JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

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JES
JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

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

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ARTICLE INFO

Article history:
Received 24 March 2016
Revised 6 June 2016
Accepted 7 June 2016
Available online xxxx

Keywords:
PFOS
Activated carbon
Anion exchange resin
Sorption kinetics modeling
Sorption isotherm
Selectivity of sorption

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.*, N_2 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 β_s. The big difference in the initial mass transfer coefficient $\beta_{s,0}$, 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.

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

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http://dx.doi.org/10.1016/j.jes.2016.06.011

Please cite this article as: Schuricht, F., et al., Removal of perfluorinated surfactants from wastewater by adsorption and ion exchange — Influence of material properties..., J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.06.011

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 2006/122/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 (Destaillats 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 funnels which were put into a shaking bath for 48 hr ($f = 250$ min^{-1}). For each

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