and more stringent regulations including tighter limit concentrations of selected pollutants. The improvement of water treatment processes is related to the growing consumption of energy and chemicals, which in turn increases the costs of water treatment and imposes a further environmental impact. Due to the hydrophilic nature of pharmaceutical compounds their complete removal at WWTPs is nearly impossible. Therefore these compounds persist and can even be found in drinking water [1]. The most frequent pharmaceutical pollutants found in drinking water include non-steroidal anti-inflammatory drugs as well as antibiotics. Another known pharmaceutical group found in the aquatic environment is represented by gonadal steroid hormones which may negatively affect aquatic life [2].

1.2. Over the counter (OTC) analgesics

Over the counter analgesics are divided according to their clinical effect into analgesic-antiphlogistic (ibuprofen, naproxen, diclofenac, dexketoprofen), analgesic-antipyretic (acetylsalicylic acid, paracetamol, propyphenazone)

* Corresponding author.

and according to the number of substances into single and combination analgesics [3]. For the research reported in this article four simple analgesics were used, namely: ibuprofen, diclofenac, naproxen and paracetamol.

The selected drugs can also be classified according to the Anatomical Therapeutic Chemical Classification (ATC), which is the international system of drug classification that has been used by the World Health Organization (WHO) since 1976. In the ATC classification system, active substances are divided into different groups according to the organ systems on which they act and their therapeutic, pharmacological and chemical properties. According to the ATC classification, ibuprofen, diclofenac and naproxen are classified in group M – musculoskeletal system, subgroup non-steroidal anti-inflammatory drugs (NSAIDs). Paracetamol is classified in group N – nervous system, subgroup anilides [4].

Non-steroidal anti-inflammatory drugs (NSAIDs) include both prescription and over-the-counter drugs with analgesic, antipyretic, and anti-inflammatory effects [5]. Analgesics reduce pain sensation but do not eliminate its cause. Antipyretics reduce fever. Known representatives of the analgesic and antipyretic group include ibuprofen, diclofenac, naproxen, metamizole, indomethacin and others. In addition to the desired effects, these drugs can also have adverse effects such as headache, allergic reactions, gastric inflammations, or even severe renal disorders in the case of overdose [6].

Anilides include drugs that are classified among analgesics and antipyretics, but do not have an anti-inflammatory effect. This group of drugs includes, for example, paracetamol, propacetamol, bucetin and phenacetin. Drugs of this group are used against pain and high temperature [4].

1.3. Methods of removing drugs from water

Known methods for the removal of drugs from water include membrane processes, oxidation processes and adsorption. Membrane processes contain a membrane that acts as a selective barrier to restrict the passage of impurities such as organic compounds, suspended particles, metal ions, nutrients and microorganisms, allowing the treated water to pass through the membrane. The various commonly used membrane processes can be divided into four main categories: microfiltration, ultrafiltration, nanofiltration and reverse osmosis [2].

Advanced oxidation processes (AOP) are considered to be clean processes designed for the oxidation of a wide range of organic pollutants present in waters. Oxidation processes are a set of processes involving the production of highly reactive hydroxyl radicals (OH), which are the second most powerful oxidation group. When complete mineralization is not achieved, post-treatment is usually required, resulting in improved micropollutant removal efficiency. In the oxidation process, the by-products of the reaction are biodegradable and less toxic than the original compounds [2].

In addition to drugs, oxidation processes reliably remove other types of contaminants such as aromatic hydrocarbons, pesticides, dyes, heavy organic compounds, and others. Oxidation processes can be applied differently depending on the specific characteristics of the treated water. These processes can be implemented using ultraviolet radiation (UV), oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2), or even a combination of some of them [2].

Adsorption can be another method for removing drugs from water. This method is described in more detail in the following chapter.

1.4. Adsorption and desorption

Adsorption on various sorption materials is used for the removal of micro-contamination from water. Adsorption is a type of the phase transfer process, widely used in practice for the removal of substances from fluids (gases or liquids). This process can also be observed as a natural process in various environmental components. As adsorption is a superficial process, the surface area is a key parameter of adsorbent quality. Adsorbents are typically highly porous materials with surface areas ranging between 10^2 and 10^3 m^2/g [7]. Sorption processes represent and are a widely used and proven technological procedure for the removal of drugs from drinking water. At present they probably represent the most effective universal method of water treatment. In specific cases they may be complemented with water pre-oxidisation with ozone, or ozone plus UV radiation [2]. Desorption is a process opposite to adsorption. The reasons for desorption occurrence may include exhausted sorbent capacity as well as different properties of the adsorbed pollutants. As desorption is a process opposite to adsorption, all conditions leading to adsorption reduction increase the volume of adsorbate that may be desorbed. Desorbed adsorbate is an aqueous solution that can be affected by properties such as concentration, temperature, and pH, in comparison to the original adsorbate, in the case of the present experiment, the model water [7].

Adsorption is usually described by isotherms – Freundlich, Langmuir and BET [8]. For adsorption from solutions, the Freundlich or Langmuir isotherm is usually suitable. The Freundlich isotherm is usually valid for physical adsorption and for adsorption on heterogeneous surfaces with different active sites. The Langmuir isotherm is usually valid for chemisorption or electrostatic adsorption, where only a monomolecular layer is formed on the adsorbent surface and all active sites on the surface are equivalent [9].

2. Materials and methods

2.1. Selected adsorbents

Four adsorbents were selected for the laboratory experiment on the removal of over the counter (OTC) analgesics from water. The charcoal brands Filtrasorb F100 and F400 were selected for their common use in micro-pollution removal from water [2]. Adsorption material brands Bayoxide E33 and GEH were chosen for their positive results in the laboratory removal of metals from water [10]. The characteristics, properties, photos and structures of the selected adsorbents can be found below.

2.1.1. Filtrasorb F100

Filtrasorb F100 granular activated carbon (Fig. 1) is used for the removal of dissolved organic compounds from water. Filtrasorb F100 granular activated carbon is manufactured

by Chemviron Carbon, Feluy, Belgium. The granulated product F100 is made of selected bitumen coals by a process called re-agglomeration. Charcoal is capable of resistance to the wear connected with repeated rinses, hydraulic transport and reactivation for reuse. The raw coal is extracted in the United States and subsequently processed by GAU to ensure the top quality and consistence of the final product. The activation is carefully controlled to produce a significant volume of both low- and high-energy pores for the effective adsorption of a broad spectrum of organic contaminants [11]. The technical and physical parameters of Filtrasorb F100 can be found in Table 1.

2.1.2. Filtrasorb F400

Filtrasorb F400 granulated charcoal (Fig. 2) is quite similar in composition to Filtrasorb F100, but differs in the size of the adsorption surface. Filtrasorb F400 granular activated carbon is manufactured by Chemviron Carbon, Feluy, based in Belgium. The process of re-agglomeration assures the correct wetting and elimination of floating material. Filtrasorb F400, thanks to its high mechanical compactness in comparison to other materials reduces contamination by backwash. Segregation of the carbon bed is preserved even after repeated rinses and ensures an unchanged adsorption profile, which maximises the filter bed life. This carbonaceous material is dense, which increases adsorption capacity per volume unit [12]. For the technical and physical parameters of Filtrasorb F400, Table 1.

2.1.3. GEH

The adsorption material identified as GEH (Fig. 3) is a high-performance iron-hydroxide-based adsorbent made by a special patented process and designed for the selective adsorption of arsenic by a specific process. The GEH sorption material was developed at the University of Berlin's Department of Water Quality Control for the removal of arsenic and antimony from water. It is manufactured by the German company GEH-Wasserchemie GmbH [13]. This agent is ideal for drinking water treatment as it does not release any chemical compounds into the treated water and leaves its pH unchanged. The treatment technology is based on adsorption of the contaminant on granulated iron hydroxide (GEH sorbent), loaded in a reactor which the treated water flows through. The adsorption capacity of

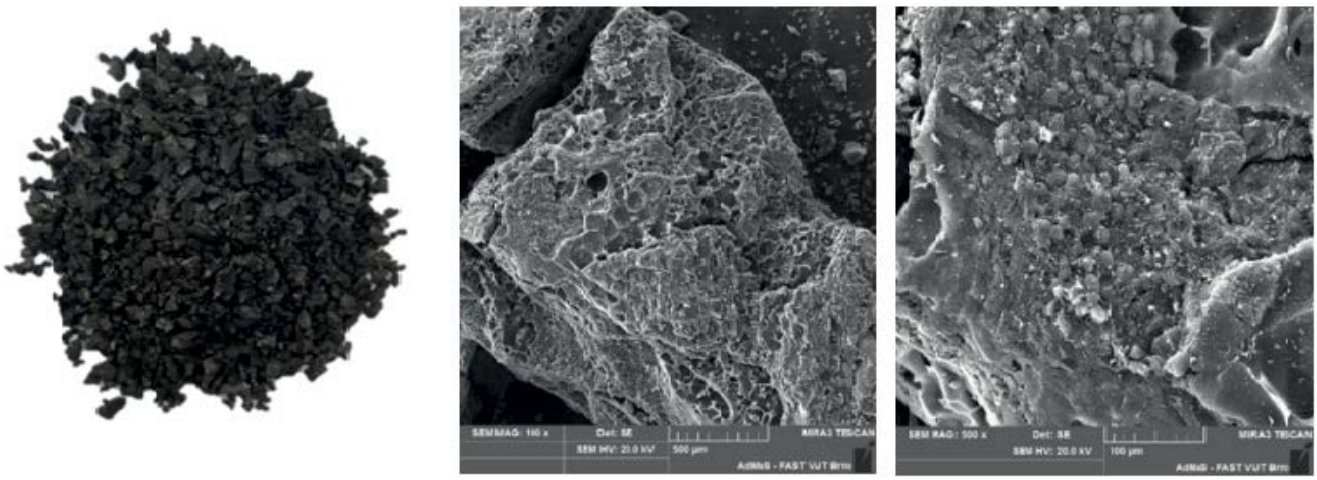


Fig. 1. Filtrasorb F100 sorption material in the original size and in microscopic enlargement.

Table 1
Technical and physical parameters of sorption materials [12–14,16]

Parameter	F100		F400		E33		GEH	
Specific adsorption surface, m^2/g	850		1050		120–200		250–300	
Bulk density, kg/cm^3	0.5		0.45		0.4–0.6		1.25	
Median particle size, mm	1		1.6		0.5–2		0.3–2	
Sieve analysis, mm; %	<0.6	<4	<0.425	<4	<0.5	Max. 20	<0.3	<10
	>2.36	<15	>1.7	<5	>2.0	Max. 5	>2.0	<10
Coefficient of uniformity	1.9		1.7		*		*	
Working pH	Mildly basic		Mildly basic		5.5–8.5		5.5–6.5	
Porosity, %	*		*		85		72–77	
Material colour	Black		Black		Brown		Brownish red	

*Not specified by the manufacturer.

the material depends on the operation conditions [14,15]. The properties of the adsorbent are shown in Tab. 1.

2.1.4. Bayoxide E33

The iron-oxide-based crystalline sorption medium Bayoxide E33 (Fig. 4) is produced by the British manufacturer Severn Trend Services mainly for the purpose of the removal of arsenic and other metals from water. The adsorption material manages to clear arsenic down to below 4 μg/L. The sorbent is used in the granulated form as Bayoxide E33 or in tablets as Bayoxide E33P. The advantages of the material include long life under continuous operation, low investment and operation costs and the long life of the dry

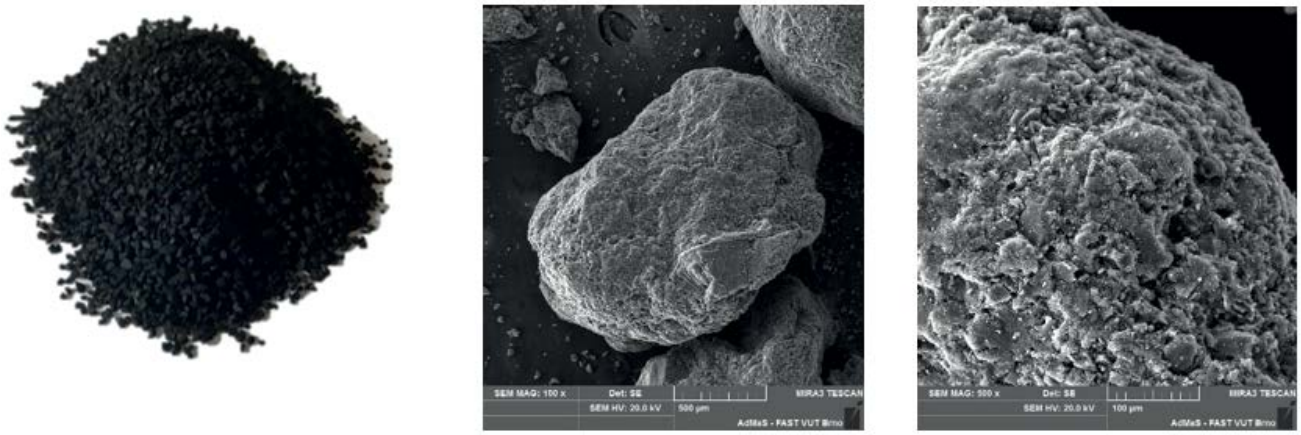


Fig. 2. Filtrasorb F400 sorption material in the original size and in microscopic enlargement.

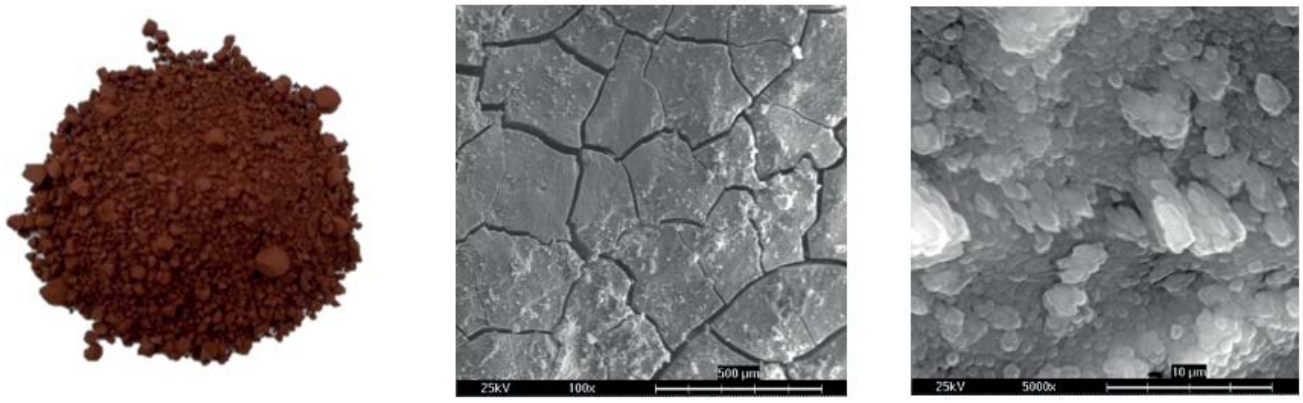


Fig. 3. GEH sorption material in the original size and in microscopic enlargement.

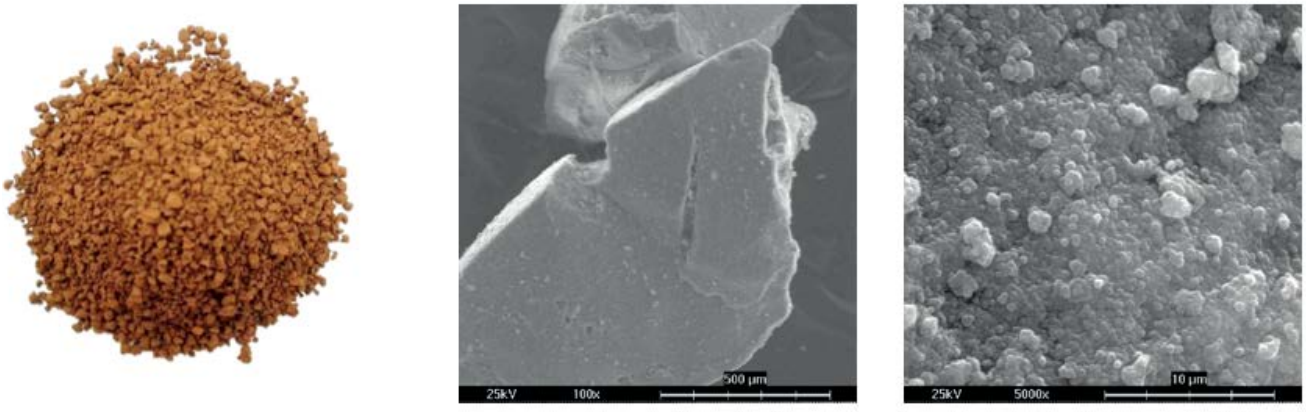


Fig. 4. Bayoxide E33 sorption material in the original size and in microscopic enlargement.

medium [16]. The technical and physical parameters of the adsorbent can be found in Table 1.

2.2. Selected representatives of over the counter (OTC) analgesics

Since each drug has a different composition and properties and each group of drugs may have a different course of removal during adsorption, individual drugs belonging to the group of OTC simple analgesics were selected for the experiment. They included ibuprofen, diclofenac, naproxen and paracetamol. Their respective descriptions follow.

2.2.1. Ibuprofen

Ibuprofen is a known drug with analgesic and antipyretic effects. This drug has been proven to be up to thirty times stronger than aspirin and twenty times more effective than antipyretics. It is used against mild to moderate pain of various origins, including joint, muscle and tooth aches etc. The drug can be bought over the counter in limited doses. Higher doses of ibuprofen require a medical prescription [6,17,18]. In response to interest, the monitoring of the drug presence in water has been performed in the Czech Republic. Ibuprofen concentrations at WWTP outflows reached up to 11.2 μg/L. Maximum ibuprofen concentration measured in surface water was 4.4 μg/L. Surface water may, of course, be a source of drinking water. Therefore the presence of the drug in the drinking water was analysed too. Ibuprofen concentrations in drinking water reached max. 0.12 μg/L [19].

2.2.2. Diclofenac

Diclofenac is a strong analgesic administered in low doses. It resorbs well after administration, but nearly half of the administered dose is subject to pre-systemic elimination in the liver. The elimination halftime of diclofenac is 1–2 h. Thanks to its analgesic effects, diclofenac is widely used in a large spectrum of patients. Adverse effects affect 12% of the treated patients in total, with 10% exhibiting digestive problems. This is where diclofenac differs from other antiphlogistic acids [6]. The maximum concentration of diclofenac measured at WWTP outlets in the content of water drug content monitoring in the Czech Republic was 2.51 μg/L. Measured surface water concentrations of this drug reached maximum 0.272 μg/L, and no drug was detected in drinking and groundwater [19].

2.2.3. Naproxen

Naproxen is a drug used in chronic rheumatic inflammations. Its antiphlogistic (anti-inflammatory) effect is good and adverse effects are rare. Very rare adverse effects include massive bleeding from the digestive tract. As its elimination is slow, it is especially suitable for chronic therapies [6]. The maximum measured concentration of naproxen at WWTP outlets in the context of the water drug monitoring project implemented in the Czech Republic was 12.5 μg/L. The measured surface water concentrations were lower, up to 0.25 μg/L. No drug was detected in drinking and groundwater [19].

2.2.4. Paracetamol

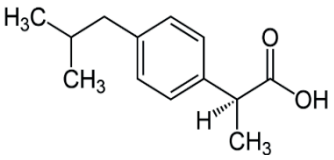
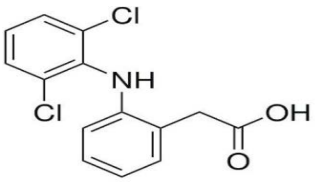
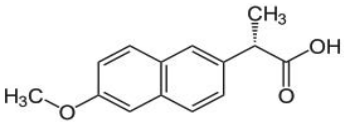
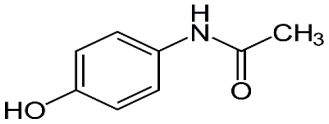
Paracetamol (p-acetaminophen) is a p-aminophenol derivate with a good analgesic and antipyretic effect. The substance resorbs well after administration and is excreted through kidneys after biotransformation in the liver. The elimination halftime is about 2 h. Adverse effects include allergic reactions, mainly dermal. Chronic overdose of paracetamol alone is rarely manifested, but it more often appears when paracetamol is combined with stimulants, such as caffeine. Long-term administration of these composite drugs may cause renal damage [6]. Paracetamol was also one of the objectives of water drug monitoring in the Czech Republic and its maximum concentration measured at WWTP outlets was up to 5.704 μg/L. this analgesic was also found in surface water in the maximum concentration of 0.464 μg/L. Groundwater monitoring revealed no paracetamol content but there were trace concentrations found in drinking water on the level of 0.01 μg/L [19].

2.3. Measurement methodology

A 4-h static test was performed for the assessment of adsorbent adsorption capacity. The tested sorption material was pre-filled in the prepared 1 L beakers in the volume of 10 g and the beaker was then topped up with 1 litre of model water. The model water was a mix of tap drinking water mixed with a standard of the selected drugs. The standard was prepared by the accredited laboratory ALS Czech Republic. Samples were taken in predefined time intervals of 1, 2 and 4 h. The model water and sorbent were mixed after each sample taking. At the sample taking times, the drug concentration together with the water temperature and pH were measured in each beaker. For the reason of the analysis complexity, the samples taken were provided for analysis to the above-mentioned accredited laboratory. As the analysis of ibuprofen levels in water differs from analyses of the levels of diclofenac, naproxen and paracetamol, the samples were filled in two different samplers. As the static test was performed in parallel there were 49 samples in total, of which 1 was a model water sample. The experiment was performed twice, with a total of 8 beakers, 2 beakers always with the same sorbent and all beakers with the same model water. Samples were collected in two sample cups as required by the accredited laboratory for accuracy of analysis. Table 3 shows tap water quality on the trial day and Fig. 5 shows a graph preview of the static test.

The pH value is very important in hydrochemistry, for its effect on most physical–chemical, chemical and biochemical processes taking place in water. Water reaction is a dimensionless indicator also affected by water temperature. At water temperatures over 25°C, its pH value is lower than 7 and at temperatures below 25°C the pH is higher than 7. Temperature is also a significant drinking water indicator significantly affecting the chemical and biochemical reactivity of water within a relatively narrow temperature range between 0°C to about 30°C [21]. The laboratory experiment used a pH meter with a thermometer by XS Instruments pH5 for water pH and temperature measurements. This instrument is a high-standard pH meter with a microprocessor and a high-standard replaceable electrode.

Table 2
Properties of selected drug representatives [6,17–19]

Name	Structural formula	Summary formula	Molar weight (g/mol)	Melting temperature (°C)
Ibuprofen		$C_{13}H_{18}O_2$	206.280	76
Diclofenac		$C_{14}H_{11}Cl_2NO_2$	296.148	284
Naproxen		$C_{14}H_{14}O_3$	230.094	152–154
Paracetamol		$C_8H_9NO_2$	151.163	169

The later display of the tester shows both pH and temperature values simultaneously. The meter by XS Instruments is water- and humidity-proof. Its functions include calibration with the help of a three-point button with five buffer values in the USA for ±0.01 pH accuracy. The instrument further reads mV for pH electrode diagnostic [9].

2.4. Method of drug residue specification

As the laboratory of the Department of Municipal Water Management is unable to specify residual drug concentrations in water, the water levels of the tested drugs were analysed by the accredited laboratory ALS Czech Republic. Drug residues in the samples were specified by ultra-high-performance liquid chromatography in combination with tandem weight detection UPLC-MS/MS (Waters XEVO TQ-XS).

2.4.1. Liquid chromatography

Liquid chromatography is a separation technique based on different speeds of distribution of sample components between the stationary and the liquid mobile phase. In relation to the stationary phase there is thin-layer chromatography (TLC), paper chromatography (PC) and column liquid chromatography (LC). Column liquid chromatography can be divided into an open and a closed system chromatography. The closed system chromatography types include high-performance liquid chromatography (HPLC) or, in the case of use of higher pressure, ultra-high-performance liquid chromatography (UPLC) [22].

Table 3
Quality of drinking water used as model water [20,21]

Indicator	Value	Limit acc. to Decree 70/2018 Coll.
Colour, mg·Pt/L	4	20
Turbidity, NTU	0	5
Iron, mg/L	0.01	0.2
pH	7.48	6.5–9.5
Total hardness, mmol/L	2.08	2–3.5
Ammonia ions, mg/L	<0.03	0.5
Nitrates, mg/L	27	50
Nitrites, mg/L	<0.00	0.5
Chlorides, mg/L	17.9	100
VOC, mg/L	1.74	5
Free chlorine, mg/L	<0.03	0.3
Coliform bacteria, CFU/100 mL	0	0
Escherichia coli, CFU/100 mL	0	0

2.4.2. Weight spectrometric detection

Weight spectrometer can be defined as any instrument capable of the production of ions from neutral types and providing means for the specification of the weights of these ions on the basis of the weight proportions in the ion charge and ion numbers. Today, weight spectrometers can be used for the specification of element isotope distribution, elementary or molecular composition of samples or compound structure or its molar weight. A combination of two or

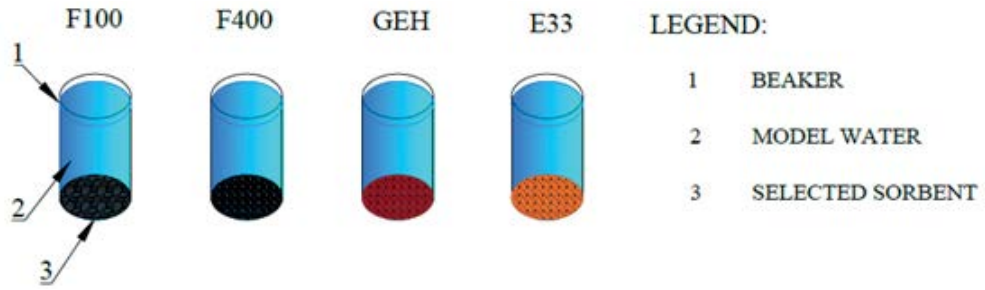


Fig. 5. Graph image of the static test.

Table 4
Calculated adsorption capacity of adsorbents in the elimination of ibuprofen

Time	Ibuprofen – adsorption capacity (μg/g)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	4.335	4.967	0.720	0.010	4.474	4.968	0.580	0.150
2	4.919	4.941	0.690	–0.230	3.320	4.956	0.720	0.040
4	4.938	4.924	0.890	–0.110	4.989	4.950	0.680	–0.170

Table 5
Calculated adsorption capacity of adsorbents in the elimination of diclofenac

Time	Diclofenac – adsorption capacity (μg/g)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.322	0.311	0.083	–0.019	0.320	0.320	0.055	–0.001
2	0.313	0.322	0.036	–0.009	0.306	0.323	0.014	0.009
4	0.314	0.322	–0.102	0.003	0.322	0.324	–0.042	–0.017

more analysers, commonly identified as MS/MS, or tandem weight spectrometry, is a highly specific means for mixture separation, fragmentation process study and fluid phase reaction analyses. As MS/MS can be combined with chromatographic separation techniques this method has found a broad range of applications in analytic chemistry [23].

2.5. Comparison of drug removal efficiencies of selected sorbents

Removal of some drugs by adsorption using these sorbents was already carried out in previous years. This involved the removal of ibuprofen and diclofenac dynamically through a column with Filtrasorb F100, Bayoxide E33 and GEH sorbents [24,25].

The initial concentration of ibuprofen in the model water was 1.02 μg/L. The activated carbon Filtrasorb F100 reduced the concentration to 0.29 μg/L after 6 min, and the sorbent Bayoxide E33 to 0.15 μg/L. The GEH sorbent did not perform well in removing ibuprofen from water. After 6 min of removal, a concentration of 2.11 μg/L was measured. The final concentration was higher than that of ibuprofen in the model water. In this case, desorption may have occurred [24].

In the second experiment, the concentration of diclofenac in the model water was 1.29 μg/L. After 6 min of removal, Filtrasorb F100 activated carbon almost removed diclofenac from the water. The laboratory determined a value < LOD, which means that a value below the detection limit was measured. The limit value for diclofenac was 0.006 μg/L. The sorbent Bayoxide E33 reduced the concentration of the drug to 0.97 μg/L. The GEH sorbent material already removed diclofenac from the water within 1 min of removal as a value < LOD was measured at times 1, 2, 4 and 6 min [25].

2.6. Specification of adsorbent adsorption capacity

The quantity of the adsorbed substance is not commonly expressed as the substance weight or quantity adsorbed per unit of adsorbent weight. In water technology, where

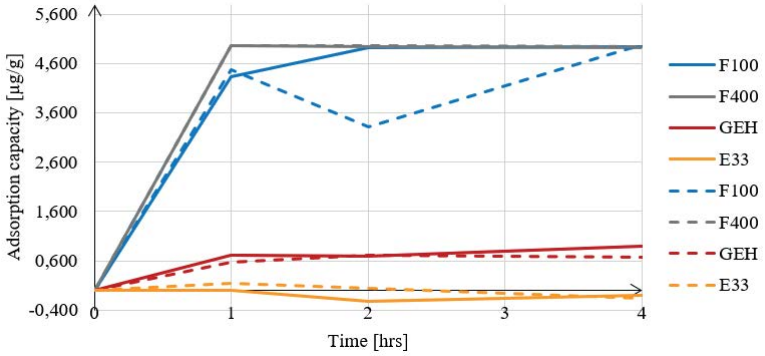


Fig. 6. Adsorption capacity of sorbents in the elimination of ibuprofen.

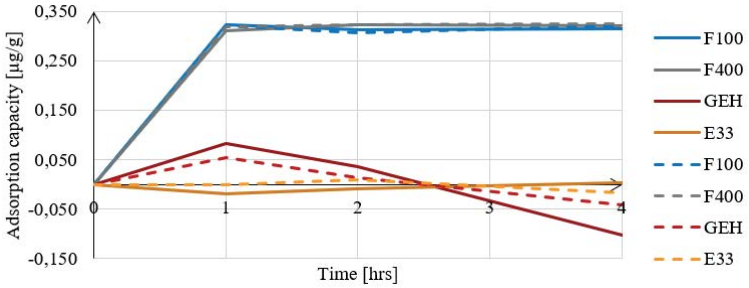


Fig. 7. Adsorption capacity of sorbents in the elimination of diclofenac.

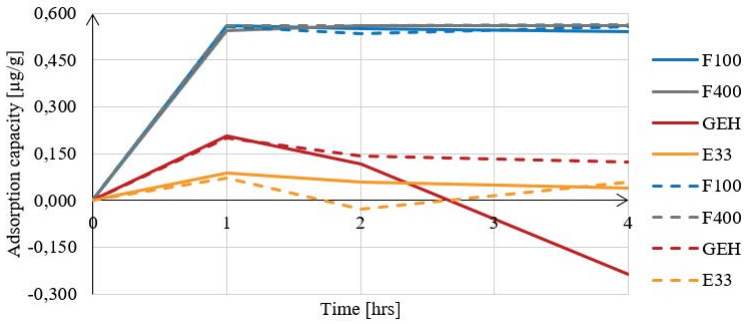


Fig. 8. Adsorption capacity in elimination of naproxen.

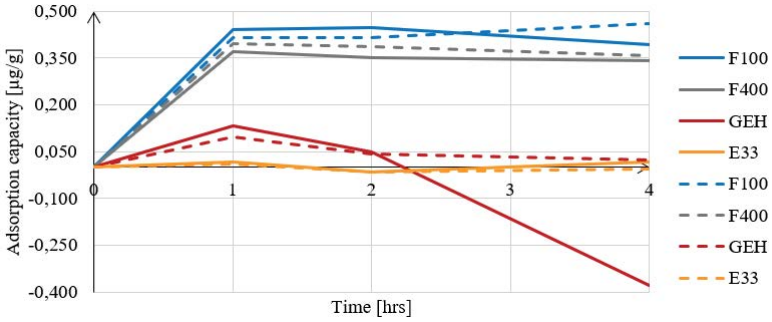


Fig. 9. Adsorption capacity in the elimination of paracetamol.

Table 6
Calculated adsorption capacity of adsorbents in the elimination of naproxen

Time	Naproxen – adsorption capacity (μg/g)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.562	0.543	0.206	0.088	0.557	0.561	0.200	0.071
2	0.552	0.560	0.118	0.060	0.534	0.561	0.144	–0.027
4	0.542	0.561	–0.238	0.041	0.559	0.562	0.122	0.060

Table 7
Calculated adsorption capacity of adsorbents in the elimination of paracetamol

Time	Paracetamol – adsorption capacity (μg/g)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.442	0.369	0.134	0.017	0.415	0.396	0.098	0.012
2	0.446	0.351	0.050	–0.016	0.416	0.386	0.044	–0.014
4	0.394	0.341	–0.380	0.016	0.459	0.358	0.025	–0.005

substance mixtures of unknown compositions are encountered, the following formula is used (1) [26]:

$$a_t = \frac{(c_0 - c_m)V}{m} \tag{1}$$

where c_0 is the concentration in time t = 0 h (μg/L); c_m is the concentration in time t (μg/L); V is the aqueous solution volume (L); m is the sorption material weight (g); a_t is the instantaneous adsorption capacity (μg/g).

2.7. Dependence of adsorption on adsorbate concentration

The effect of adsorbate concentration on adsorption is described by adsorption isotherms. Langmuir and Freundlich isotherms were used to evaluate the adsorption from solution. The Langmuir isotherm is expressed by the relation [9]:

$$a_t = a_{\max} \cdot \frac{b \cdot c_r}{1 + b \cdot c_r} \tag{2}$$

where a_t is the instantaneous adsorption capacity (μg/g); $a_{\max}$ is the maximum adsorption capacity (μg/g); b is the constant; c_r is the equilibrium concentration of the adsorbed substance (μg/L).

To verify that the measured data fit this isotherm, Eq. (2) was converted into a linearized form from which the maximum adsorption capacity $a_{\max}$ and the constant b were calculated using the least squares method:

$$\frac{1}{a_t} = \frac{1}{a_{\max} \cdot b} \cdot \frac{1}{c_r} + \frac{1}{a_{\max}} \tag{3}$$

Table 8
Measured pH values during static test

Time	pH (–)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	7.03	7.03	7.03	7.03	7.03	7.03	7.03	7.03
1	7.36	7.59	7.52	7.58	7.45	7.67	7.48	7.56
2	7.28	7.62	7.50	7.47	7.50	7.69	7.50	7.54
4	7.35	7.62	7.57	7.43	7.53	7.56	7.45	7.51

Table 9
Measured temperature values during the static test

Time	Temperature (°C)							
(h)	F100	F400	GEH	E33	F100	F400	GEH	E33
	1	2	3	4	5	6	7	8
0	18.8	18.8	18.8	18.8	18.8	18.8	18.8	18.8
1	19.4	19.1	19.0	19.0	19.2	19.0	19.0	19.0
2	19.6	19.6	19.6	19.6	19.6	19.4	19.4	19.5
4	20.3	20.2	20.3	20.3	20.3	20.3	20.3	20.3

The Freundlich isotherm is described by the relation [9]:

$$a_t = k \cdot c_r^{1/n} \tag{4}$$

where a_t is the instantaneous adsorption capacity (μg/g); n is the constant; c_r is the equilibrium concentration of the adsorbed substance (μg/L).

To verify that the measured data fit this isotherm, Eq. (4) was converted into a linearized form from which the constants n and k were calculated using the least squares method:

$$\log a_t = n \log c_r + \log k \tag{5}$$

3. Results and discussion

3.1. Adsorption capacity of selected adsorbents

Eq. (1) was used for assessment of adsorption capacity of the materials. The assessment was performed by drug type for clarity with comparison of adsorption capacities of the individual adsorbents. As the static test was performed in parallel, the parallel adsorption capacities of the individual materials are shown by dashed lines in the diagram. The calculated values of adsorption capacities of the individual sorption materials are shown in the tables below, followed by diagrams of the progress of adsorption capacity of the adsorbents in the course of the static test. The following input concentrations for individual drugs were measured in the model water: ibuprofen 50.1 μg/L, diclofenac 3.35 μg/L, naproxen 5.8 μg/L and paracetamol 4.76 μg/L. The model water contained the selected drugs at different concentrations. Compared to the concentrations detailed in Section

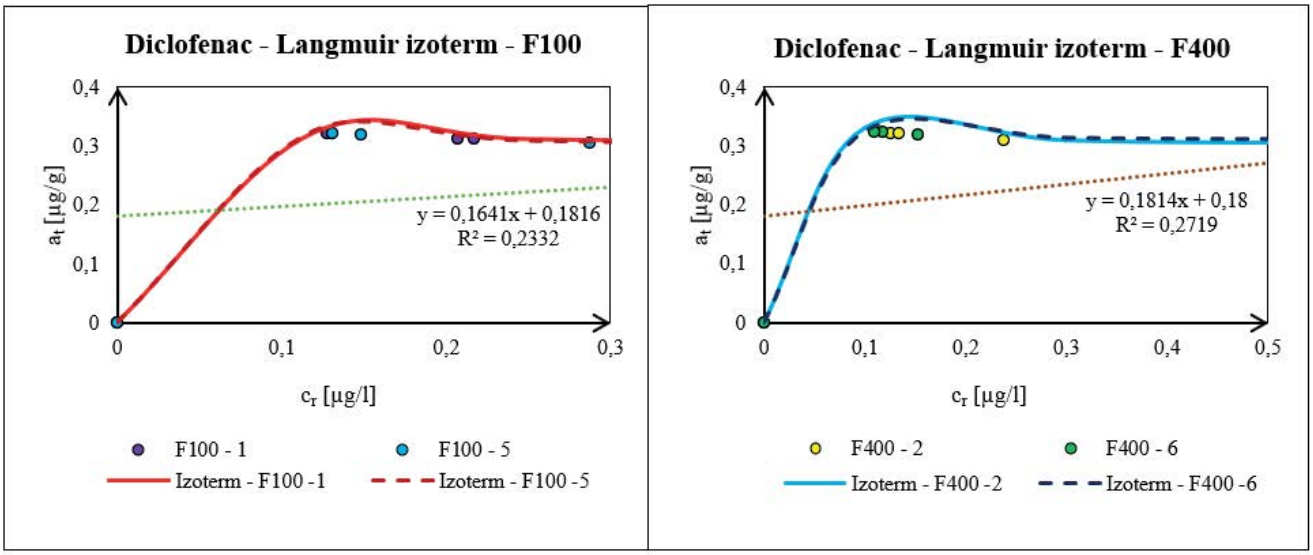


Fig. 10. Diclofenac removal process – Langmuir isotherm.

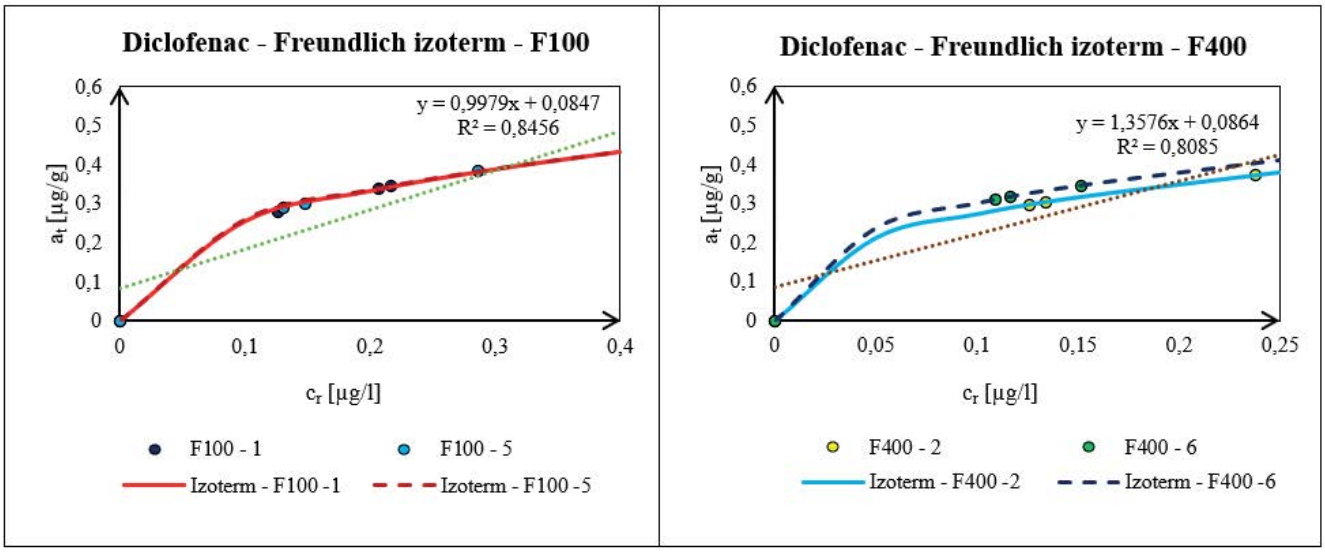


Fig. 11. Diclofenac removal process – Freundlich isotherm.

2.2 Selected Representatives of Over the counter (OTC) analgesics, the input concentration of all the drugs used for laboratory removal was higher.

3.1.1. Adsorption capacity of adsorbents in the elimination of ibuprofen

In ibuprofen elimination, both charcoal types proved to be suitable adsorbents. The highest adsorption capacity was achieved by Filtrasorb F400, with the value 4.968 µg/g. Just in the case of charcoal Filtrasorb F100, parallel measurements showed a decreased adsorption capacity after 2 h, which may be a wrong measurement considering the adsorption capacity was measured in the first beaker. Adsorbent GEH reached its peak adsorption capacity at 0.890 µg/g, probably due to the lower specific surface area of the material when compared to charcoal. The sorption material called Bayoxide E33 did not prove to be ideal for elimination of ibuprofen. The adsorption capacity values reached negative values after only 2 h, which may point to the desorption process occurrence.

3.1.2. Adsorption capacity of adsorbents in the elimination of diclofenac

The drug diclofenac was best eliminated by charcoal. Both Filtrasorb F100 and Filtrasorb F400 achieved similar values of about 0.3 µg/g after a mere 1 h. The adsorbents GEH and Bayoxide E33 did not prove to be suitable sorption materials for diclofenac elimination. The material GEH

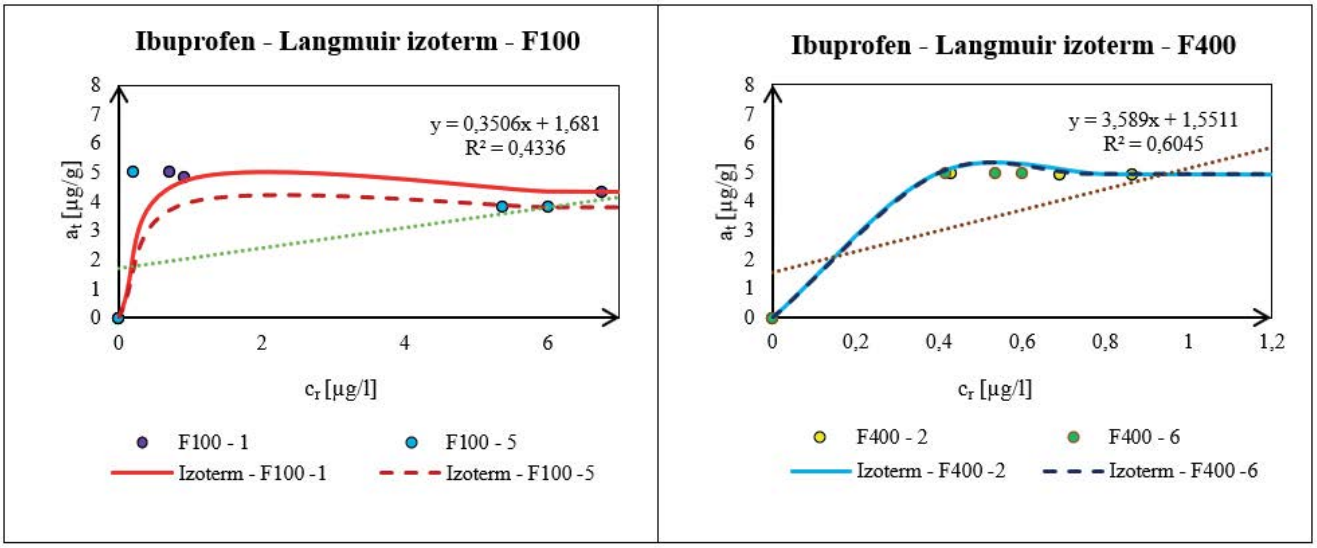


Fig. 12. Ibuprofen removal rate – Langmuir isotherm.

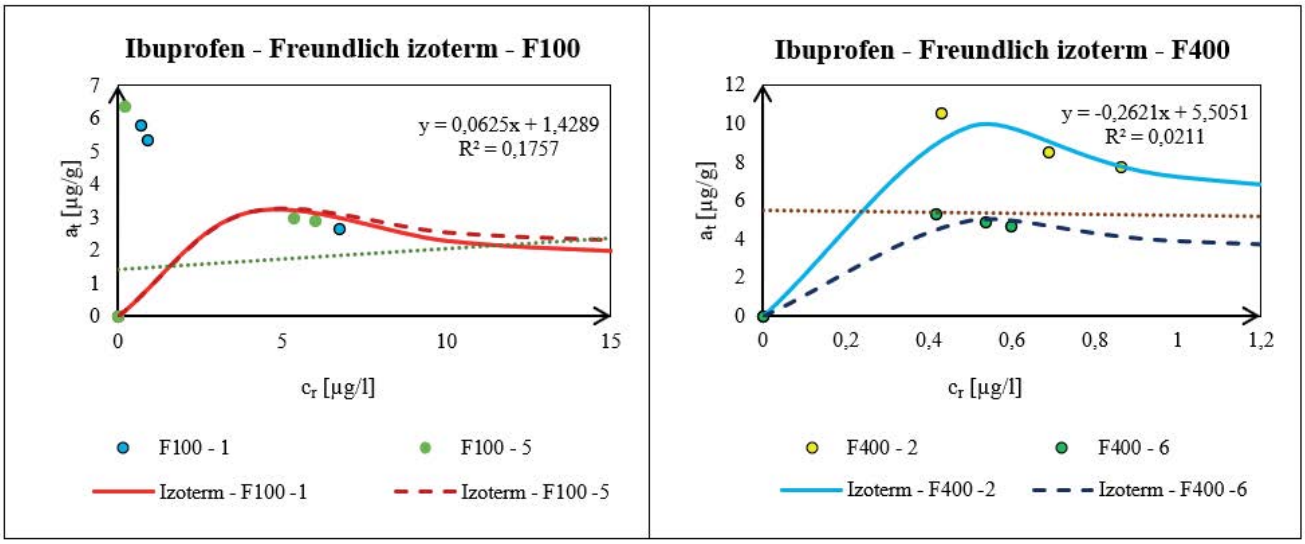


Fig. 13. Ibuprofen removal process – Freundlich isotherm.

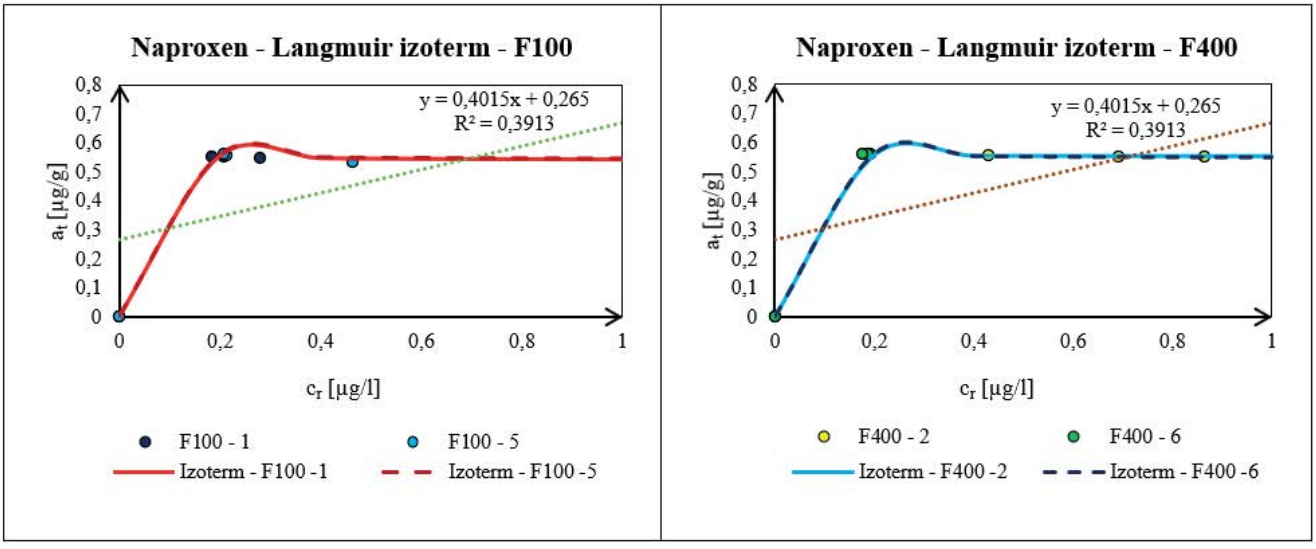


Fig. 14. Naproxen removal process – Langmuir isotherm.

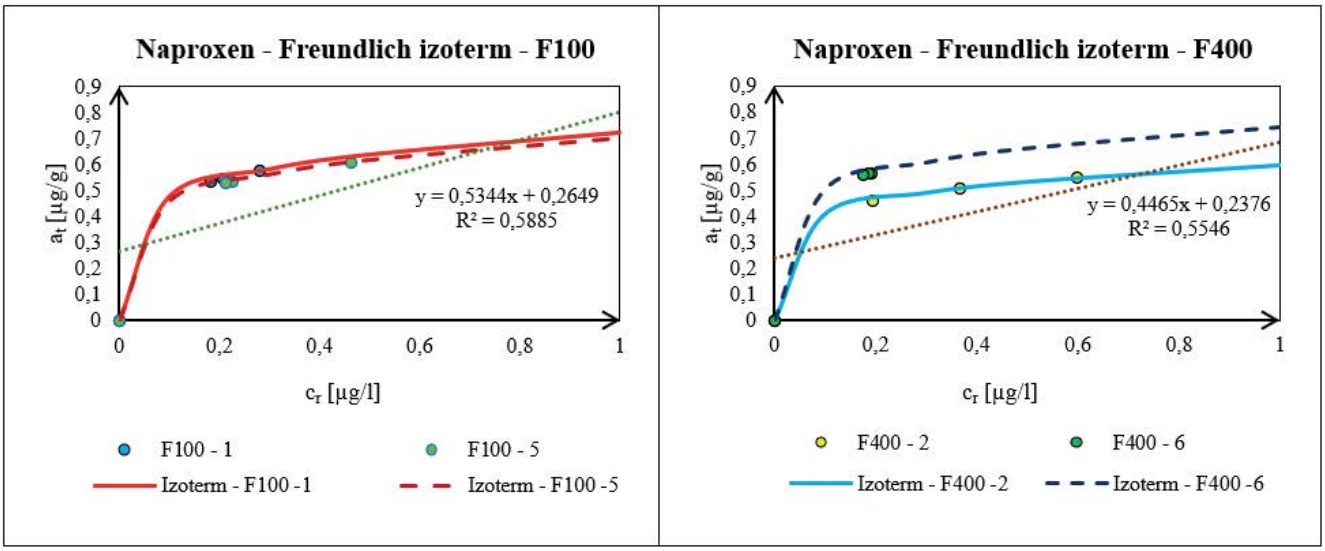


Fig. 15. Naproxen removal process – Freundlich isotherm.

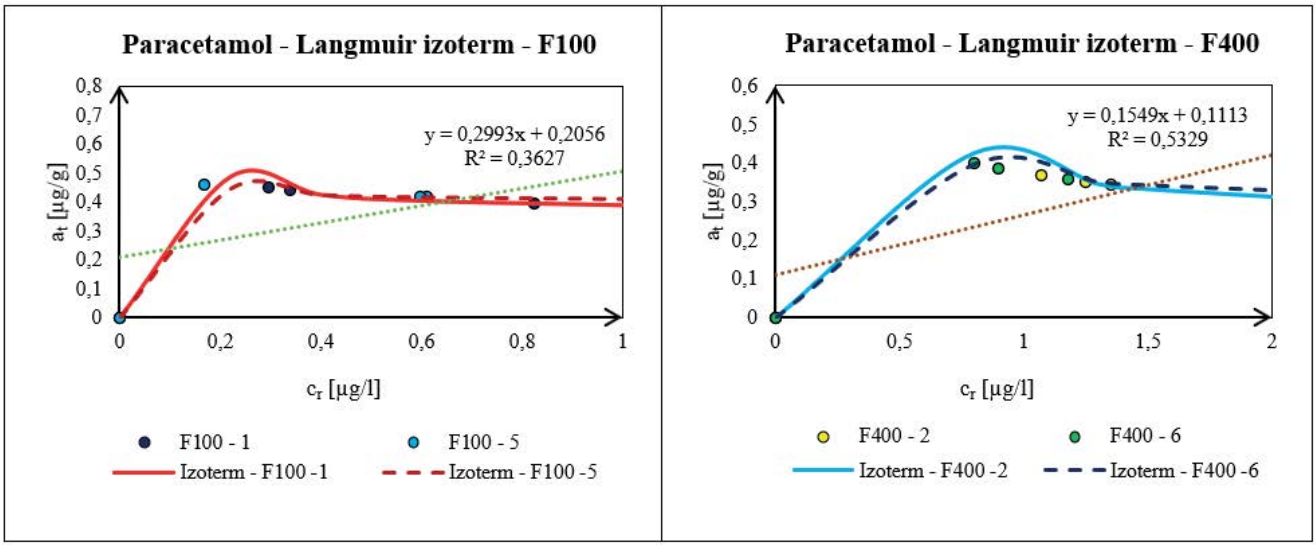


Fig. 16. Paracetamol removal process – Langmuir isotherm.

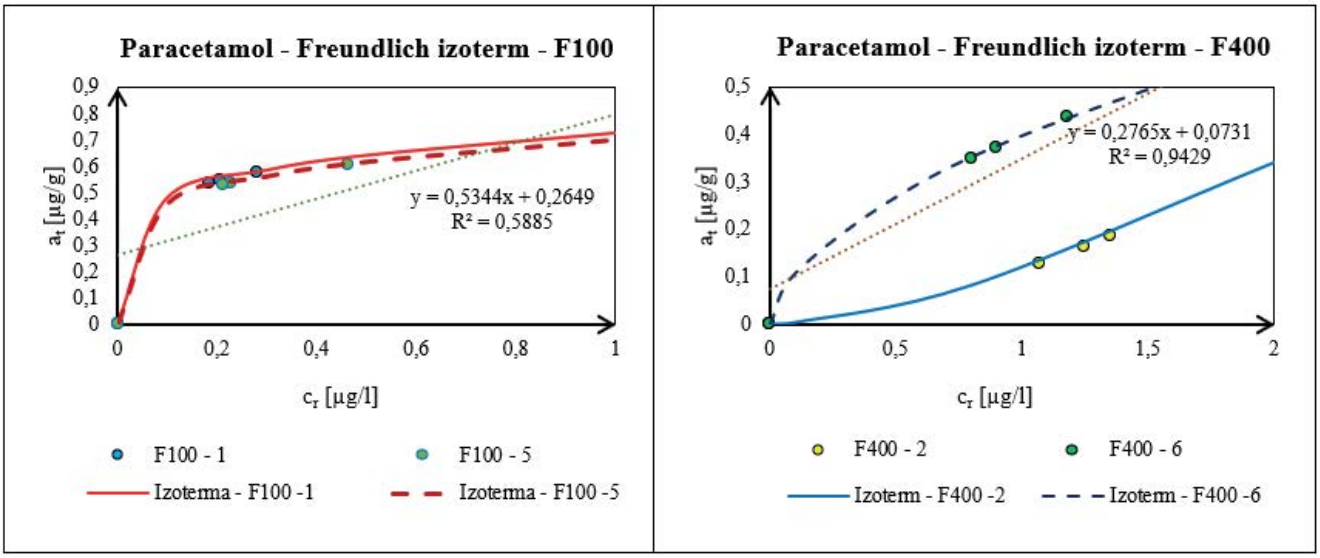


Fig. 17. Paracetamol removal process – Freundlich isotherm.

adsorbed the drug after 1 h but then reverted to desorption. Bayoxide E33 desorbed the drug nearly from the start of measurement.

3.1.3. Adsorption capacity of adsorbents in the elimination of naproxen

In the elimination of naproxen, charcoals again proved to be suitable adsorbents for the elimination of the drug from water. The large specific surface area increases the values of adsorption capacity. The sorbents GEH and Bayoxide E33 adsorbed the drug well after 1 h but then all beakers with these materials showed desorption, that is, the adsorption capacity of the GEH sorption material reached negative values.

3.1.4. Adsorption capacity of adsorbents in the elimination of paracetamol

The progress of adsorption capacity of the selected sorbents in the elimination of paracetamol was similar to the elimination of naproxen. The adsorption capacity of Filtrasorb F100 and Filtrasorb F400 charcoals reached up to 0.459 μg/g. The adsorption capacity of GEH in the first beaker reached negative values but a positive adsorption capacity was calculated for the parallel beaker. For the beakers with Bayoxide E33, the sorbent the adsorption capacity dropped after 2 h but after that the values began to rise again. Despite this, the adsorption capacity of Bayoxide E33 was not sufficient for paracetamol adsorption.

3.2. Evaluation of adsorption using adsorption isotherms

Langmuir and Freundlich isotherms were used to evaluate the dependence of adsorption capacity on adsorbate concentration. From the evaluation, it was found that both activated carbons satisfied both Langmuir and Freundlich isotherms. Due to the decreasing trend of adsorption capacity for GEH and Bayoxide E33 adsorbents, it was not possible to present the measured values by Langmuir or Freundlich isotherm. Therefore, only the values for Filtrasorb F100 and Filtrasorb F400 activated carbon are shown in the graphs below. As few measurements were taken during the experiment, the isotherms cannot be plotted according to the classical isotherm function. From the measured values it can be seen that they are close to the course of the isotherms. The adsorption isotherms are plotted for each drug separately according to the individual beakers with sorbents.

3.2.1. Evaluation of diclofenac removal by Langmuir and Freundlich isotherm

The measured values of diclofenac indicate that they are in the vicinity of both the Langmuir and Freundlich isotherms. In the case of more measurements, the tendency of the isotherm would be optimal.

3.2.2. Evaluation of ibuprofen removal by Langmuir and Freundlich isotherm

The initial concentration of ibuprofen was quite high compared to the other drugs, but still both sorption materials removed the drug reliably. The measured values reliably represent the progress of the Langmuir and Freundlich isotherms.

3.2.3. Evaluation of naproxen removal by Langmuir and Freundlich isotherm

During the removal of naproxen, drug concentration values were measured that follow the Langmuir and Freundlich isotherms. The Freundlich isotherm indicates the optimum function.

3.2.4. Evaluation of paracetamol removal by Langmuir and Freundlich Isotherm

From the measured values during the removal of paracetamol, it is evident that the drug was removed from the water immediately after the first measurement, and the ideal course of the Langmuir and Freundlich isotherms is indicated.

3.3. Evaluation of measured values of pH and temperature

The static test progress involved pH and temperature measurements. The pH values of model water, as well as of model water with sorbent, complied with the limit defined by Decree 70/2018 Coll., for they ranged between 6.5 and 9.5. The model water pH reached 7.030 but increased in all beakers after adsorbent addition.

The temperature measured in the model water was 18.8°C. In the course o3f the static test, the temperature increased slightly up to 20.3°C. That was probably caused by slight heating by the ergonomic temperature in the laboratory which ranged around 20°C.

4. Conclusion

The purpose of the performed experiment was the specification of the adsorption capacity of selected adsorbents by a performed static laboratory test of the removal of over the counter (OTC) analgesics from water. The experiment was performed on over the counter (OTC) analgesics for the reason of their recent extensive consumption as well as for the reason of their proven presence in drinking water sources [2,19]. Charcoal is known to typically be used in practice for the removal of this kind of contamination but other materials available on the market, and used for the removal of other micro pollutants, have not yet been tested for drug removal from water. The materials selected have shown efficacy in the removal of metals from water [10].

Both charcoal types proved to be suitable adsorbents for the removal of the selected drugs from water by the experiment performed. Both Filtrasorb F100 and Filtrasorb F400 achieved the highest values of adsorption capacity among the tested materials thanks to their large specific surface area. The sorption materials GEH and Bayoxide E33 did not prove sufficient efficacy in the removal of NSAIDs from water in the present experiment. In most cases, these materials rather led to desorption for the calculated adsorption capacity values were negative values. The adsorption of selected drugs on Filtrasorb F100 and Filtrasorb F400

sorption materials was also evaluated using Langmuir and Freundlich isotherms. The graphs presenting the course of isotherms in individual beakers show that the measured values fulfilled the adsorption conditions. The pH and temperature values specified in the course of the experiment met both appropriate laboratory condition requirements of the material manufacturers and the applicable legislative requirements. On the basis of the experiment performed, we conclude that Filtrasorb F100 and F400 charcoals are suitable means of removal of over the counter (OTC) analgesics from water. The research will also include the removal of selected drugs through sorbents dynamically, that is, by a column filled with the sorbents. However, these results will be presented in another paper and the resulting values from the static test will be used for comparison.

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