Removal of perfluorinated surfactants from wastewater by adsorption and ion exchange — Influence of material properties, sorption mechanism and modeling

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ABSTRACT

Perfluorooctane sulfonate (PFOS) has attracted increasing concern in recent years due to its world-wide distribution, persistence, bioaccumulation and potential toxicity. The influence of sorbent properties on the adsorptive elimination of PFOS from wastewater by activated carbons, polymer adsorbents and anion exchange resins was investigated with regard to their isotherms and kinetics. The batch and column tests were combined with physico-chemical characterization methods, e.g., N₂ physisorption, mercury porosimetry, infrared spectroscopy, differential scanning calorimetry, titrations, as well as modeling. Sorption kinetics was successfully modelled applying the linear driving force (LDF) approach for surface diffusion after introducing a load dependency of the mass transfer coefficient βs.

The big difference in the initial mass transfer coefficient βs,0, when non-functionalized adsorbents and ion-exchange resins are compared, suggests that the presence of functional groups impedes the intraparticle mass transport. The more functional groups a resin possesses and the longer the alkyl moieties are the bigger is the decrease in sorption rate. But the selectivity for PFOS sorption is increasing when the character of the functional groups becomes more hydrophobic. Accordingly, ion exchange and hydrophobic interaction were found to be involved in the sorption processes on resins, while PFOS is only physisorptively bound to activated carbons and polymer adsorbents. In agreement with the different adsorption mechanisms, resins possess higher total sorption capacities than adsorbents. Hence, the latter ones are rendered more effective in PFOS elimination at concentrations in the low μg/L range, due to a less pronounced convex curvature of the sorption isotherm in this concentration range.

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Introduction

Perfluorinated acids and their salts have been produced in industrial scale for more than six decades (Schmeisser and Sartori, 1964; Pearlson, 1986). Since then, they have found application as surfactants in many fields of industry, comprising polymer synthesis, fire retardants and paper coatings, as well as plating solutions (Kissa, 2001). This broad range of applications is not only a consequence of the high surface activity of fluorosurfactants, but also of their outstanding thermal and chemical stability (Krafft and Riess, 1998; Kissa, 2001). Their inherent high persistence is a major drawback though when these substances are released to the environment. They are not biodegradable and especially long-chain fluorosurfactants tend to accumulate in
the environment (OECD, 2002). For example, perfluorinated surfactants were not only found in aquatic systems (Hansen et al., 2002; Exner and Färber, 2006; Suja et al., 2009) and in animals like fish and birds (Giesy and Kannan, 2001; Kannan et al., 2001; Martin et al., 2003), but also in human blood (OECD, 2002; Olsen et al., 2003, 2007). In order to protect health and environment, the use of perfluorooctane sulfonate (PFOS), the main perfluorinated pollutant, was restricted by the EU directive 2006/126/EC (EU, 2006). For certain branches of industry, in which PFOS cannot be replaced to date, a special permit was established, so that its usage can be sustained (EU, 2006). In electroplating, perfluorinated surfactants, in particular perfluorooctane sulfonate, are still indispensable for a large number of wet chemical processes, not only due to their chemical properties, but also for reasons of process reliability and industrial safety (Schwarz et al., 2010). To alleviate environmental problems related to fluorosurfactants, development of technologies to eliminate such compounds, especially from wastewaters, is of great interest. In general, two ways can be followed in order to achieve this goal—a decomposition of PFOS or its adsorptive removal. The drawbacks of such degradative methods as advanced oxidation processes (Schröder and Meesters, 2005; Schröder et al., 2010), photolysis, photocatalysis (Yamamoto et al., 2007; Wang et al., 2008; Panchangam et al., 2009), and sonolysis (Destaillets et al., 2001; Moriwaki et al., 2005; Vecitis et al., 2008) are high energy demand, special reaction conditions or incomplete mineralization of the fluorosurfactants, which impedes the application of these methods on an industrial scale. In contrast, sorption processes have been successfully implemented in many wastewater treatment applications and showed promising results regarding the removal of perfluorinated surfactants (Yu et al., 2008; Carter and Farrell, 2010; Senevirathna et al., 2010). But so far, the sorption of fluorosurfactants onto activated carbons, polymer adsorbents and anion exchange resins was mainly investigated in solutions containing only the sorptive and deionized water. In this matrix, the length of the fluorocarbon chain and the nature of the functional group influenced the adsorption of the anionic surfactants onto activated carbons—the adsorption was stronger for PFOS than for perfluorooctanoic acid (PFOA) and perfluorobutane sulfonate (PFBS) (Ochoa-Herrera and Sierra-Alvarez, 2008; Hansen et al., 2010). Due to their higher surface area, powdered activated carbons demonstrated higher capacities for perfluorinated compounds than granulated activated carbons (GACs) (Yu et al., 2009; Hansen et al., 2010). However, both values are significantly lower than the perfluorinated compounds capacity of anion exchange resins (Carter and Farrell, 2010; Senevirathna et al., 2010), which is probably the result of different sorption mechanisms on both materials (Yu et al., 2009). These findings were confirmed for a more complex matrix by our own investigations regarding the removal of PFOS from electroplating wastewaters (Schuricht et al., 2014a; Schuricht et al., 2014b). While the PFOS capacity of sorbents increases with the number of functional groups; their presence has a negative effect on sorption kinetics. Apparently, functional groups hinder the diffusion of PFOS molecules inside the pores. To have a closer look at this phenomenon, in the present work, modeling tools were applied to describe the kinetics of PFOS sorption onto activated carbons, polymer adsorbents and anion exchange resins, possessing a different number or kind of functional groups. In addition, the influence of these material properties on the selectivity and the mechanism of the sorption of PFOS were discussed.

1. Experimental

1.1. Adsorbents and adsorbent characterization

A large number of commercially available and for the adsorption of PFOS suitable adsorbents provided by Cabot Norit Inc. and Dr. Felgenträger & Co. GmbH were screened in the conducted experiments. The selection of materials comprised the best materials after screening tests such as: activated carbons (ACs), polymeric adsorbents (PAs) and anion exchange resins (AS resp. AW) (Tables 1 and 2). As reference material the Activated Charcoal Norit GAC 1240 was used. Mercury porosimetry and nitrogen physisorption were applied to characterize the porosity and the inner surface of the adsorbents. In addition, the total capacity of anion exchange resins was determined by titration according to DIN 54402. A summary of the material properties is given in Tables 1 and 2.

Furthermore, virgin and used samples were characterized by infrared (IR) spectroscopy and differential scanning calorimetry (DSC) to gain insight into the mechanism of the adsorption of PFOS onto different types of materials. Attenuated total reflection infrared spectroscopy (ATR IR) spectra were collected on a Nicolet 5700 spectrometer (Thermo Fisher Scientific), equipped with a MCT detector, in the wave number range of 4000–650 cm⁻¹. For the DSC measurements, 10 mg of the samples was sealed in an aluminum crucible and heated to 300°C with a rate of 3 K/min using the DSC 1 of Mettler Toledo. Because of low thermal stability, resins could only be heated to 120°C.

In addition, the capacity of anion exchange resins was determined by acid/base titration before and after adsorption of PFOS. For this purpose, a suspension of 1.5 g resin (dry mass) in 100 mL 0.1 mol/L NaOH was stirred for 1 hr. Afterwards, potentiometric titrations with 0.1 mol/L HCl were carried out to determine the remaining NaOH concentration. The capacity was calculated based on the concentration difference. In order to confirm the obtained results, this procedure was repeated with the processed samples using 100 mL 0.1 mol/L HCl for stirring and 0.1 mol/L NaOH for titration.

1.2. Adsorption experiments

Kinetic curves are usually determined by the adsorption equilibrium. Firstly, adsorption isotherms were recorded at 25°C by varying the initial PFOS concentration between 1 and 1000 mg/L. While such high concentrations of perfluorinated surfactants do not appear in the environment (PFOS has a solubility of approximately 550 mg/L in water at 25°C), they represent typical concentrations in wastewater and process water streams in electroplating industry. As PFOS source its tetraethyl ammonium salt was used, which was dissolved in 0.1 mol/L sulfuric acid. This matrix was chosen to simulate the conditions of a typical electroplating wastewater stream regarding sulfate concentration and pH value. The tests were carried out in thoroughly sealed Erlenmeyer flasks which were put into a shaking bath for 48 hr (f = 250 min⁻¹). For each...
test 200 mL of the acidic PFOS solution and 100 mg adsorbent (dry mass) were used.

PFOS concentrations were determined by high-performance liquid chromatography/electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS) according to DIN 38407-42 using an API 4000 and API 5500 of Applied Biosystems. In this method the HPLC (high pressure liquid chromatography) is coupled with the mass spectrometry (MS). The analyte ions required for the MS are generated by electrospray ionization (ESI). This method allows identification and thus a selective determination of PFOA from amount of a few ng/L.

In the second step, kinetic studies in a batch reactor at 25°C were carried out. The initial PFOS concentration was set to 100 mg/L by dissolving the required amount of NEt₄-PFOS in 0.1 mol/L sulfuric acid. To start a kinetic experiment 100 mg adsorbent (dry mass) was added to 200 mL of the acidic PFOS solution, which was then stirred for 16 to 20 hr at a stirring speed of 350 r/min. In this case, in contrary to experiments in Erlenmeyer funnels, PFOS concentration was continuously monitored during the experiment by surface tension measurements using the SITA science line t60 tensiometer. This method was described in detail in previous publications (Haberland, 2004; Schuricht et al., 2014b).

1.3. Adsorbent regeneration

The adsorbents were firstly loaded with PFOS according to the previously described procedure. Afterwards, they were filtered off and washed with small amounts of water. For regeneration, these samples and 200 mL de-ionized water were put into Erlenmeyer funnels, which were placed in a shaking bath for 24 hr (f = 250 min⁻¹). The adsorbents were filtered off again and the regeneration procedure was repeated, using firstly methanol and then a 9:1 volume mixture of methanol and ammonia. PFOS concentration was determined by HPLC-ESI-MS/MS on each step, prior to filtration.

2. Results and discussion

2.1. Adsorption isotherms

The isotherms of the PFOS adsorption onto several adsorbents are compared in Fig. 1. In agreement with the results previously reported in literature (Yu et al., 2009; Carter and Farrell, 2010; Senevirathna et al., 2010), the adsorption capacities of adsorbents for PFOS increase in the following order: PA > AC > anion exchange resins (AS, AW). This finding is the result of the magnitude of the adsorbent’s inner surface area and the availability of cationic functional groups, respectively. The nature of these groups, weak (AW) or strong basic (AS), seems to have no impact on the adsorption isotherms, if resins of similar structure are compared (AW-F100, AS-F520).

The aforementioned remarks are only valid for mesoporous adsorbents as a comparison of these materials with the gel-type resin AS-L K6362 reveals. Due to the predominantly microporous structure of AS-L K6362, its sorption isotherm shows a lower slope and strives against a lower limit for PFOS loading. The surfactant molecules, especially the branched isomers, cannot access the micropores, because either they are intrinsically too large or the pore access is blocked by previously adsorbed molecules. Only a small part of the total base capacity of this material is thus available for the sorption of PFOS at most part of the tested inlet concentration range. However, the last isotherm point does not fit into this scheme since the adsorbent loading suddenly increases again, after forming a stable plateau before (Fig. 1a). Such behavior is usually assigned to a change in orientation of adsorbed surfactant molecules (Giles et al., 1960), resulting in swelling of the polymer network due to the formation of micelles inside its pores. In the case of the gel-type AS-L K6362, this is more likely to happen in its macroporous transport channels, which were introduced in the microporous polymer by post-crosslinking. Accordingly, the macropores might be filled
completely with adsorbent molecules, causing the salt up in the isotherm at the highest concentration applied.

Regarding the acrylate-based anion exchange resin AS-F860, it generally needs to be assumed that PFOS is not only bound to the functional groups of this resin, but is also stored in the form of micellar aggregates inside of its pores. The adsorption isotherm of this material exhibits a very steep slope and doesn’t show any signs of saturation yet, even at the highest inlet concentrations applied. At this point, a PFOS amount of about 2000 mg/g was already stored on the resin, which matches quite exactly the total capacity of the material (Table 2). Regarding capacity, the higher polarity of the polymer backbone of this resin seems to have a positive effect on the adsorption of PFOS, at least when high initial concentrations are applied. This behavior is not relevant for practical applications at high concentrations, therefore it wasn’t closely investigated in the present study.

In contrast, at start concentrations in the low μg/L range, a hydrophobic polymer structure is beneficial for the sorption of PFOS, as a comparison of the hydrophobic resin AW-F 100 and the hydrophilic resin AS-F 860 reveals (Fig. 1b). This result indicates that hydrophobic interactions also participate in the sorption of PFOS onto resins, in addition to the ionic interactions. Nonetheless, at such low PFOS concentrations the selectivity for PFOS sorption is generally poor, as indicated by the convex curvature of the experimental adsorption isotherms at equilibrium concentrations in the low μg/L range. The appearance of the resulting S-shaped isotherms is not unusual for adsorption processes taking place in the liquid phase, because this kind of adsorption generally requires a replacement of previously adsorbed species which cover the surface of the adsorbents. At such low PFOS concentrations the driving force is simply too weak to displace these species effectively — water molecules in case of AC and PA and ionic species in case of resins — by the adsorptive PFOS. The ionic interactions between the functional groups of the adsorbent and their counter ions are stronger than physical interactions of water molecules with the surface of the adsorbent. Hence, water molecules can thus be easily replaced, which is why activated carbons and polymer adsorbents are more effective adsorbents for PFOS at concentrations in the μg/L range than resins (Fig. 1b).

2.2. Isotherm modeling

Adsorption isotherms can be described by numerous mathematical models. In the present work, the classical approaches of Freundlich and Langmuir, as well as their “combination” in the models of Sips and Redlich-Petersen, have been applied to model the experimental data. In addition, the models of Zhukhovitskii and Frumkin were also considered, since S-shaped isotherms can be described by their approaches. Modeling according to those equations and experimental data was carried out in Scilab (ver. 5.4.1) using the optimization routines fminsearch and optim, which are based on the Nelder–Mead method or the quasi-Newton method, respectively. As optimization criterion the sum of squared residuals (SSRs) of calculated and observed data was applied.

Unfortunately, none of the mathematical models was able to describe the adsorption isotherm of AS-F 860, because the isotherm didn’t show any saturation in the tested concentration range. For similar reasons, in the case of AS-L K6362, the last data point had to be neglected for successful isotherm modeling.

Generally, already the classical approaches of Langmuir and Freundlich described the adsorption isotherms of the materials sufficiently well (Table 3). Due to the rather defined structure of the synthetic adsorbents and the strong ionic interactions in case of PFOS sorption onto resins, the adsorption sites of these materials can be assumed to be energetically pretty homogeneous, a prerequisite of the Langmuir model. Hence, better fits were usually obtained applying this approach. An exception in this regard was only the activated carbon Norit GAC 1240, which is more heterogeneous in its properties, since it is derived from a natural product. The sorption of PFOS onto this adsorbent was better described by a Freundlich isotherm. As this model presumes a logarithmic decrease in adsorption enthalpy with increasing surface coverage it is intrinsically applicable to
materials with energetically heterogeneous adsorption sites. Because the perfluorinated surfactants are only bond by physisorption to the non-functionalized materials, the influence of such heterogeneity is usually more pronounced for this kind of adsorbents. This is probably the reason why both models describe the isotherm of the adsorption of PFOS onto PA-F 2600 equally well.

Basically all adsorbents, also the synthetic ones, possess different kinds of adsorption sites. Therefore, a better mathematical description can generally be achieved by introducing an additional parameter in the Langmuir equation, which characterizes this heterogeneity, like in the isotherms of Redlich–Petersen and Sips (Table 4). Despite the rather low SSR values, none of the before-mentioned models can describe the convex curvature at the beginning of the observed isotherms. But also modeling the experimental data according to the approaches of Zhukhovitskii and Frumkin did unfortunately not lead to a significant improvement in the accuracy of the mathematical description, especially in the low concentration range (Appendix A Fig. S1), even though these approaches are basically applicable to S-shaped isotherms. Accordingly, one might argue if it is reasonable to use those more complex isotherm models, especially if the error margin of the analytical methods (±10%) is considered as well. For this reason, only the approaches by Langmuir and Freundlich were used to characterize the adsorption equilibrium in kinetic modeling.

2.3. Kinetics of the PFOS adsorption

The kinetics of the PFOS adsorption onto different kinds of materials is compared in Fig. 2. In contrast to the increase of equilibrium capacity in the presence of functional groups, adsorbent functionalization influences adsorption kinetics negatively.

For styrene-based materials, the PFOS adsorption rate, which correlates with the number and kind of functional groups present, decreased in the following order: PA-F2600 > AW-F111 > AW-F100 > AS-F500 ≈ AS-F520 > AS-F530. The most significant drop in adsorption rate can be observed, when a non-functionalized adsorbent and a functionalized resin are compared. Within the group of resins, the diffusion of surfactant molecules into and inside the pores is...
hindered to a greater extent, when their functional groups become more voluminous. Already by adding just another methyl moiety at the ion exchange function of the AW-F100, like in the case of its strong-base counterpart AS-F500, a distinct effect can be observed. On the other hand, the rate of PFOS adsorption onto AS-F500 and AS-F520 is basically identical, even though the functional groups of these resins possess alkyl moieties of different lengths — methyl rests in the case of AS-F500 and ethyl rests in the case of AS-F520. However, the latter material has a lower total base capacity. Obviously, the negative effect of more voluminous functional groups on the adsorption rate is compensated by the lower number of these groups. Such compensation is not possible anymore if the alkyl on the functional groups than C2 moieties. For this reason, the PFOS uptake of AS-F530 is very low and slow.

Besides material functionalization, grain size has also a major impact on the kinetics of PFOS adsorption, which is typical for diffusion controlled processes. In the case of surface diffusion, the higher rate of PFOS uptake, when the mean particle diameter is reduced, can be explained by shorter diffusion lengths inside the pores and thus a better accessibility of adsorption sites. As can be seen in Fig. 3, for a distinct improvement in adsorption rate the grain size needs to be reduced significantly. Especially powdered adsorbents and resins provide excellent adsorption kinetics. However, they are not applicable in classic adsorption columns due to a too high pressure drop over bed length (Hansen et al., 2010).

2.4. Modeling of adsorption kinetics

The kinetic data of the adsorption experiments was successfully described applying LDF model. In this approach, surface diffusion is assumed to be the rate-determining step of the adsorption. The change in PFOS concentration over time may thus be expressed by differential Eq. (1). Therein, $\eta$ is given by the material balance (Eq. (2)) and $q_s$ is related to the concentration in the bulk liquid by the adsorption isotherm. For the above-mentioned reasons, only the approaches of Freundlich (Eq. (3)) and Langmuir (Eq. (4)) were used to describe the adsorption equilibrium in the kinetic models.

The initial conditions for the mass transfer equation are: $c = c_0$, $\eta = 0$ at $t = 0$.

$$\frac{dc}{dt} = -\rho_k \cdot \beta_s \cdot \eta \cdot (q_s - \eta) \quad (1)$$

$$\eta = \frac{V}{m_{Ad}} \cdot (c_0 - c) \quad (2)$$

$$q_s = K_F \cdot c^n \quad (3)$$

$$q_s = q_{max} \cdot \frac{K_L \cdot c}{1 + K_L \cdot c} \quad (4)$$

where, $c$ (mg/L) is the concentration at external particle surface; $\beta_s$ (cm/min) is the mass transfer coefficient for surface diffusion; $aV$ (cm$^2$/L) is the external adsorbent particle area related to reaction volume; $\eta$ (mg/g) is the adsorbed amount, adsorbent loading; $q_s$ (mg/g) is the adsorbent loading at external particle surface; $m_{Ad}$ (g) is the adsorbent mass; $K_L$ (L/mg) is the adsorption equilibrium constant in Langmuir isotherm; and $K_F$ (mg$^{-1-n}$ L$^n$ g$^{-1}$) is the adsorption equilibrium constant in Freundlich isotherm.

The first modeling results revealed that the intraparticle mass transfer coefficient $\beta_s$ depends on adsorbent loading. This relation was taken into account by introducing the following exponential approach for $\beta_s$:

$$\beta_s = \beta_{s,0} \cdot \exp(\omega \cdot \eta) \quad (5)$$

Solving the equation system (1)–(5) under minimization of the sum of least absolute residuals (SLAR) per data point in Scilab, the values of mass transfer coefficient at maximum loading ($\beta_{s,0}$) and $\omega$ (load dependency of the mass transfer coefficient $\beta_s$) were determined. The SLAR was calculated according to Eq. (6):

$$\text{SLAR} = \sum_{i=1}^{n} \left| \frac{c_{\text{exp}} - c_{\text{mod}}}{n} \right| \quad (6)$$

Since multiple roots of the equation system could exist and the gradient of the SLAR was very small, the whole relevant parameter range had to be investigated. Hence, the equation system was solved in each node of a parameter network (Fig. 4). The parameter set with the lowest SLAR value was then chosen for the further minimization procedure.

The influence of the parameter $\omega$, which characterizes the load dependency of $\beta_s$, on the SLAR values is clearly illustrated in Fig. 4. This load dependency might be explained by strong interactions between adsorbent and adsorptive, especially if they are of ionic nature like in the case of resins. For this reason, adsorbed species can hardly be displaced by new surfactant molecules, slowing thus down the inner diffusion processes due to the rather large chain-length and rigidity of the PFOS molecule.

No distinct optimum of the error function can be observed in Fig. 4. It even seems to be independent of $\beta_{s,0}$ in the tested parameter range, but by analyzing the red contour line in detail an optimum can be identified. Due to the special character of this function with very similar SLAR values over a broad parameter range a comparison of different materials is nonetheless difficult.
In agreement with the results of isotherm modeling, a better match of the surface diffusion model with the experimental data was generally obtained, when the adsorption equilibrium was described by a Langmuir isotherm. In the case of the activated carbon GAC 1240 the accuracy of the modeled kinetic curve was again better, when the Freundlich approach was applied. The worse adsorption kinetics of this material in comparison with the circular activated carbon AC 43767 — the initial mass transfer coefficient $\beta_{s,0}$ is by a factor of 2 smaller (Table 5) — can be attributed to its more microporous character and thus a smaller average pore diameter.

Of course, the impediment of the diffusion processes in the presence of functional groups is confirmed by results of kinetic modeling as well. The intra particle mass transfer coefficient for surface diffusion $\beta_{s,0}$ of the weak-base resin AW-F 100 is about one order of magnitude smaller than the value obtained for the polymer adsorber PA-F 2600. Replacing the methyl moieties at the ion exchange function of the AW-F100 by ethyl, like in the case of AS-F 520, the mass transfer coefficient is further decreased by a factor of about 2. The more voluminous the functional group becomes, the bigger is obviously its effect on the rate of surface diffusion.

A comparison of the different adsorbents on the basis of calculated mass transfer coefficients was reasonable, because the $\omega$ values of all materials are very similar (−0.018 to −0.015). Only the gel-type resin AS-1 K6362 is an exception in this regard. Considering its microporous character in combination with the presence of functional groups, the intrinsic impediment of the diffusion processes is assumed to be large in comparison to the additional hindrance by already adsorbed surfactant molecules.

The kinetic curve of this resin was better described by a model including the Langmuir isotherm, while no distinct

| Table 5 – Linear Driving Force (LDF) model for surface diffusion — calculated values for model parameters considering validity of Langmuir or Freundlich isotherm. |
|-----------------|-----------------|-----------------|-----------------|
| Adsorbent       | $\beta_{5,0}$ (cm/min) | $\omega$ (g/mg) | SLAR (mg/L)     |
| GAC 1240        | $1.81 \times 10^{-5}$ | −0.01813        | 1.013           |
| AK 43767        | $3.64 \times 10^{-5}$ | −0.01533        | 1.259           |
| PA-F 2600       | $1.26 \times 10^{-5}$ | −0.01662        | 1.182           |
| AW-F 100        | $1.62 \times 10^{-5}$ | −0.01664        | 1.051           |
| AS-F 520        | $0.88 \times 10^{-5}$ | −0.01527        | 1.163           |
| AS-L K6362      | $0.80 \times 10^{-5}$ | −0.00792        | 2.027           |

*a For these adsorbents only the approaches of Freundlich was used.
differences between both classical approaches were observed in isotherm modeling. For PA-F 2600 the situation is similar, but in this case the accuracy of the kinetic model was better when the Freundlich approach was included in the system of equations. The SLAR values might still appear comparably large (Table 5), despite optically very good fitting results. However, it can be easily explained by the scattering of the experimental data.

2.5. Selectivity of PFOS-adsorbent interactions

Regarding the selectivity of PFOS-adsorbent interactions two aspects need to be considered, the adsorption of different PFOS isomers and the interaction of PFOS with different kinds of functional groups. To answer the latter question, the loading of different materials was divided by the total base capacity of the anion exchange resins. The normalized loading can then be used as an indicator for the selectivity of PFOS adsorption onto different functional groups. As can be seen in Fig. 5, materials whose functional groups possess a more hydrophobic character due to their longer alkyl rests show a higher normalized PFOS loading: AS-F500 < AS-F520 < AS-F530. This result can be explained by the more hydrophobic nature of the PFOS anion in comparison with the sulfate ion. It also indicates that hydrophobic interactions have a share in the adsorption of PFOS onto resins.

The only small difference in selectivity between AS-F520 and AS-F530 at the higher inlet concentration might be ascribed to AS-F530 being already saturated with PFOS at this isotherm point because of its lower number of functional groups. However, the advantage in selectivity of such functional groups with longer-chain alkyl rests (C < 2) cannot be kept when their number is increased, like in AS-F555. Assumably, pore accessibility is not completely ensured in this case anymore.

The above-mentioned explanations are generally valid for the removal of PFOS, but in detail there are differences in the adsorption of the different PFOS isomers. The isomer composition of the technical-grade product, which was used as feed, was determined by HPLC-ESI-MS/MS as follows: 70% unbranched PFOS and 30% mono- and double branched isomers (Fig. 6), the latter one present only in a minimal amount. An exact quantification is unfortunately impossible, because the MS response factors cannot be estimated for most of the isomers, since they are not available as pure substance. Nonetheless, on the basis of the relative peak areas in the chromatograms representing the three isomer groups, conclusions regarding changes in isomer composition can still be drawn.

In Fig. 6, the chromatograms of feed and product for the polymer adsorber PA-F2550 are compared. It shows that the unbranched isomer is preferably adsorbed. This can either be explained by the higher packing density of unbranched molecules in the adsorbate layer or by the worse adsorption kinetics of branched isomers. The rate-limiting diffusion processes proceed at a lower speed due to the larger diameter...
of branched molecules in comparison to their unbranched analogs (Einstein et al., 1956). Especially the fraction of double branched isomers is thus increased.

The trend to preferential binding of the unbranched PFOS isomer is less pronounced in resins than in non-functionalized materials. PFOS is bound to resins mainly by ionic interaction with the functional groups. Because of the thus higher adsorption enthalpy, packing density is of less importance in this case. Lateral interactions between the perfluorinated surfactant tails only affect the adsorption at higher loadings or when double and multi-branched molecules are adsorbed. The greater is the ionic character of the exchange function, the smaller is the influence of the lateral interaction. Therefore, fewer differences in relative isomer selectivity, which was calculated as the quotient of the relative peak area of an isomer in eluate and in feed, were observed for the strong base resin AS-F500 than for its weak base analog AW-F100 (Table 6).

Probably, these generally appearing differences in the selectivity of the adsorption of the different PFOS isomers are the reason for breakthrough curves forming a plateau at normalized concentrations <1 (Appendix A Fig. S2), especially as a decomposition of the adsorptive can be excluded due to the excellent chemical stability of perfluorinated surfactants.

2.6. Characterization of used adsorbents — mechanistic implications

The adsorption experiments suggest that PFOS can only bond to activated carbons and polymer adsorbents by physisorption, while it is primarily bound to resins by ionic interactions. To verify these assumptions regarding the mechanisms of PFOS adsorption onto different kinds of adsorbents, used samples were characterized by several physicochemical methods and their regeneration using several solvents was tested.

In Table 7 some characteristic IR bands of PFOS are summarized. An interpretation of the IR spectra (Appendix A Fig. S3) is generally challenging, because the characteristic bands of PFOS can be found at wave numbers between 1500 cm$^{-1}$ and 600 cm$^{-1}$, where the adsorbents also show a strong absorption of infrared radiation. Hence, when the IR spectra of pure PFOS and PFOS loaded samples are compared, no systematic shifts of IR bands in dependence of the material type can be observed, with one exception. The band of the symmetric stretching vibration of the sulfonate group $\nu_\text{s}(R-SO_3^-)$ is for resins further shifted towards lower wave numbers than for polymer adsorbents. This hints on different adsorption mechanisms on both materials, as mentioned at the beginning of this subsection. The existence of the doublet at 1210 cm$^{-1}$ and 1240 cm$^{-1}$ in the IR spectra of all materials furthermore indicates that no chemical bonds are formed between adsorptive and adsorbent (Gao and Chorover, 2012), confirming thus indirectly the ionic character of the bond between the cationic exchange functions of the resins and the sulfonate group of the surfactant.

To evaluate if the adsorption mechanism of weak and strong base anion exchange resins is identical, the capacity of virgin and used samples was determined by acid/base titration and compared with the total capacity provided by the manufacturer (Fig. 7). Differences in the weight capacity of virgin samples of strong-base resins and their total capacity

### Table 6 – Relative selectivity of PFOS sorption onto different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Relative isomer selectivity</th>
<th>Unbranched</th>
<th>Single br.</th>
<th>Double br.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-F2550</td>
<td>0.646</td>
<td>1.455</td>
<td>3.050</td>
<td></td>
</tr>
<tr>
<td>AC 43767</td>
<td>0.997</td>
<td>0.786</td>
<td>2.155</td>
<td></td>
</tr>
<tr>
<td>AW-F100</td>
<td>0.773</td>
<td>1.266</td>
<td>2.660</td>
<td></td>
</tr>
<tr>
<td>AS-F500</td>
<td>0.934</td>
<td>1.082</td>
<td>1.418</td>
<td></td>
</tr>
<tr>
<td>AW-F111</td>
<td>0.881</td>
<td>0.754</td>
<td>1.108</td>
<td></td>
</tr>
</tbody>
</table>

Values <1 indicate a preferred adsorption of the respective isomer.

### Fig. 7 – Capacities of several virgin and used resins.

### Table 7 – Infrared (IR) bands of PFOS prior to and after sorption onto different kinds of adsorbents.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Wave number (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEA-PFOS</td>
</tr>
<tr>
<td>$\nu_\text{(C-C)}$</td>
<td>1037</td>
</tr>
<tr>
<td>$\nu_\text{(R-SO_3^-)}$</td>
<td>1068</td>
</tr>
<tr>
<td>$\nu_\text{s}(\text{CF}_2)$</td>
<td>1147</td>
</tr>
<tr>
<td>$\nu_\text{as}(\text{CF}_2)$</td>
<td>1197</td>
</tr>
<tr>
<td>$\nu_\text{as}(\text{R-SO_3^-})$</td>
<td>1224</td>
</tr>
<tr>
<td>$\nu_\text{as}(\text{CF}<em>2) + \nu</em>\text{as}(\text{R-SO_3^-})$</td>
<td>1240</td>
</tr>
<tr>
<td>$\nu_\text{as}(\text{CF}_2)$</td>
<td>1328</td>
</tr>
<tr>
<td>$\nu_\text{ax}(\text{CF}_2)$</td>
<td>1369</td>
</tr>
</tbody>
</table>

n.b. = no band.
can be ascribed to the test conditions, under which a complete exchange of sulfate ions by hydroxide ions is impossible, due to a higher selectivity of the functional groups for $SO_4^{2-}$. The weak-base resin AW-F100 doesn’t show this behavior, because instead of replacing the counter ions, the functional groups are deprotonated by the hydroxide ions. In contrast to the interaction between the cationic functional group and the sulfate ion, the bond with the sulfonate group of PFOS is strong enough to prevent the neutralization from taking place, which was confirmed by regeneration experiments using NaOH and NH$_3$. For this reason, used samples of this resin could not be transformed into their free base form completely. After deprotonation of those functional groups, which were occupied by sulfate, the combined capacity for PFOS and $SO_4^{2-}$ was larger than the total capacity of the virgin material. This over-capacity suggests either that PFOS is partly bound to the nonpolar polymer matrix by hydrophobic forces or that micellar structures form inside the pores of the resin. For strong-base resins over-capacities were not observed, but the capacity of used samples was also significantly higher than that of virgin samples, confirming thus the higher selectivity for PFOS in comparison to sulfate.

Unfortunately, the DSC measurements could not provide further insights into the adsorption of PFOS onto weak and strong base resins, because no endothermic desorption peaks could be detected in the narrow temperature range, predefined by material stability. In the case of physisorptively bound PFOS on AC 43767 and PA-P2600, desorption peaks appeared in their thermograms at 208°C and 268°C (Appendix A Fig. S4), respectively, suggesting thus a stronger adsorption of PFOS onto polymer adsorbents than onto activated carbons. This might be explained by a slightly lower hydrophobicity of the carbon matrix due to the presence of heteroatoms.

The above-mentioned conclusions regarding the adsorption mechanism on different kinds of materials are also supported by the results of regeneration experiments. Accordingly, PFOS was completely desorbed from polymer adsorbents using pure methanol, while desorption from resins required a mixture of ammonia solution and methanol. However, due to the large amounts of solvent necessary for desorption, regeneration is not feasible for economic reasons.

3. Conclusions

In the adsorption experiments, it was found that the total PFOS capacities of the adsorbents increase in the following order: polymer adsorbents (PA) > activated carbons (AC) > anion exchange resins (AS, AW) which is the result of the magnitude of the adsorbent’s inner surface area and the availability of cationic functional groups, respectively. The nature of these groups determines the selectivity of the adsorption process — the more hydrophobic the character of the functional groups the higher the selectivity for PFOS adsorption. In combination with over-capacities observed for weak-base resins, this result suggests at the same time that hydrophobic interactions participate in the adsorption of perfluorinated surfactants onto resins, but predominantly ionic bonds are formed. As expected, physisorption was found to be the dominating adsorption mechanism on activated carbons and polymer adsorbents.

Adsorption isotherms of all materials could be described sufficiently well by the models of Langmuir and Freundlich, respectively. Only, the convex curvature of the isotherm in the low µg/L range could not be reproduced by any of the tested models, even by more complex approaches. Differences in the convex curvatures render polymer adsorbents more effective in PFOS elimination in the before-mentioned concentration range than activated carbons and especially resins.

Kinetics of PFOS adsorption is generally determined by diffusion processes; especially the inner mass transport limits the adsorption rate. Therefore, the presence of functional groups impedes these transport processes. The more functional groups a resin possesses and the longer the alkyl moieties are the bigger is the decrease of adsorption rate. Kinetic modeling quantified the difference in the initial mass transfer coefficient $\beta_{\text{m}_0}$ between non-functionalized polymer adsorbents and resins by a factor $\geq 10$. All kinetic curves were successfully described, applying the LDF approach for surface diffusion, if the mass transfer coefficient $\beta_{\text{m}}$ was defined as a function of the adsorbent loading. Diffusion limitation of PFOS adsorption furthermore causes preferred adsorption of the unbranched PFOS isomer.

Regeneration of the adsorbents is possible, if methanol (polymer adsorbents) or ammonia/methanol mixtures (resins) are used as solvents, but due to the large amounts of solvent necessary for desorption, regeneration is not feasible for economic reasons.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.06.011.

REFERENCES


