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Adsorption kinetics and adsorption isotherms for the elimination of organic micropollutants and dissolved organic carbon from municipal wastewater by activated carbon

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ABSTRACT

Activated carbon is used increasingly in the post-treatment of municipal wastewater in order to reduce micropollutant loads in aquatic systems. However, there is lack of knowledge concerning the capacity and kinetics of adsorption on activated carbon. Using treated municipal wastewater spiked with organic micropollutants in this study assesses the elimination efficiency of six different activated carbon products and investigates the adsorption capacity and kinetics of these products. Elimination efficiency was assessed for dissolved organic carbon (DOC), benzotriazole, carbamazepine, diclofenac and sulfamethoxazole. A comparison of different isotherm equations using equivalent molar radius and Stokes radius as parameters was also investigated focusing on adsorption kinetics as well as adsorption isotherms. Kinetics of DOC elimination were comparable for all activated carbons tested with an elimination of about 50% occurring within the first 5–10 min. Carbamazepine and diclofenac showed high elimination of more than 90% with carbon dosages of 5 mg/L or more. For benzotriazole and sulfamethoxazole 90% elimination could only be achieved with carbon dosages of 20 mg/L or more, depending on the activated carbon used. Analytical data for micropollutant elimination were found to be best represented by Freundlich isotherm.

Keywords: Adsorption kinetics; Adsorption isotherm; Activated carbon; PAC; GAC; Micropollutants; Benzotriazole; Carbamazepine; Diclofenac; Sulfamethoxazole

1. Introduction

Wastewater treatment plant (WWTP) effluents are one of the major pathways for organic micropollutants into aquatic ecosystems [1]. Although most of these micropollutants and their ecotoxicological potential are neither known nor quantified, the precautionary principle of the European Union suggests the reduction of micropollutant loads in wastewater; subsequently limiting their concentration and potential effects in aquatic ecosystems [2].

In this context, end of pipe technologies such as the utilisation of ozone or activated carbon [3,4] might be practical technological solutions as they are non-selective and can therefore serve to reduce micropollutant concentrations at municipal WWTPs. While ozone reacts with certain functional groups capable of donating electrons (e.g., C=C double bonds [5]), activated carbon adsorbs micropollutants with fairly different chemical and physical characteristics [6]. An advantage of adsorption on activated carbon is that no by-products, which are potentially more toxic than their precursors, are formed [7].

Due to the vast amount of different micropollutants found in wastewater, it nevertheless remains a challenge to identify particularly efficient activated carbon products for this use. At the moment, there are no indicator substances or parameters that are able to represent all these micropollutants [8].

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Thus, a deeper knowledge of adsorption capacities of different activated carbon products used in wastewater treatment could be helpful. In the present study, the adsorption capacity of six types of activated carbon was tested regarding the removal of four different micropollutants (benzotriazole, carbamazepine, diclofenac and sulfamethoxazole) representing a range of different chemical and physical characteristics. A pan-European study highlighted carbamazepine, diclofenac and sulfamethoxazole as the most frequently found compounds in ground water (in up to 42% of all samples [9]). Various other studies verify the frequent occurrence of all four micropollutants tested in this study [10–12]. Prior to micropollutant removal experiments, dissolved organic carbon (DOC) removal was also tested with the aim to compare activated carbons tested in a non-substance specific way and single out the most promising products.

Building on the experimental part of this work, the achieved adsorption was described by means of isotherm equations in order to find out whether the results can be modelled. To do so, Freundlich and Langmuir isotherms were used by the authors [13,14]. While the isotherm equations themselves are well known and widely applied [15,16], a new approach has been utilised which uses and compares both the equivalent molecular radius (EMR) and Stokes radius as a parameter in the Langmuir isotherm.

2. Materials and methods

2.1. Wastewater and micropollutants

The adsorption capacity of each of the six types of activated carbon was tested using real wastewater so that potential implications of the background matrix could be accounted for. By doing so an overestimation of the adsorption capacity of the activated carbon was avoided [17]. The wastewater was sampled from a municipal WWTP in Aachen, Germany. The plant incorporates conventional biological treatment and sand filtration as the last treatment step. In 2010, the WWTP served a population equivalent of 312,000 producing 24,750,000 m³ of wastewater. The samples were taken after the final clarification step and prior to the sand filtration; and were subsequently stored frozen at –14°C until further use. Before each experiment the required amount of wastewater was thawed and DOC of the sample was measured. This initial DOC ranged from 4.0 to 6.5 mg/L.

The micropollutants investigated in the present study were chosen to represent a great diversity of physical and chemical properties such as molecular structure, molecular mass and water solubility. Products used were all of analytical quality and purchased from Sigma-Aldrich, Germany (Table 1).

2.2. Types of activated carbon

The types of activated carbon tested in the present study represent four commercially available powdered activated carbon products and one granular activated carbon (GAC) whose properties are detailed in Table 2. Tests with powdered activated carbon were carried out with fresh activated carbon as delivered by the manufacturer. In order to assess the possibility of reusing the activated carbon in an application where a lower quality is needed, the granular carbon was tested both as delivered and also after 4 years of use in a filter bed at a drinking water treatment plant. The granular carbon samples were milled, producing a powder with similar properties to those of the other carbon samples. Thus, six types of then powdered activated carbon were assessed during the course of the present work. All activated carbon samples were dried at 105°C for 24 h prior to each test in order to be able to weigh the products without water content.

2.3. Test design

To assess DOC reduction, 1.5 L of wastewater was dosed with 5, 10, 20 or 50 mg/L of activated carbon in a 2-L glass bottle. The mixture was shaken continuously by means of a rotary shaker. Samples were taken before activated carbon dosage and at 5, 10, 15, 30, 45, 60, 90 and 120 min as well as 24 h after dosage. For sampling, a syringe and a 0.45 μm filter were used. The samples were stored at –14°C before being analysed for DOC via high temperature catalytic oxidation and non-dispersive infrared detection using Dimatoc 2000 (Dimatec, Essen, Germany).

DOC adsorption tests were mainly carried out to compare activated carbon products with each other in a way that is not substance specific and therefore allows for a general

Table 1
Micropollutants used in the present study with information about their molecular formula, molar mass, water solubility (where available respective temperature is provided in °C), hydrophobicity ($\log P_{oct/wat}$) and CAS number

Name	Molecular formula	Molar mass (g/mol)	Solubility in water (g/L)	$\log P_{oct/wat}$ (–)	CAS no.
Carbamazepine *Anticonvulsant*	$C_{15}H_{12}N_2O$	236.27	0.0177 (25°C)	2.45[a]	298-46-4
Diclofenac natrium *Analgesic*	$C_{14}H_{11}Cl_2NO_2Na$	318.13	1.5 (20°C)	1.1[a]	15307-79-6
Sulfamethoxazole *Antibiotic*	$C_{10}H_{11}N_3O_3S$	253.28	0.61 (37°C)	0.89[b]	723-46-6
Benzotriazole *Complexing agent*	$C_6H_5N_3$	119.13	20 (25°C)	1.44[b]	95-14-7

[a][18].
[b][19].

Table 2
Types of activated carbon used in the present study together with their properties

	Material	Inner surface (BET) (m^2/g)	Iodine number (mg/g)	Mean particle size D_{50} (μm)	Activation process
PAC1	Not known, other than bituminous coal	1,300	1,250	30.3	Steam activation
PAC2	–	1,150	1,050 (min. 1,000)	15	Steam activation
PAC3	Charcoal	>1,050	>1,050	25	Steam activation
PAC4	Coconut shell	–	min. 950	–	Steam activation
GAC1 (new) GAC2 (pre-used)	–	~1,000	950 ± 50	34.0 (re-use)[a] 26.3 (new)[a]	–

[a]Particle size obtained by means of milling with a blade granulator.
Note: BET – Brunauer–Emmett–Teller

evaluation of activated carbon performance. The results were also used to select the most relevant samples to be tested for micropollutant elimination.

The analytical approach of DOC adsorption tests was also used for investigations of the adsorption of micropollutants. Additionally, 200 μg of one of the selected micropollutants was added per litre of wastewater prior to activated carbon dosage. As these micropollutants possess a relatively low solubility in water, they were dissolved in methanol before dosing. One sample was taken after 24 h of shaking by means of a rotating shaker. Thus, it is assumed that equilibrium concentrations had been achieved. All samples were stored at –80°C and then concentrated in a solid phase extraction column. Following liquid chromatography separations, the samples were analysed with an LTQ Orbitrap (Thermo Fisher Scientific, Schwerte, Germany). The analytical procedures are described in detail by Gebhardt and Schröder [20].

An additional sample was chemically characterised to determine the background concentration of each of the four micropollutants in the wastewater. None of the four micropollutants exceeded the limit of quantification, which was 0.2 μg/L. Therefore, background concentrations can only add a maximum of 0.1% on top of the initial spike concentration of each of the micropollutants, which the authors consider negligible.

2.4. Isotherm equations

Adsorption isotherms were first calculated using the Freundlich equation (Eq. (1)) [13]:

$$q_E = K_F c_E^n \tag{1}$$

where q_E is the equilibrium load defined as mass of adsorbate per mass of adsorbent (mg/g), c_E is the equilibrium concentration of adsorbate in solution (g/L) and K_F as well as n represent Freundlich constants for a given combination of adsorbate and adsorbent.

The Freundlich isotherm was chosen because it is one of the most widespread isotherms used for adsorption of compounds from aqueous solutions and often results in a good fit with analytical data [21]. However, for very low concentrations the adsorption equilibrium can often be described by a linear function, which would result in Freundlich constant n converging to 1. For very high concentrations the isotherm's slope decreases. Therefore, Freundlich isotherm is best used in a medium concentration range.

A second approach was carried out by use of the Langmuir equation (Eq. (2)) [14]:

$$q = q_{\mathrm{m}} \frac{K_L \cdot c}{1 + K_L \cdot c} \tag{2}$$

Here, q is the equilibrium load defined as mass of adsorbate per mass of adsorbent (mg/g), q_m is the load for a complete monolayer on the activated carbon surface (g), c is the remaining concentration at equilibrium (g/L) and K_L is the Langmuir adsorption coefficient.

When calculating Eq. (2), the adsorbate's molecular radius r_{mol} (nm) is needed in order to determine the load q_m. However, in many cases the molecular radius of a certain substance is missing and cannot be easily determined, which makes calculation of q_m impossible. Consequently, r_{mol} has to be either calculated or fitted. A logical approach would be the determination of density by means of a chemical structure model. Hereafter actual calculation of the EMR can be undertaken as shown in Eq. (3), where molecular volume V_{mol} (m^3/mol) is derived from the chemical structure model as the quotient of mass and density.

$$r_{\mathrm{mol}} = \left(\frac{3}{4} \frac{V_{\mathrm{mol}}}{\pi \mathrm{N_A}} \right)^{\frac{1}{3}} \tag{3}$$

where $\mathrm{N_A}$ is Avogadro constant (1/mol).

In this paper, an alternative approach for the calculation of the Langmuir isotherm is made by use of the Stokes radius R_H (Eq. (4)) (also known as hydrodynamic radius). This radius does not describe the geometric radius of a molecule. In contrast to this, the Stokes radius is a concept used to describe the radius of a sphere which has the same diffusion rate as the original molecule.

$$R_H = \frac{k_B T}{6\pi\eta D} \tag{4}$$

As shown in Eq. (4), calculation of the Stokes radius R_H involves Boltzmann constant k_B (J/K), temperature T (K), viscosity η (kg/(s·m)) as well as the diffusion coefficient D (m^2/s). Values for Stokes radius in this work are derived from the literature.

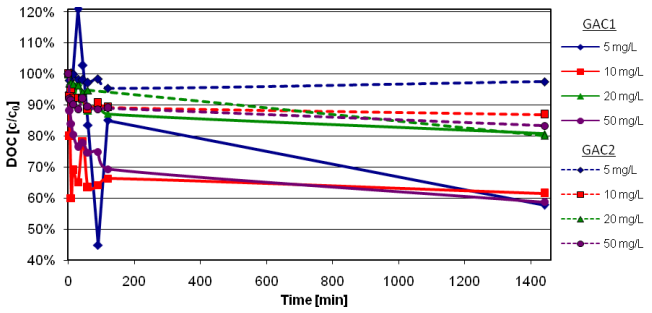

Fig. 1. Kinetics of DOC adsorption for GAC1 (unused) and GAC2 (pre-used).

3. Results and discussion

3.1. Elimination of DOC

All six activated carbons were tested regarding their DOC elimination in order to assess their overall adsorption capacity. Fig. 1 shows DOC adsorption kinetics of the two milled GACs (GAC1 and GAC2). Both of them represent the same commercially available product, with GAC1 being new and unused and GAC2 being the used material taken out of a filter bed from a municipal drinking water treatment plant after 4 years of utilisation. DOC adsorption results for the four PAC samples assessed during the course of the present study as well as for both GAC are shown in Table 3 and Fig. 2. With regard to the results in Fig. 1 and Table 3 it is important to keep in mind that initial DOC of the wastewater was similar, but not the same in all tests. Therefore, the lowest DOC at a certain time does not necessarily represent the highest proportionate elimination. Initial DOC of tests with the used carbon only varies slightly between 5.5 and 5.7 mg/L. At the

Table 3
DOC adsorption data for all activated carbon samples

	PAC1				PAC2				PAC3			
Dosage	5 mg/L	10 mg/L	20 mg/L	50 mg/L	5 mg/L	10 mg/L	20 mg/L	50 mg/L	5 mg/L	10 mg/L	20 mg/L	50 mg/L
Initial DOC (mg/L)	5.79	5.10	5.67	5.58	6.45	5.60	6.19	5.49	5.43	5.28	5.42	5.39
DOC Removal (%)												
5 min	13.8	7.3	21.5	31.5	–4.8	–1.3	17.0	32.1	5.0	11.2	15.9	28.4
10 min	5.4	10.4	25.9	36.9	5.7	8.7	24.2	37.7	–4.1	12.5	17.0	30.2
15 min	13.0	7.5	27.3	45.0	5.9	10.5	31.5	43.9	4.2	13.4	19.4	33.4
30 min	12.1	12.0	33.3	52.2	–1.9	7.0	34.1	48.8	6.3	15.0	22.0	37.1
45 min	16.2	14.5	32.6	52.9	9.6	13.8	34.4	52.5	0.0	17.2	22.1	40.3
60 min	2.4	13.9	30.9	57.0	4.8	9.3	36.5	51.7	5.5	21.4	25.1	40.1
90 min	17.8	17.5	36.5	60.0	10.9	10.0	38.4	52.1	5.7	21.6	26.0	42.9
120 min	17.1	15.5	37.9	60.9	9.6	18.6	39.9	56.1	9.0	19.1	29.5	44.5
1,440 min	18.3	20.2	44.8	69.7	15.0	11.1	42.6	64.1	12.7	22.2	37.6	50.1
	PAC4				GAC1				GAC2			
Dosage	5 mg/L	10 mg/L	20 mg/L	50 mg/L	5 mg/L	10 mg/L	20 mg/L	50 mg/L	5 mg/L	10 mg/L	20 mg/L	50 mg/L
Initial DOC (mg/L)	5.59	5.88	5.65	5.70	3.96	4.13	5.40	5.39	5.73	5.66	5.51	5.65
DOC Removal (%)												
5 min	–25.2	6.5	14.0	7.0	6.1	20.1	5.0	11.9	2.1	6.9	3.1	8.1
10 min	–32.6	12.9	15.2	11.9	3.5	40.0	7.2	16.0	–0.2	4.8	3.1	8.3
15 min	–19.7	10.9	14.3	1.8	0.0	31.0	9.8	19.5	0.2	8.0	3.3	9.7
30 min	–0.2	11.1	9.2	16.7	–21.0	34.9	2.6	23.6	1.9	7.6	3.6	11.3
45 min	2.3	4.3	15.6	11.1	–2.8	21.5	8.1	22.1	1.9	8.0	6.0	8.0
60 min	2.7	4.9	16.1	10.0	16.4	36.6	11.9	25.2	2.8	11.5	5.3	10.4
90 min	4.7	6.3	15.0	19.6	55.1	35.8	9.6	25.0	1.6	9.4	–187.8	11.3
120 min	–8.4	13.1	16.3	21.4	14.9	33.7	12.8	30.6	4.5	10.8	–14.0	11.0
1,440 min	–9.8	8.3	15.8	24.2	42.2	38.5	19.3	41.2	2.4	13.1	19.8	16.6

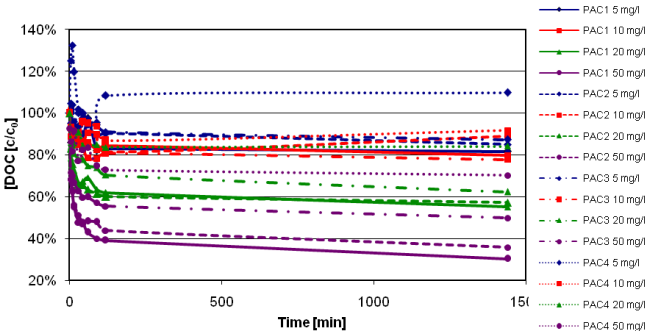

Fig. 2. Kinetics of DOC adsorption for PAC1, PAC2, PAC3 and PAC4.

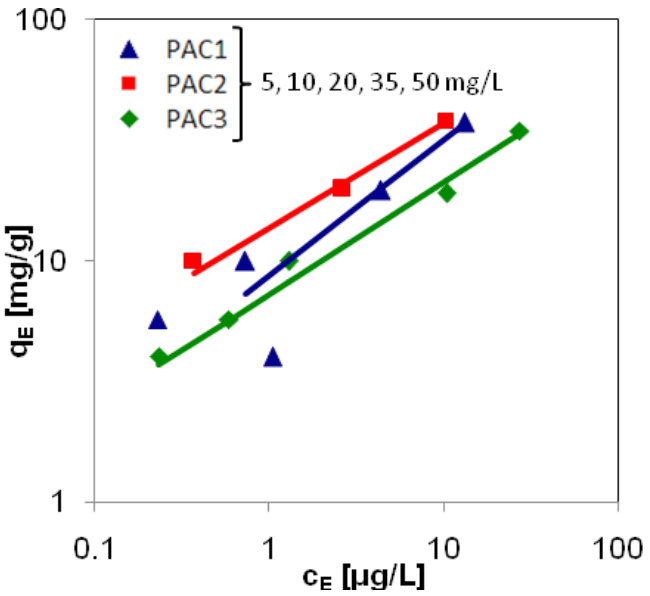

Fig. 3. Adsorption results for carbamazepine: carbon load q_E vs. residual concentration c_E after 24 h (solid lines indicate Freundlich isotherms).

same time, initial DOC of the tests with the new carbon ranges from 4.0 to 5.4 mg/L.

All six activated carbon products eliminated an average of 49% of DOC within only 5 min after dosage. After 10 min the elimination increased to 53%, while only 22% of the elimination took place between 2 and 24 h after activated carbon dosage. The results suggest that easily accessible adsorption sites are full after 10 min thus slowing the rest of the adsorption process. These kinetics were similar for all activated carbon concentrations. Moreover, no correlation between the elimination rate at the beginning and the overall elimination achieved after 24 h could be established, e.g., rapid elimination in the beginning does not necessarily lead to a high overall elimination. This indicates that adsorption in the beginning is dominated by a factor other than activated carbon surface available for adsorption.

The overall elimination achieved after 24 h ranges between 17% and 70% for the highest activated carbon dosage (50 mg/L) and from –10% to 18% for the lowest dosage, i.e., 5 mg/L. Lowest elimination after 24 h was achieved with pre-used product GAC2 at dosage of 50 mg/L and with PAC4 at dosages 5, 10 and 20 mg/L. Comparing GAC1 and GAC2 showed that for most activated carbon dosages the used carbon GAC2 (average of 13%) has a considerably poorer elimination than the fresh carbon GAC1 (average of 35%).

Some of the measurements show an increase in DOC concentration over time thus resulting in negative eliminations. This can be observed several times for activated carbon concentrations of 5 and 10 mg/L and once for an activated carbon concentration of 20 mg/L. As elimination is comparably low for dosages of 5 and 10 mg/L, low negative eliminations might well derive from variability of measurement in these cases. However, this is unlikely for the negative elimination observed after 90 min for GAC2 at a dosage of 20 mg/L. As GAC2 had been previously used, both desorption of previously adsorbed DOC as well as contamination in the experiment are possible. As DOC increase is immediate and high, the latter explanation seems to be more likely. All in all, best elimination of DOC was achieved with PAC1, PAC2 and PAC3. Subsequently, these samples were chosen to be tested for micropollutant elimination in the following step. Although GAC2 had performed rather poorly regarding DOC elimination, it was still included in the experiments regarding elimination of benzotriazole and sulfamethoxazole. In this case, the benefits of downcycling a used carbon were expected to still be given even with a comparably low performance.

3.2. Elimination of micropollutants

Elimination of carbamazepine at an activated carbon dosage of 10 mg/L was more than 94.5% for all activated carbons tested. 99% of carbamazepine was adsorbed at an activated carbon concentration of 20 mg/L in all tests (see Fig. 3). Even the lowest concentration of 5 mg/L led to an elimination of 93% or more for PAC1 and PAC2. However, PAC3 showed considerably lower elimination of 86.4% at this dosage.

Activated carbon load ranged between 34.6 and 38 mg/g for an activated carbon concentration of 5 mg/L. The difference between the loads of the different carbons tested decreases with increasing activated carbon concentration. For an activated carbon concentration of 50 mg/L calculated load was 4.0 mg/g for all PAC due to the fact that the residual concentrations are in the low µg/L range and elimination reaches nearly 100%. While absolute difference in loads is very small for an activated carbon concentration of 50 mg/L, relative difference is high with a factor of 26 between residual concentrations of carbamazepine for PAC1 and PAC3.

The experimental results are comparable to those reported by Abegglen et al. [22]. In their study, the authors tested the elimination of micropollutants with an activated carbon concentration of 10 mg/L. Regarding carbamazepine, Abegglen et al. [22] measured an average elimination of 95% with what is named PAC2 in this study. Metzger [23] also stated an elimination of 95% for 10 mg/L activated carbon and complete elimination for 20 mg/L of activated carbon. In the present study, elimination ranges from 94.8% to 98.7% for 10 mg/L and 99.4% or higher for 20 mg/L, verifying the findings from the other authors. However, it should be noted that Abegglen et al. [22] and Metzger [23] used treated wastewater which they did not spike as was done in this study.

Adsorption of diclofenac is the highest adsorption observed amongst all micropollutants tested in this study. At an activated carbon dosage of 10 mg/L at least 97.1% elimination was achieved. For all activated carbons, residual concentrations of diclofenac are below the limit of quantification at an activated carbon dosage of 20 mg/L thus resulting in at least 99.9% elimination. Because of that there are only two values displayed for each carbon in Fig. 4.

For an activated carbon concentration of 5 mg/L PAC1 shows a better result than PAC2, with activated carbon loads of 38.5 and 37.9 mg/g and residual concentrations being 7.6 and 10.7 μg/L, respectively. Increasing the activated carbon concentration to 10 mg/L leads to residual concentrations of 1.8 μg/L for PAC1 and 2.0 μg/L for PAC2. All in all, elimination of diclofenac with activated carbon PAC3 is always lower than with PAC1 and PAC2, as was also found for carbamazepine elimination. One reason could be the fact that PAC3 has the lowest inner surface of the PACs tested.

The results for diclofenac differ from those in the literature. While Abegglen et al. [22] state an elimination of about 85% and Metzger [23] about 90% for 10 mg/L activated carbon, values in the present study range from 97.1% to 99.1% although PAC2 was used by both Abegglen et al. [22] and Metzger [23]. An explanation for the difference in elimination might be rather low and varying initial micropollutant concentrations which both Abegglen et al. [22] and Metzger [23] reported due to the fact that they did not spike.

Elimination of benzotriazole is lower than that of diclofenac and carbamazepine as can be seen in Fig. 5. With an activated carbon dosage of 5 mg/L, an elimination ranging from 73% to 81% was achieved. The elimination increases to 94.7% for a dosage of 50 mg/L using GAC2 which is nearly as good as PAC3, thus showing that a pre-used carbon might well be suitable to replace fresh carbons regarding specific applications.

The best results were attained with PAC2, its load is 31.7 mg/g for an activated carbon concentration of 5 mg/L which is 2.2 mg/g more than PAC1. Residual concentrations range from 37.4 to 53.3 μg/L. High residual concentrations remain for low activated carbon concentrations (5 and 10 mg/L). Nevertheless, the highest specific load of activated carbon is achieved in these cases. As can also be seen in the results of DOC elimination, an increase in activated carbon dosage does not lead to a proportional increase in elimination.

Benzotriazole was found to be eliminated to slightly less than 90% on average in investigations reported by Abegglen et al. [22]. This is similar to the results achieved with PAC1 and PAC2 in the present paper while with PAC3 only about 80% elimination was achieved.

Regarding sulfamethoxazole, the Freundlich isotherms in Fig. 6 show that activated carbon load was comparably low resulting in the lowest elimination results of all tested micropollutants. With 5 mg/L activated carbon a residual sulfamethoxazole concentration of below 118.5 μg/L was achieved thus resulting in an elimination of just 40.7%. For the other micropollutants tested, no residual concentration higher than 53.2 μg/L was found even at low activated carbon dosages. In order to achieve 90% elimination of sulfamethoxazole at least 20 mg/L activated carbon had to be used. Besides PAC1, PAC2 and PAC3; GAC2 was tested for activated carbon concentrations of 35 and 50 mg/L. Despite these rather high concentrations, an elimination of sulfamethoxazole of only 14.0% and 43.9%, respectively, was measured in this case.

Highest loads were achieved with activated carbons PAC1 and PAC2, as it is the case with all other substances as well. PAC2 shows a slightly higher load than PAC1 for high residual concentrations, i.e., low activated carbon concentrations. For PAC3 only three values are shown in Fig. 6 as with activated carbon concentrations of 5 and 10 mg/L an increase in sulfamethoxazole concentration was measured which cannot

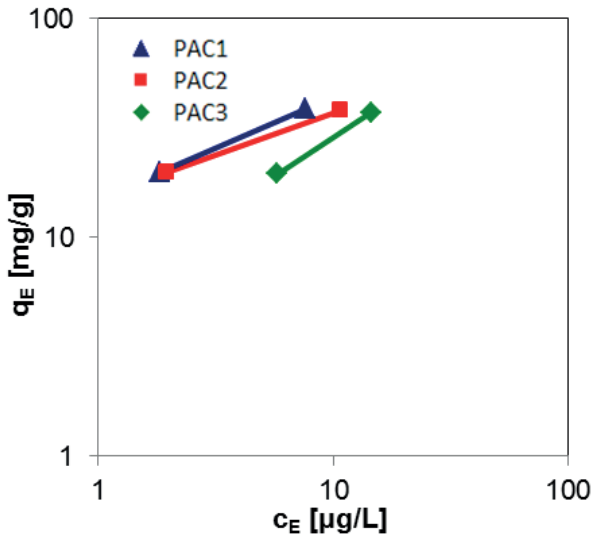

Fig. 4. Adsorption results for diclofenac: carbon load q_E vs. residual concentration c_E after 24 h (solid lines indicate Freundlich isotherms).

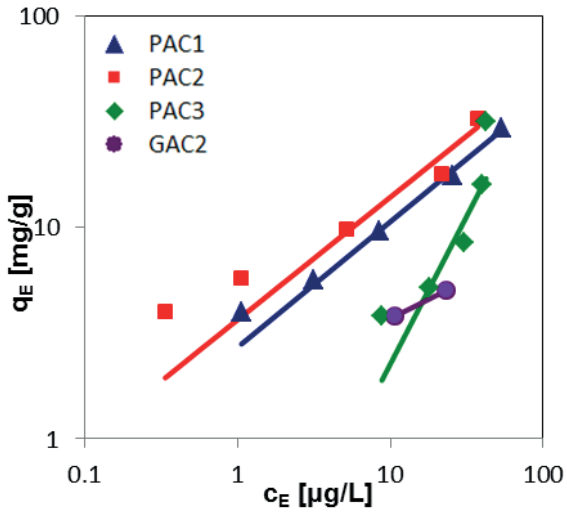

Fig. 5. Adsorption results for benzotriazole: carbon load q_E vs. residual concentration c_E after 24 h (solid lines indicate Freundlich isotherms).

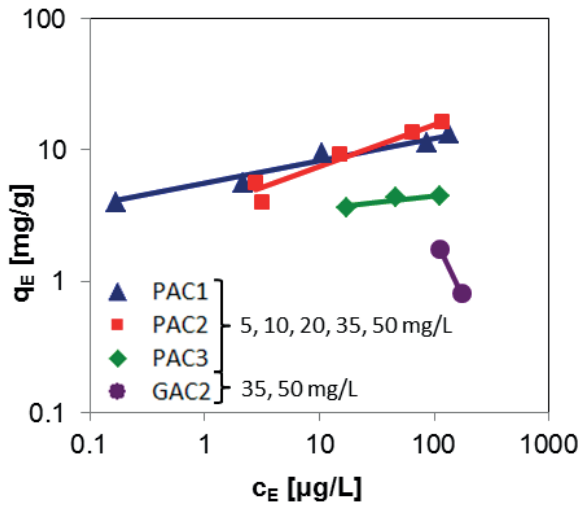

Fig. 6. Adsorption results for sulfamethoxazole: carbon load q_E vs. residual concentration c_E after 24 h (solid lines indicate Freundlich isotherms).

be displayed on a logarithmic scale. Adsorption of sulfamethoxazole with pre-used activated carbon GAC2 results in eliminations as low as 14.0% and 43.9% for activated carbon concentrations of 35 and 50 mg/L.

All in all, the experiments on the adsorption of sulfamethoxazole resulted in being the substance that was least adsorbed of all substances tested in this study. This finding was also made by Abegglen et al. [22]. Low adsorption can be explained by the fact that sulfamethoxazole has a higher polarity than the other micropollutants tested.

3.3. Adsorption isotherms

A Freundlich isotherm was fitted to the experimental data obtained for each activated carbon. The values in Table 4 show that a good description of micropollutant adsorption data can be achieved in most cases. However, the fitting of the Freundlich isotherm is slightly better for carbamazepine and diclofenac then for benzotriazole and sulfamethoxazole. Regarding DOC elimination, only the isotherm calculated for PAC3 fitted the data well ($r^2 > 0.91$) while PAC1 and PAC2 results could not be described using the isotherms. In these two cases, the load achieved with a dosage of 10 mg/L is lower than the load achieved with 20 mg/L thus resulting in an outlying value. Part of the reason for this might be the fact that in both cases the initial DOC of the 10 mg/L dosage was lower than that used for the 5 mg/L dosage.

Çalışkan and Göktürk [24] also fitted data for adsorption of sulfamethoxazole to the Freundlich isotherm. Resulting parameters are K_F = 68.89 and n = 0.31. While for PAC2 a similar value for n was achieved, the K_F value in this paper is significantly lower. A closer inspection of Çalışkan and Göktürk's experiments shows that initial micropollutant concentrations are 5–10 times higher than in this study and residual concentrations are even up to 200 times higher. This may explain the differences as Freundlich isotherm fitting depends on the concentration range where it is used. Similar values for K_F were found be Yu et al. [25]. In their experiments on adsorption of micropollutants on different natural soils the authors found a K_F of 5.5 for benzotriazole, 14.3 for carbamazepine and 18.7 for sulfamethoxazole for the adsorption on Euro 5.

Regarding elimination no correlation between adsorption and molar weight, solubility or logK_{OW} of the micropollutants could be found. Adsorption increases with hydrophobicity, expressed as log$P_{oct/wat}$, for sulfamethoxazole (log$P_{oct/wat}$ = 0.89), benzotriazole (1.44) and carbamazepine (2.45). However, the best adsorption results were achieved with diclofenac (log$P_{oct/wat}$ = 1.10) despite its comparably low log$P_{oct/wat}$. At the same time diclofenac has the highest molar weight (318.13 g/mol) and the second lowest adsorbed sulfamethoxazole (253.28 g/mol). A reason for the poor sulfamethoxazole elimination might be the highest number of H-bond donors and acceptors.

3.4. Comparison of different isotherm equations using different ways of calculating molecular radius

One of the required parameters for the Langmuir isotherm is the load corresponding to a complete monolayer adsorption of the selected micropollutant. As the size of the micropollutant molecule is often unknown, the complete monolayer is frequently taken as another parameter to be fitted to the data [26]. This can lead to a very good fit of the isotherm equation obtained. At the same time the value for the complete monolayer might not represent the true situation very well. Therefore, in this paper the load corresponding to a complete monolayer adsorption was calculated beforehand. In order to do so the molecular size of the micropollutants need to be taken in consideration, e.g., represented

Table 4
Freundlich parameters for adsorption of DOC and micropollutants for five different activated carbon dosages

	DOC			Carbamazepine			Sulfamethoxazole			Diclofenac			Benzotriazole		
	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2
PAC1	0.0056	0.774	0.422	8.70	0.56	0.914	5.61	0.17	0.959	14.99	0.47	0.985	2.71	0.59	0.994
PAC2	0.0186	0.437	0.122	13.70	0.43	0.975	3.61	0.32	0.977	15.31	0.38	1.000	3.65	0.58	0.935
PAC3	0.0003	1.405	0.916	7.24	0.46	0.983	2.85	0.10	0.779[a]	5.59	0.71	1.000	0.00	3.54	0.821

[a]Only three dosages fitted, other two dosages with negative elimination.
[b]Only three dosages fitted, as three highest dosages resulted in elimination under quantification limit just lowest of these was taken.

Table 5
Molecular radius, stokes radius and values for complete monolayer, calculated values given in italics

	Equivalent molecular radius				Stokes radius			
	r_{mol} (nm)	Monolayer load PAC1 (mg/g)	Monolayer load PAC2 (mg/g)	Monolayer load PAC3 (mg/g)	Stokes radius (nm)	Monolayer load PAC1 (mg/g)	Monolayer load PAC2 (mg/g)	Monolayer load PAC3 (mg/g)
Benzotriazole	*3.27*	*7.65*	*6.76*	*6.18*	–	–	–	–
Carbamazepine	*4.24*	*9.05*	*8.00*	*7.31*	0.37[a]	*1,186*	*1,049*	*958*
Diclofenac	*4.35*	*10.78*	*9.53*	*8.71*	–	–	–	–
Sulfamethoxazole	*4.10*	*10.38*	*9.18*	*8.38*	0.38[a]	*1,205*	*1,066*	*973*

[a][27].

Table 6
Langmuir isotherm parameter K_L calculated using stokes and molecular radius, respectively

		Carbamazepine		Sulfamethoxazole		Diclofenac	Benzotriazole
		Stokes radius	Molecular radius	Stokes radius	Molecular radius	Molecular radius	Molecular radius
PAC1	K_L	2.64E–03	3.00E+02	9.39E–05	1.30E+02	4.14E+02	2.64E+02
	R^2	0.84	–0.47	0.65	0.84	0.88	0.49
PAC2	K_L	3.94E–03	8.50E+02	1.54E–04	1.62E+02	4.63E+02	3.18E+02
	R^2	0.61	0.01	0.68	0.66	0.88	0.01
PAC3	K_L	1.47E–03	1.21E+01	5.25E–05	7.55E+01	4.96E+02	3.22E+02
	R^2	0.80	–0.42	–34.79	–	0.88	0.00

by their radius. As an alternative to the calculation of EMR, Stokes radius was tested regarding its feasibility in this work. Equivalent molecular radius for all micropollutants was calculated using Eq. (4) and Stokes radius was taken from the literature. Resulting values are displayed in Table 5.

These values were used to calculate the activated carbon load for one complete layer of the compound as is assumed by Langmuir isotherm. Results are presented in Table 5.

The values for complete monolayer coverage, which have been calculated using Stokes radius, are about 1 g per gram of activated carbon.

Parameter K_L (see Eq. (2)) can be fitted to the experimental data using the values in Table 5. The results of this fit are presented in Table 6. Stokes radius leads to an acceptable fit for carbamazepine, whereas the use of molecular radius leads to very low values for R^2 in this case.

For all other micropollutants no trend comparing quality of fit with the Stokes radius and with the molecular radius can be observed. However, fitting is always far better using the Freundlich isotherm than using the Langmuir isotherm with either of the two radii.

4. Summary

Six activated carbons were tested regarding the kinetics and capacity of the adsorption of DOC, benzotriazole, carbamazepine, diclofenac and sulfamethoxazole from treated wastewater.

The main findings regarding DOC elimination can be summarised as follows:

- For all activated carbons tested about 50% of the elimination takes place within 5–10 min after activated carbon dosage. Later adsorption occurs at a much slower pace as easy accessible adsorption sites are already full.
- The adsorption rate in the beginning does not correlate with the overall elimination after 24 h. This result suggests that adsorption rate in the beginning is dominated by factors other than the total activated carbon surface which is available for adsorption.

Concerning the elimination of four micropollutants it was found that:

- Carbamazepine and diclofenac showed high elimination of more than 90% with carbon dosages of 5 mg/L or more. While carbamazepine has the highest KOW and the lowest number of H-bond acceptors of all micropollutants tested, it was eliminated slightly less than diclofenac.
- For benzotriazole and sulfamethoxazole 90% elimination can be achieved with carbon dosages of 20 mg/L or more, depending on the activated carbon used. Lowest elimination was observed for highly polar sulfamethoxazole.
- Freundlich isotherm provides a good fit for the experimental data in most cases.

Additionally, an alternative approach to calculate Langmuir isotherm using the Stokes radius was discussed. However, a better fit than with Freundlich isotherm could not be achieved with the use of Stokes radius nor with EMR. More data are needed to further compare both calculation methods. As Langmuir isotherm is based on the assumption

that there is only a monolayer of adsorption, it would also be interesting to compare the above findings with a fitting of Brunauer–Emmett–Teller isotherm.

For better understanding of adsorption onto activated carbon further research focusing on the correlation of the physical and chemical parameters of the activated carbon parameters and the substances to be adsorbed is needed.

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Symbols

c and c_E	—	Mass of adsorbate in solution at equilibrium, μg/L and g/L
D	—	Diffusion coefficient, m^2/s
k_B	—	Boltzmann constant, J/K
K_F	—	Freundlich constant for given combination of adsorbate and adsorbent
K_L	—	Langmuir adsorption coefficient
n	—	Freundlich constant for given combination of adsorbate and adsorbent
η	—	Viscosity, kg/(s·m)
N_A	—	Avogadro constant, 1/mol
q, q_E	—	Mass of adsorbate per mass of adsorbent at equilibrium, mg/g
q_m	—	Load for a complete monolayer on the activated carbon surface, mg/g
R_H	—	Stokes radius, m
r_{mol}	—	Equivalent molecular radius, nm
T	—	Temperature, K
V_{mol}	—	Molecular volume, m^3/mol

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