Report by UWI doctoral researcher Geert Aschermann (T5)

Project number: T5

First and last name of doctoral researcher: **Geert Aschermann**

(Working) title of doctoral project: **Desorption kinetics and irreversibility in applications of technical adsorbents for water treatment**

Name of supervisors: Prof. Dr. Martin Jekel (TUB), Prof. Dr. Eckhard Worch (TU Dresden), Prof. Dr. Juliane Hollender (Eawag)

2. Description of doctoral project and research results achieved to date:

Motivation

Despite their trace-level concentrations, organic micropollutants (OMP), such as pharmaceuticals and household chemicals, are suspected to be a potential risk for aquatic ecosystems as well as for human health. Therefore, there are ongoing discussions on potential measures for the reduction of OMP. A promising technique for the removal of OMP in drinking and waste water treatment processes is the application of activated carbon (AC) [1, 2]. Due to the chemical structure and the high internal surface of AC, many organic water constituents show a high affinity for adsorption onto its surface. Although the application of AC is well established in water treatment, the processes at this solid-water interface are still not completely understood.

The adsorption of water contaminants onto AC is generally expected to be reversible [3, 4]. Therefore, it seems likely that previously adsorbed compounds can also desorb again under certain conditions, which could lead to an undesired increase of OMP concentrations in the effluent of the treatment process (Figure 1). In general, different scenarios are conceivable that can theoretically lead to an occurrence of desorption in running AC processes, e.g. (i) the displacement of an adsorbate on an adsorption site by subsequent adsorption of another adsorbate or (ii) a reversal of the reaction pathway due to high OMP loadings on the AC surface and low OMP concentration in the bulk aqueous phase.

Whereas the process of adsorption of OMP onto AC itself has been the object of a number of research project in the last years, the process of desorption in AC applications has only been of minor focus of investigations up to date. Despite its potential relevance in AC processes indicated above only very few publications deal with desorption of OMP. Thus, the goal of this project is to get a better mechanistic understanding of the OMP desorption from activated carbon. It is known that activated carbon treatment processes are strongly influenced by dissolved organic matter (DOM) that is present in every drinking or waste water [5]. The main focus of the work was therefore to study the impact of DOM on OMP desorption, with respect to the desorption kinetics as well as to the extent of desorption (or, or in other words, the reversibility of OMP adsorption).

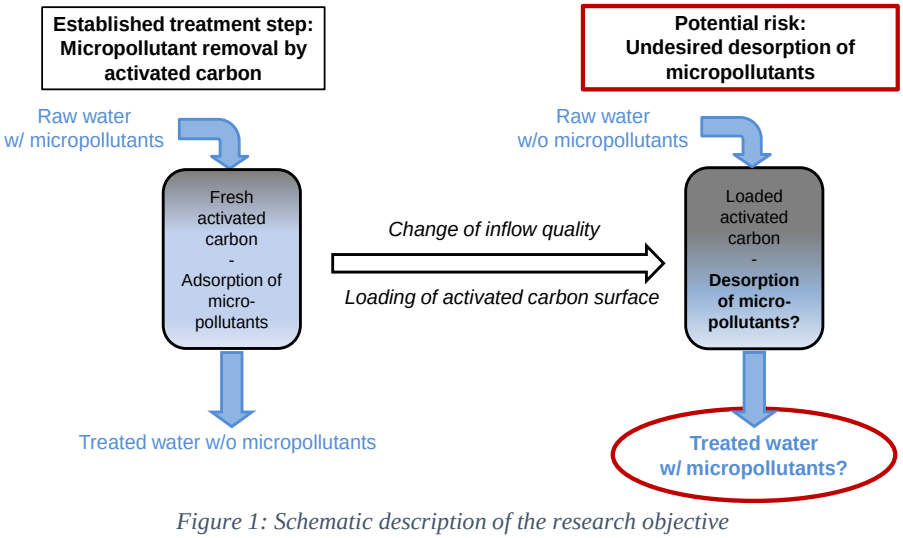

Figure 1: Schematic description of the research objective

Methodology

The research in this study is based on lab scale experiments, where potential OMP desorption scenarios are simulated. Therefore, the activated carbon is first loaded with OMP by addition of a spiked solution (adsorption phase) and subsequently transferred into an OMP-free solution (desorption phase). By varying adsorption and desorption conditions (e.g. with or without background DOM) the impact of certain factors on desorption are studied. Furthermore, different AC products are tested in parallel to examine the effect of different AC characteristics on desorption. On the one hand, batch tests are conducted. By evaluating the resulting adsorption and desorption isotherms in equilibrium state, statements about the extent of desorption can be made. On the other hand, small scale column test are conducted to study the desorption kinetics under different adsorption and desorption conditions. In all tests six substances that reflect typical OMP were examined in these experiments.
The experiments are combined with different analytical methods. OMP concentrations are analyzed with a LC-MS/MS device. Thereby, experiments can be conducted with OMP concentrations of several µg/L to ng/L and, thus, in an environmentally relevant range. DOM characteristics and adsorption are analyzed by DOC and UV_{254nm} measurements. Furthermore, liquid chromatography coupled with online carbon detection (LC-OCD) is used to analyze the adsorption of different DOM size fractions and the resulting effect on OMP desorption. Pore size distributions of the tested AC products are analyzed by BET measurements.

Current State of Work

In batch tests, the extent of OMP desorption under different background conditions was examined. These experiments were evaluated by use of the resulting adsorption and desorption isotherms. Under ideal conditions (adsorption and desorption in a pure water matrix) all tested OMP show a highly to completely reversible adsorption in case of all tested AC. With respect to systems with continuous inflow (like AC filters) this indicates a potentially complete desorption of adsorbed OMP. Under real conditions (adsorption and desorption in drinking water) additional DOM adsorption affects desorption in different ways depending on the AC pore structure (Figure 2). For AC with overall smaller pores, an increased irreversibility of OMP adsorption is found, which shows that DOM adsorption decreases the extent of OMP desorption. This can be referred to pore blockage effects of DOM. For macroporous AC, DOM adsorption leads to an enhanced OMP desorption which can be attributed to displacement processes. These results show that smaller pores tend to be blocked by DOM which hinders OMP from desorption. This work was published in a journal paper [6].
The experiments were repeated with additional AC products (7 in total). The results show a good and clear correlation between (micro-)porosity of the AC´s and irreversibility of OMP adsorption. With regard to real AC treatment systems, it can be expected that systems with macroporous AC might be affected stronger by undesired desorption in case of fluctuating inflow concentrations. Based in these results, pore size analyses of the used AC might be a tool for operators to evaluate the desorption risk in their systems.

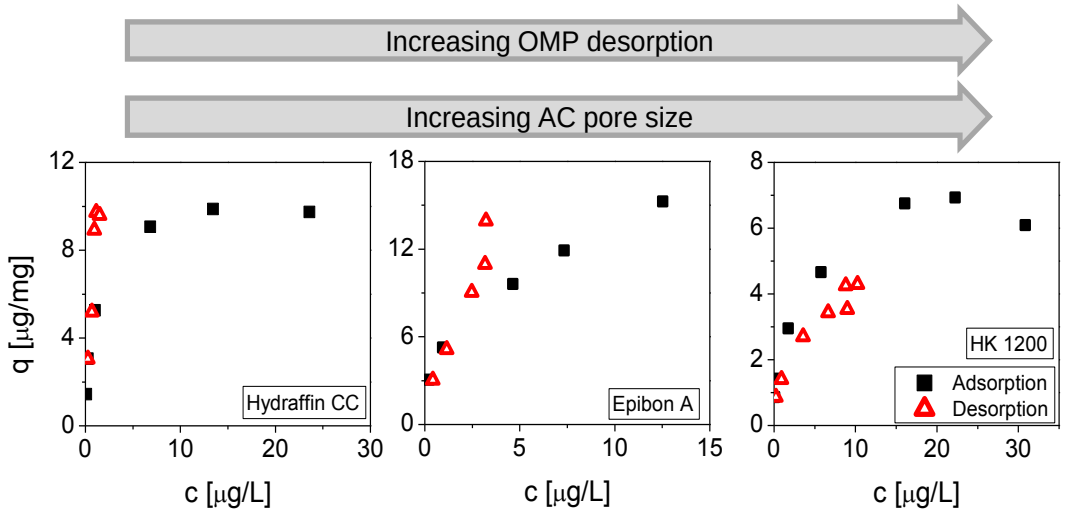

Figure 2: Adsorption and desorption isotherms of carbamazepine for three tested AC products (Hydraffin CC, Epibon A, HK 1200) from a batch experiment in Berlin drinking water; the shift of the desorption isotherm in comparison to its corresponding adsorption isotherm (from left/above to right/below) shows the increasing desorption from microporous Hydraffin CC to macroporous HK 1200.

Further experiments with different DOM fractions (low molecular weight DOM and high molecular weight DOM) were conducted to get a better mechanistic understanding of the DOM impact on OMP desorption. Batch tests (as described above) with these solutions led to results that show very similar effects of these fractions. This indicates that the gained results can also be transferred to other waters with different DOM composition. This is supported by results of batch tests with waste water treatment plant effluent. Despite

different DOM characteristics the results in terms of OMP desorption are very similar in comparison to drinking water.
First column experiments show that the adsorption of DOM also impacts the kinetics of OMP desorption. In comparison to pure water conditions, OMP desorption is slower under real water conditions in case of all tested AC products. Among these AC´s macroporous products showed a faster desorption rate than microporous AC.

Future Work planned

Further kinetic tests will be conducted to get a deeper understanding of the mechanistic effects of DOM on desorption kinetics. These results should be published a journal paper. Also the (unpublished) results of the batch experiments will be subject of two additional research papers (in preparation).

Collaboration

Collaborative LC-MS/MS analyses were conducted with projects N1, N3, N4 and N6 (including data processing and evaluation) as part of the common topic group “micropollutants”. Activated carbon pore analyses were carried out by the Chair of Soil Sciences at TU Berlin and included common discussions on methods and results.
Prior to and during the research stay at NC State University (USA) close collaboration was established with Prof. Detlef Knappe and his team and resulted in discussions on improvement of used and adaption of new methods.

References

1. Altmann,J., Ruhl,A.S., Zietzschmann,F. & Jekel,M. (2014): Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water Research* **55**, 185-193
2. Westerhoff,P., Yoon,Y., Snyder,S. & Wert,E. (2005): Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environmental Science & Technology* **39**(17), 6649-6663
3. Crittenden,J.C., Trussell,R.R., Hand,D.W., Howe,K.J. & Tchobanoglous,G. (2005): Water Treatment - Principles and Design (2nd Edition), John Wiley & Sons, Hoboken, USA
4. Worch,E. (2012): Adsorption Technology in Water Treatment, Fundamentals, Processes, and Modeling. De Gruyter, Boston (USA)
5. Zietzschmann,F., Aschermann,G. & Jekel,M. (2016): Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents. *Water Research* **102**, 190-201
6. Aschermann,G., Zietzschmann,F. & Jekel,M. (2018): Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption. *Water Research* **133**, 123-131

3. Comments on the qualification programme and supervision strategy:

Due to its thematic diversity the research training group helped to broaden my scientific horizon and to get insights in other research fields. On the one hand, the core courses at the initial phase of projects were very helpful to gain a better understanding of research basics in other fields (e.g. civil engineering). This also facilitated further discussions with the other doctoral students. On the other hand, the annual summer schools as well as the interim workshop gave the possibility to get insights into the actual research projects in these fields, to exchange ideas with the other doctoral researchers and to present my research results in front of an audience that (partly) has another scientific background.
The possibility of doing an internship abroad gave me the great opportunity to conduct part of my research in the USA, which broadened my network with researchers and gave me insights in research facilities and topics overseas.
Furthermore, I would like to emphasize the benefit of the support of young parents in UWI. The possibility of home office days and the funding of corresponding equipment (e.g. a laptop) allowed me to have flexible working hours. This improved the balance between my work and family life.

Participation in the following Research Training Group events:

1. Core courses
   - I – Urban interface processes – fluxes, transport, interactions (3 ECTS)
   - II – Modelling and measuring concepts of interface processes (3 ECTS)
   - III – Urban freshwater ecology (3 ECTS)
2. Elective courses
   - Spring school “Water in Urban Areas” (TU Berlin, 7. – 11.03.2016, 6 ECTS)
   - Proposal writing workshop (TU Berlin, 16.03.2018)
3. UWI lectures: Participated in all UWI lectures
4. Colloquium of the Chair of Water Quality Control
5. Other UWI events
   - Orientation Seminar and UWI Opening Ceremony (08. – 09.09.2015)
   - Exposé Talks (08.12.2015)
   - Summer School 2016 (13. – 14.09.2016)
   - Summer School 2017 (5. – 6.09.2017)
   - Kollegiate Seminar (22.09.2016)
   - Interim Meeting (19.05.2017)
   - Student research council (17. – 18. 03.2017)
   - Summer School (18.-20.09.2018)

Research stays or internships at other research institutions both at home and abroad:
2.11.2017 – 10.03. 2018: Research stay at NC State University (Raleigh, USA) (Supervision: Prof. Detlef Knappe)

Participation in conferences, congresses, etc., at home and abroad:
2016:
- Student workshop "Innovations around adsorption" (14.06.2016, Duisburg)
- 27. Mülheimer Wassertechnisches Seminar – Adsorption in der Wasseraufbereitung: Renaissance einer bewährten Technologie (15.06.16, Mühlheim (Ruhr))

2017:
- Wasser Berlin International (28. – 31.03.2017, Berlin)
- Wasser 2017 – Jahrestagung der Wasserchemischen Gesellschaft (22. – 24. 05.2017, Donaueschingen)
- Essener Tagung (22. – 24.03. 2017 , Aachen)
- AWWA Water Quality Technology Conference (12. – 16.11.2017, Portland (OR), USA)

2018:
- Wasser 2018 - Jahrestagung der Wasserchemischen Gesellschaft (7. – 9.05.2018, Papenburg)

4. Individual publications:

I. Articles:

- Aschermann,G., Zietzschmann,F. & Jekel,M. (2018): Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption. *Water Research* 133: 123-131
- Zietzschmann,F., Aschermann,G. & Jekel,M. (2016): Comparing and modeling organic micro-pollutant adsorption onto powdered activated carbon in different drinking waters and WWTP effluents. *Water Research* 102: 190-201
- Aschermann,G., Jeihanipour,A., Shen,J., Mkongo,G., Dramas,L., Croue,J.P. & Schäfer,A. (2016): Seasonal variation of organic matter concentration and characteristics in the Maji ya Chai River (Tanzania): Impact on treatability by ultrafiltration. *Water Research* 101: 370-381

II. Conference, poster presentations etc.:

- Aschermann,G., Neubert,L. & Jekel,M. (2018): Einfluss verschiedener DOM-Größenfraktionen auf die Desorption organischer Spurenstoffe von Aktivkohle. Wasser 2018 - Jahrestagung der Wasserchemischen Gesellschaft (7. – 9.05.2018, Papenburg, Germany), reviewed paper and oral presentation
- Aschermann,G. & Jekel,M. (2017): Effects of activated carbon pore structure on organic micropollutant desorption. AWWA Water Quality Technology Conference 2017 (12. – 16.11.2017, Portland (OR), USA), reviewed paper and oral presentation
- Aschermann,G. & Jekel,M. (2017): Einfluss der Poreneigenschaften von Aktivkohle auf die Desorption von organischen Spurenstoffen. Wasser 2017 - Jahrestagung der Wasserchemischen Gesellschaft (22. – 24.05.2017, Donaueschingen, Germany), reviewed paper and poster presentation
- Aschermann,G., Zietzschmann,F. & Jekel,M. (2017): Adsorption von organischen Spurenstoffen an Pulveraktivkohle in verschiedenen Trink-und Abwassermatrices. Essener Tagung 2017: Forum Young Scientists (22. – 24.03. 2017, Aachen, Germany), oral presentation