

Development of efficient characterization parameters for activated carbon used in drinking water treatment

Lucas Landwehrkamp, Arman Kouchaki-Shalmani, Claudia Forner, Ralph Hobby, John Eduful and Christoph Wagner

ABSTRACT

In many drinking water treatment facilities with an activated carbon (AC) purification step, polar and hydrophilic molecules are substances of concern. Many of the current test methods for AC do not really reflect AC's adsorption capacity for these substances. To develop a fast and economically reasonable parameter that characterizes AC's ability to remove these compounds, three substances, namely diclofenac, nitrobenzene, and diatrizoate were investigated as test substances. A test set of different AC samples was created by reactivating an exhausted AC in three different ways. Additional AC samples were obtained by sampling different depths of a full-scale AC filter at regular intervals during the operation time of the filter. Several adsorption tests were performed with the three test substances, including adsorption isotherms in the concentration range mg/L, single-point adsorption tests in the concentration range $\mu\text{g/L}$, and pilot-scale fixed bed filter experiments. The results suggest that diatrizoate allows for a sensitive comparison of different AC samples. A characteristic figure, the 'diatrizoate number' was developed. This diatrizoate number allows for a sensitive, cheap, and quick comparison of different ACs. A similar survey with special focus on problematic substances present on site is recommended for other water treatment facilities.

Key words | activated carbon, adsorption isotherm, diatrizoic acid, diclofenac, drinking water treatment, reactivation

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INTRODUCTION

Activated carbon (AC) adsorption has been used in drinking water treatment for decades to meet varying challenges. Whereas the primary goal was the removal of residual chlorine and the improvement of the organoleptic properties of the water, the objectives of AC use in Germany have shifted since then (Worch 2012). For about 30 years, AC has increasingly been used to remove a variety of organic micropollutants. Depending on the specific location, these micropollutants can include chlorinated hydrocarbons, crop protection products, perfluorinated compounds, and pharmaceuticals (Kaplan 2013; Richardson & Ternes 2014). Hence, AC adsorption can be seen as an essential step in the production of safe and esthetic drinking water,

especially in a highly developed country like Germany, where the combination of a dense and aging population (increased drug use) with a high grade of industrialization leads to intensive use of the available water resources.

For an economically reasonable choice and a sustainable application of AC, it is important to have tools for the description of the adsorption properties on hand. An essential question to be answered is: which parameters are suitable to describe the performance in drinking water treatment regarding:

- raw water properties (pH, dissolved organic carbon background, etc.);

- substances of concern/micropollutants;
- the performance after reactivation/regeneration.

As the AC used in the municipal water treatment plants in Düsseldorf, Germany, is granular activated carbon (GAC) in fixed bed filters, this article deals specifically with the characterization of GAC.

To choose a GAC type for a specific application, it is recommended to perform pilot-scale fixed bed filter tests. As these tests can be performed with the raw water that has to be treated later on and the original particle size of the GAC, they are a valuable and frequently applied tool for the assessment of AC in water and waste water treatment (Ho *et al.* 2011; Kennedy *et al.* 2015; Meinel *et al.* 2015). The major drawback of this method is, however, that it is very time-consuming. The runtime of pilot-scale filters varies from a few weeks to several months, depending on the adsorbate, the adsorbent, the filter bed height, and several other parameters (Marcus 2005; Poddar *et al.* 2013). Hence, these tests are not suitable for situations that require quick decisions, such as adjustments in the (re)activation process or intake controls. Although there is a variety of quicker characterization methods on hand (Table 1), these often do not reflect the site-specific treatment situation.

Many drinking water treatment facilities in Germany are facing the problem that their ‘substances of concern’ are polar, hydrophilic organic molecules. Detailed reviews analyzing the occurrence and importance of specific

contaminants are available in the literature (Kaplan 2013; Richardson & Ternes 2014). It should be noted that the occurrence of these substances in the raw water is not an exclusively German problem but a challenge in many densely populated areas of the world facing anthropogenically influenced raw water sources (Focazio *et al.* 2008; Heeb *et al.* 2012; Kuzmanovic *et al.* 2015). Polar and hydrophilic substances can significantly shorten the lifetime of AC filters due to their poor adsorption behavior on the hydrophobic surface of ACs. Consequently, the adsorption performance of an AC in regard to these substances is of particular importance. The main objective of this study was, therefore, to find a parameter that reflects AC’s ability to remove these compounds, with specific regard to compounds present in the raw water of the municipal water treatment facilities of Düsseldorf, Germany. This parameter should be quickly measurable, reproducible, and economically reasonable.

MATERIALS AND METHODS

To find a suitable parameter, it was first checked which substances are frequently present in the raw water in Düsseldorf. Based on this analysis, a relatively good adsorbable substance (diclofenac) and a poorly adsorbable substance (diatrizoate) were selected as test substances. Nitrobenzene was also included as a test substance in the analysis program because it is recommended as a test substance in the German guidelines for the testing of AC for water treatment (DVGW 2009).

For a systematic survey of all three test substances with regards to their ability to characterize the AC used in Düsseldorf, a test set of three different AC samples was created. These samples were obtained by splitting a complete exhausted filling of a full-scale AC filter into three parts. Each part was reactivated/regenerated under different conditions, which yielded three different AC samples. The following different tests were performed with these AC samples:

- adsorption isotherms using diclofenac, diatrizoate, and nitrobenzene (concentration range mg/L);
- single point adsorption tests using diclofenac and diatrizoate (concentration range µg/L);

Table 1 | Parameters for the characterization of activated carbon (ASTM D28; Sontheimer *et al.* 1988; Bandosz 2006)

Parameter	Information
Iodine number	Adsorption capacity for iodine, often correlating with the inner surface/ the general adsorption capacity
Adsorption/desorption isotherms for N ₂	Inner surface, pore volume, distribution of pore radii
Mercury intrusion	Meso and macro pore volume
Various physical tests	Density, grain size distribution, mechanical stability, wettability
Adsorption isotherm (liquid phase)	Adsorption capacity for certain substances/mixtures
Chemical purity	For example, total ash content, heavy metal content, leachable substances

- experiments in a pilot-scale fixed bed filter using real raw water and measurement of diatrizoate breakthrough.

Based on the results obtained by the examinations described above, it was decided to perform adsorption isotherms in the concentration range mg/L for nitrobenzene and diatrizoate on a larger set of AC samples. These samples were obtained by sampling different depths of a full-scale AC filter; in the following they will be called ‘depth-samples’. Samples from four different layers of the filter bed were taken every 3 weeks during operation of the filter. The migration of the mass-transition zone through the filter bed causes different residual adsorption capacities in the different filter layers. By sampling different depths of the filter it was possible to: (1) evaluate the residual adsorption capacity in the different layers, and (2) compare the sensitivity of the two test substances. This is, to our knowledge, the first time that a full-scale AC filter for drinking water production was sampled in this detailed manner.

Water treatment facilities in Düsseldorf

The three municipal water works of Düsseldorf, Germany, supply about 600,000 inhabitants of the city and its suburban municipality with drinking water, therefore relying on a mixture of river bank filtrate from the river Rhine (~70%) and groundwater (~30%) as the raw water source. The water is treated with the so-called ‘Düsseldorf process’, which consists of river bank filtration, subsequent oxidation with ozone, physical deacidification with air, and deep bed filtration in double stage filters (Figure 1). These filters consist of a layer of granular anthracite, which is backwashed at regular intervals (after 100,000 m³ treated water), and an AC layer with a height of approximately 2.5 m, which is exchanged and reactivated when exhausted. The filters possess a total surface area of 19.6 m² and are operated at filtration speeds between 6 and 13 m/h.

Reactivation of AC

For investigations on the three reactivated AC samples, a complete filling (approximately 46 m³) of an exhausted full-scale AC filter was divided into three portions. The

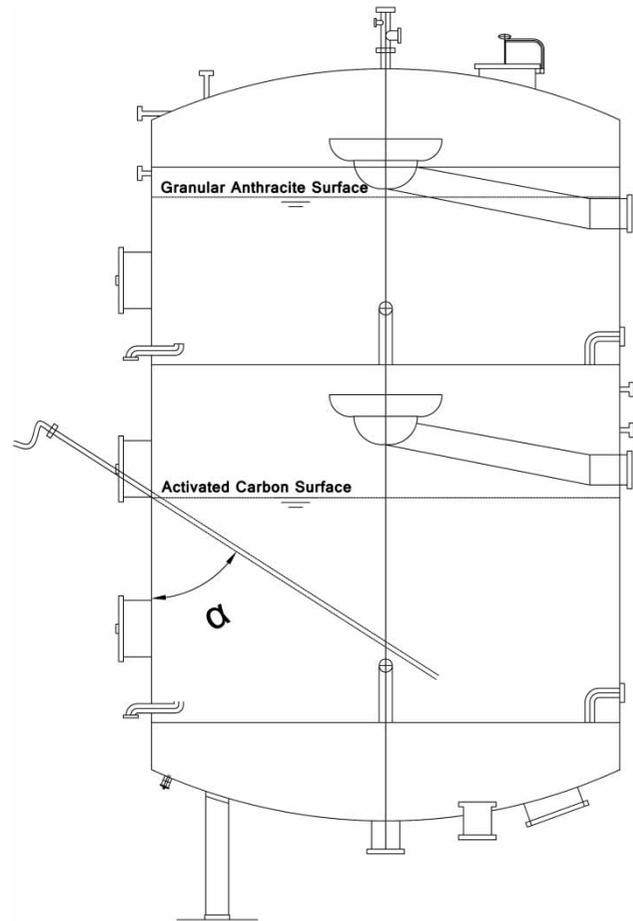


Figure 1 | Sectional view of the double stage filters. For the depth-sampling, a stainless steel pipe was stabbed through the manhole into the activated carbon bedding with a defined entrance angle α .

filter was considered exhausted after approximately 11,500 bed volumes of treated water. Each portion was reactivated separately. A list of the different samples is provided in Table 2.

Table 2 | Activated carbon sample reactivation/regeneration experiments

Samples	Type
RARK (ReActivated Rotary Kiln)	Reactivated in rotary kiln, atmosphere: N ₂ /O ₂ , temperature: 920 °C, 60 min reactivation time
RGRK (ReGenerated Rotary Kiln)	Regenerated in rotary kiln, atmosphere: N ₂ , temperature: 920 °C, 90 min regeneration time
RAFB (ReActivated Fluidized Bed)	Reactivated in fluidized bed oven, temperature: 950 °C, H ₂ O (vapor)
EXH (exhausted)	Exhausted carbon (feedstock)

Adsorption isotherms

For the performance of so-called ‘Bottle Point Isotherm Tests’ (see [ASTM D28](#) for a general description of this method), 100 mL of solution with a fixed adsorbate liquid phase concentration of 2 mg/L (see [Table 3](#) for a list of adsorbates used in this study) were exposed to various dosages of fine ground GAC (1–15 mg). It was ensured that the particle size of the fine ground GAC was in all cases smaller than 45 µm. An average of five samples for each isotherm was conducted. This means that each adsorption isotherm consisted of approximately five measured points; in all cases the number of points was higher than four. Every isotherm was at least determined two-fold; the isotherms for the reactivated AC samples were determined in a four-fold determination. All substances could, due to the high concentrations (mg/L), easily be analyzed by spectrophotometry. This allowed for a fast, precise, and cheap analysis.

The experiments were conducted in water previously filtered with a reverse osmosis module (Osmose 190, Dennerle). The reverse osmosis filtrate was adjusted to a conductivity of ~200 µS/cm and a pH of ~7.4 by the addition of MgSO₄, CaCl₂, and NaHCO₃ (Carl Roth). This procedure ensured the reproducibility of the experiments. Moreover, it provided (approximately) a single solute system as the adsorbates added were the only adsorbable compounds in the system (the background dissolved organic carbon concentration in the samples was <0.2 mg/L). In addition, samples

with a very low DOC were a prerequisite for the spectrophotometric determination of the adsorbate concentration (DOC leads to a high background signal). The samples were shaken for 24 hours on a mechanical shaker (Gerhart). Subsequently, they were filtered in order to remove the fine ground GAC (glass fiber filters, Macherey Nagel) and the residual adsorbate concentration in solution was determined with a Perkin Elmer Lambda 20 spectrophotometer.

The solid phase concentration was calculated by applying a simple mass balance:

$$q = \frac{V}{m} (C_0 - C)$$

where C_0 = initial liquid phase concentration in mg/L; C = liquid phase concentration after filtration in mg/L; q = solid phase loading in mg/mg; V = total volume of solution in L; m = mass of AC in mg.

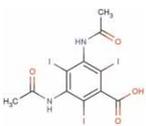
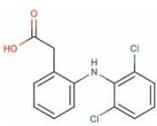
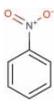
Adsorption tests, concentration range µg/L

As the determination of complete adsorption isotherms requires analysis of a comparatively large number of samples, the batch experiments in the concentration range µg/L were conducted as single point adsorption tests. For the experiments with an adsorbate starting concentration of 10 µg/L, samples with an AC mass of 0.05 mg (experiments diclofenac) and 0.25 mg/L (experiments diatrizoate) were prepared in a two-fold determination (no test was performed with nitrobenzene at this concentration level). Samples were filtered after 24 hours agitation on a mechanical shaker and the residual concentrations were analyzed by ultrahigh pressure liquid chromatography with a double mass spectrometric detection (UPLC-MS-MS) (Waters). A comparison of the relative reduction of the starting concentration (10 µg/L) allowed for a comparison of the different AC samples. This test procedure provides less information than the determination of complete adsorption isotherms, but is, at the same time, quicker and cheaper.

Pilot plant experiments

The three reactivated AC samples were tested in a pilot plant in order to establish breakthrough curves for diatrizoate.

Table 3 | Adsorbates examined in this study

	Diatrizoate	Diclofenac	Nitrobenzene
			
log D	-2.23 ^a at pH 7.15	1.64 ^a at pH 7.15; 1.77 ^b at pH 7	-1.56 ^c at pH 7.4
Supplier	Sigma-Aldrich	Cayman	Carl Roth

The logarithm of the octanol/water partition coefficient logD is a measure for the hydrophobicity of a substance; the bigger it is, the more hydrophobic is a compound. Hydrophobic molecules are usually better adsorbable onto AC as the surface of most ACs is considered hydrophobic.

^aTernes et al. (2007).

^bLarsson et al. (2014).

^cCalculated as $\log D = \log \left(\frac{K_{ow}}{1 + 10^{pH - pKa}} \right)$ with $\log K_{ow} = 1.86$ (Li et al. 2010) and $pKa = 3.98$ (University of Colorado 2014).

This pilot plant was supplied with the effluent of the first layer of the double stage filters, i.e., the same water that was also supplied to the AC layer in the full-scale filters. In the full-scale AC filters, the AC bedding sits on top of a support layer of gravel which contains several filter nozzles for the outflow of the water. This setup was downsized in the AC pilot plant filters. The pilot plant (see also Figure 2) consisted of PVC columns with a diameter of 140 mm; the filter bed height was 1 m. The bottom of the PVC columns contained a gravel support layer and a single filter nozzle. They were operated at a filtration speed of 13 m/hr, i.e., at the same speed as the full-scale filters. Owing to a down-select after the small-scale tests it was decided to perform the pilot plant experiments with diatrizoate as test substance. The average diatrizoate concentration in the inflow was 175 ng/L, with a total organic carbon background concentration of ~0.7 mg/L.

Sampling of the full-scale AC filters

A sampling device consisting of an industry vacuum cleaner and a disinfected stainless steel pipe was used for the depth-sampling of the full-scale AC filter. The graded pipe was 5 m long to be able to reach different depths of the filter. For sampling of layer 1 (see Table 4 for the definitions of the different layers), the suction pipe was stabbed into the AC bedding through the manhole (Figure 1) to the desired level (the filter was drained before). The AC sample was sucked into the vacuum cleaner. Afterward, the AC was



Figure 2 | Fixed bed filter pilot plant.

Table 4 | Layers of the full-scale filter

	Filter bed depth
Layer 1	0 m–0.6 m
Layer 2	0.6 m–1.3 m
Layer 3	1.3 m–1.9 m
Layer 4	1.9 m–2.5 m

removed from the vacuum cleaner and restored for analysis. The steel pipe was then pushed further into the bedding for sampling of layer 2, layer 3, and so on. This procedure yielded samples from each layer. It should be noted that it was important to maintain a constant entrance angle of the steel pipe into the filter.

RESULTS AND DISCUSSION

Reactivated AC samples: batch adsorption tests

The Freundlich approach (Freundlich 1906) was used for the evaluation of the bottle point isotherm results:

$$q = K_f \times C^n$$

where K_f is the Freundlich constant (an indicator of the adsorption capacity) and n is the Freundlich exponent (describes the shape of the isotherm). We defined the nitrobenzene number (NBN), the diclofenac number (DFN), and the diatrizoate number (DAN) as being the concentration of AC in mg/L that is needed to remove 90% of the initial concentration of the adsorbate under the experimental conditions defined above ($C_0 = 2$ mg/L). It can easily be obtained by a combination of the Freundlich approach and a mass balance (DVGW 2009):

$$\text{NBN} = \frac{1.8}{K_f \times 0, 2^n}$$

Consequently, the smaller these characteristic figures are, the higher is the adsorption capacity of the examined AC samples towards the specific adsorbate (providing that the experimental conditions are the same, as described above).

Analysis of the reactivated/regenerated AC samples revealed smaller values for the DFNs than for the NBNs and the DANs (Figure 3). Although a comparison of adsorption data obtained by different researchers is problematic because of different experimental conditions and diverse AC samples, diclofenac seems to be a compound that can be well removed by AC adsorption. Rigobello *et al.* (2013) reported a complete removal of diclofenac by granular AC filtration. Baccar *et al.* (2012) compared the removal of the four pharmaceuticals naproxen, ketoprofen, ibuprofen, and diclofenac by an AC prepared from an agricultural waste product and achieved the highest AC loadings for diclofenac. Comparing the logD value of the three substances examined in this study, diclofenac possesses the highest logD value, indicating a low hydrophilicity and therefore a better absorbability of this compound.

It is noteworthy that diatrizoate (a contrast agent) is a substance that was intentionally engineered with a low hydrophobicity to prevent accumulation in biological tissue during application. Therefore, it is considered as a compound that is not well adsorbable onto AC. The results indicate, however, that the adsorption capacity of the AC samples RARK and RGRK was higher for diatrizoate than for nitrobenzene.

Taking into account the minimum and maximum values (illustrated by the whiskers in Figure 3), no difference between the DFNs for the reactivated AC samples could be observed. Moreover, the NBNs for the samples RGRK

and RAFB were very similar. In contrast to that, the DANs were different for all the samples, indicating that the DAN allows for a more sensitive comparison of the samples than the DFN and the NBN.

The experiments with a diatrizoate/diclofenac starting concentration of 10 µg/L supported the results described above. As these experiments were conducted as a single point adsorption test with just one amount of AC tested (see Materials and Methods section), the removal rate – the amount of adsorbate removed from the liquid phase – was calculated in percent. Whereas the removal rate for diclofenac was approximately the same (about 70%) for all reactivated samples and 40% for the exhausted AC, the removal rate for diatrizoate revealed differences between the reactivated samples. The removal rates for the samples RARK, RGRK, and RAFB were 83, 78, and 65%, respectively. No diatrizoate was removed by the exhausted sample (Figure 4). These were important results, as they show, at least for this specific case, that the results obtained at a concentration level of 2 mg/L allow qualitative predictions about the adsorption behavior in a concentration range relevant for practical application. Ruhl *et al.* (2014) compared the adsorptive removal of acesulfame (ACS), diclofenac (DFC), and benzotriazole (BTA) from a test solution that contained 2 mg/L of these compounds and treated waste water that contained 4.2 µg/L ACS, 2.8 µg/L DFC, and 6.5 µg/L BTA. They could establish a correlation between the removal of DFC and BTA in the test solution

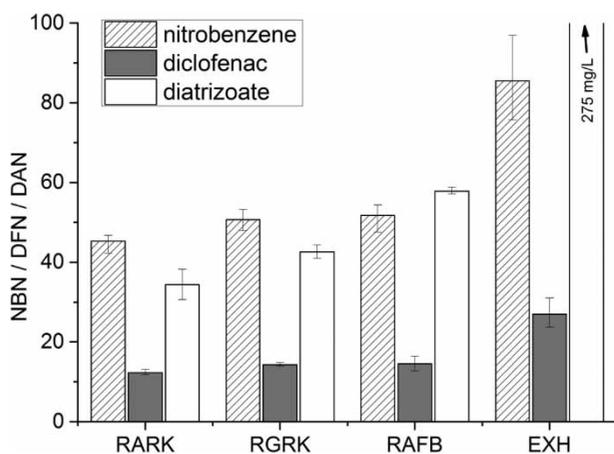


Figure 3 | NBN, DFN, and DAN of the reactivated AC samples. DAN of the exhausted AC was 275 mg/L. Error bars indicate minimum and maximum values of the four-fold analysis (equals four adsorption isotherms) of each AC sample.

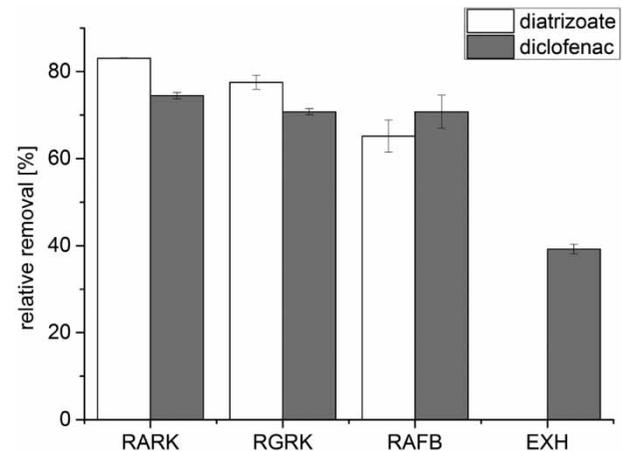


Figure 4 | Relative removal of diatrizoate and diclofenac in the concentration range µg/L. Error bars indicate minimum and maximum values of the two-fold determination.

and the treated waste water. In contrast to that, no such correlation was found for ACS. This underlines that, although a qualitative correlation between the removal at the concentration ranges mg/L and $\mu\text{g/L}$ was found in the present work, it is very important to test in each individual case whether experiments at higher concentrations allow predictions at concentration levels relevant for practical application. Differences may occur, e.g., due to competitive adsorption in real raw water that contains natural organic matter in a concentration that usually exceeds the concentration of the organic micropollutants.

Reactivated AC samples: fixed bed filter experiments

The results obtained in the fixed bed filter experiments (Figure 5) correlated with the results from the batch experiments. Despite the relatively large error associated with the analytical method, differences between the samples can be observed until a diatrizoate breakthrough of about 50%. The diatrizoate breakthrough of the column with AC sample RAFB occurred rapidly, with 50% breakthrough after a specific throughput of $\sim 20 \text{ m}^3/\text{kg}$. In contrast to that, a 50% breakthrough for sample RARK was achieved after a specific throughput of $\sim 40 \text{ m}^3/\text{kg}$. In addition, this

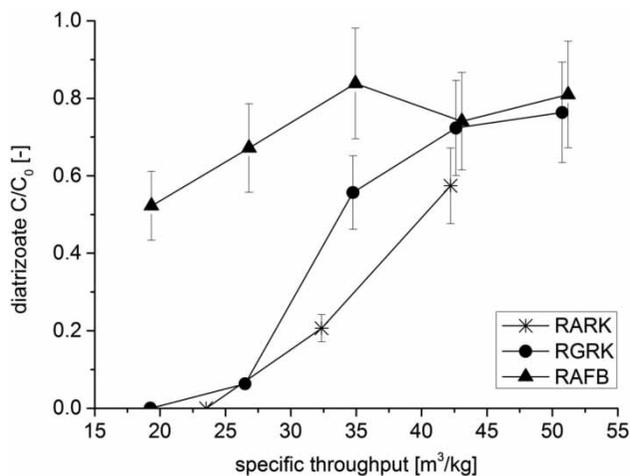


Figure 5 | Breakthrough curves for diatrizoate obtained in the pilot-scale fixed bed filter experiment. The specific throughput describes the amount of water treated per kilogram of AC. Consequently, it increases with increasing lifetime of the filter. Error bars indicate the combined measurement uncertainty obtained from the standard deviation of a 30-fold analysis of a certified reference sample.

sample expressed also a slightly slower breakthrough behavior than sample RGRK. These results suggest that the DAN allows qualitative predictions about the breakthrough behavior of diatrizoate in fixed bed filters. This is a very important finding, as diatrizoate is one of the compounds that can significantly shorten the operation time of the fixed bed filters in Düsseldorf due to its fast breakthrough behavior. The DAN allows a fairly quick and cheap test of ACs in regard to their adsorption behavior toward diatrizoate. It should be noted that the DAN does not include any kinetic effects that may influence the adsorption performance in a fixed bed filter, so experiments regarding this or the pore size distribution are a reasonable complement.

Samples from the full-scale filter

The assumption that the DAN allowed for a sensitive comparison of AC used for water treatment in the water works of Düsseldorf was underlined by the results obtained by the analysis of the depth-samples from the full-scale filter.

NBNs and DANs for the AC obtained by the depth-sampling of the full-scale AC filter are illustrated in Figures 6 and 7. In these graphs, the horizontal axis shows the specific throughput and the vertical axis shows the NBN and DAN. As was expected, in general, an increase in both NBN and DAN was observed with increasing specific throughput of the filter, indicating a decrease of the adsorption capacity

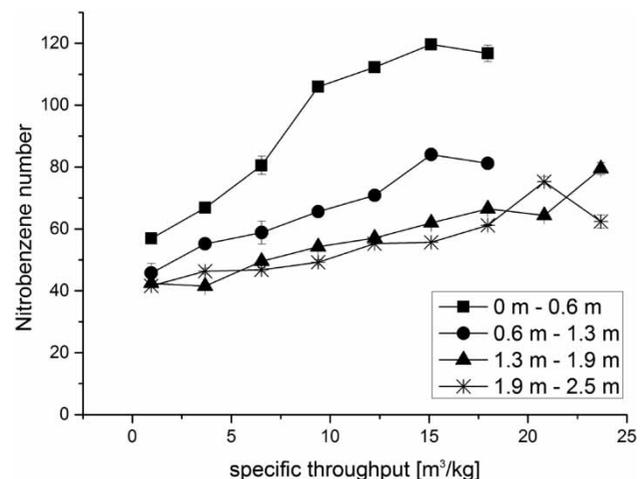


Figure 6 | Nitrobenzene numbers for the depth-samples from a full-scale filter. Error bars indicate the min/max values of the two-fold analysis of each sample.

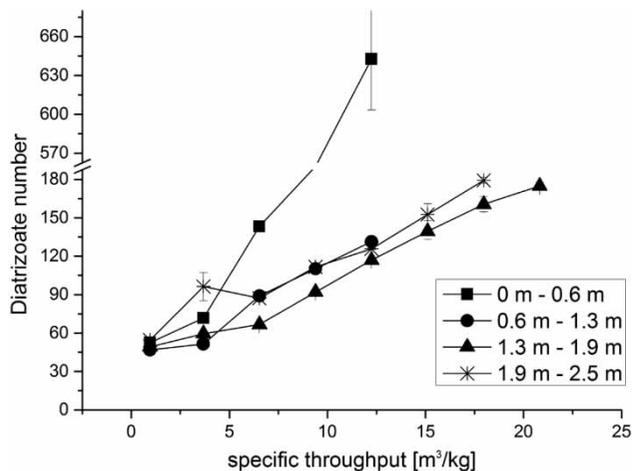


Figure 7 | Diatrizoate numbers for the depth-samples from a full-scale filter. Error bars indicate the min/max values of the two-fold analysis of each sample.

with increasing time of operation. For the NBN (Figure 6), a comparison between the carbons from different layers of the filter shows that the carbons from the upper layers of the filter bed (0–0.6 and 0.6–1.3 m) exhibit higher NBNs than carbons sampled from lower layers of the filter (1.3–1.9 and 1.9–2.5 m). This was expected, due to entering the feed water from top of the filter, the AC in the upper layers possesses a higher loading and, consequently, a lower adsorption capacity was expected for these samples. The only exceptions were the carbons sampled from the lowest layer (1.9–2.5 m), which expressed NBNs similar to the layer above. The reason for this phenomenon is that due to technical reasons, the filter was not emptied completely before it was filled with reactivated AC. Approximately 20% of the old, exhausted AC remained in the filter. Hence, the lowest filter layer represents a mixture of old spent AC and fresh AC.

The DANs of the AC samples from different filter bed depths (Figure 7) show a trend similar to the NBNs. However, a comparison between NBN and DAN reveals that with increasing specific throughput, the increase in the DANs is stronger than the increase in the NBNs (the slope of the curves is higher). These results support the idea that the DAN is a more sensitive parameter for the determination of the adsorption capacity of AC in Düsseldorf than the NBN, which is suggested as a parameter for the evaluation of AC for drinking water treatment in Germany (DVGW 2009). Also, the samples from the

lowest filter layer (1.9–2.5 m), which are a mixture of exhausted AC and reactivated AC (see above), possessed higher DANs than the ones from the layer above. This was not observed for the NBNs which were similar for both layers and, therefore, underlines the higher sensitivity of the DAN. Although diatrizoate might not be the test substances of choice for other water treatment facilities (it is recommended to use an organic micropollutant that has proven to be problematic on site), the results presented here suggest that a more hydrophilic compound may enable a more sensitive comparison of different AC samples. Further, the development of test methods similar to those presented here, that use UV spectrophotometric quantification of liquid phase concentrations, can help to keep analysis costs down. These kind of UV spectrometric test methods are not limited to drinking water treatment, but might also be useful for the testing of ACs for waste water treatment, as, for example, demonstrated by Ruhl *et al.* (2014). It should be emphasized that it is important to check whether the results obtained at higher concentrations (UV spectrometric analysis) correlate with the performance of the ACs at concentration levels relevant for practical application.

CONCLUSION

The results suggest that diatrizoate as a test substance allows the most sensitive comparison of different AC samples, followed by nitrobenzene. In contrast to this, diclofenac seems to be less suitable as a test substance. The removal of diatrizoate in the concentration range $\mu\text{g/L}$ showed the same trend as the DANs. This implies that the results obtained in the higher concentration range (mg/L) are, at least in this case, also significant for a concentration range more relevant for practical applications. Furthermore, samples that expressed a low DAN showed also a slower breakthrough behavior for diatrizoate in the pilot-scale fixed bed filter experiment. It was possible to monitor the conditions of the different filter layers of the full-scale filter with the DAN and the NBN, at which the DAN again expressed a higher sensitivity. Hence, the DAN could be used in the future as one tool to assess ACs for a possible use in the municipal drinking water plants in Düsseldorf. We recommend a similar survey with substances that are problematic on site for other water treatment facilities. A

focus on rather poorly adsorbable substances might enable a more sensitive comparison of different AC samples.

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