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Experimental investigation on the perfluorooctanoic and perfluorooctane sulfonic acids fate and behaviour in the activated sludge reactor

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ABSTRACT

Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the most investigated compounds in the class of perfluoroalkyl substances for their persistence and wider diffusion in the environment. However, fate and behaviour of PFOA and PFOS in the Wastewater Treatment Plants (WWTPs) have not been fully understood yet. The aim of the present study was to obtain a better understanding of the processes occurring to PFOS and PFOA in the activated sludge reactor. Several experimental tests were performed in the presence of activated sludge and sterilized sludge. PFOA and PFOS showed removals from the liquid phase from 59 % to 68 % and from 66 % to 96 %, respectively, for initial concentrations from 200 ng/L to 4000 ng/L in the presence of activated sludge. A significant fraction of the initial contaminant load was found adsorbed on the sludge, mainly in the case of PFOS. Other processes occurred, not fully identified, which were responsible of a further loss from the system. Leaching tests showed negligible release of the adsorbed pollutants from the sludge. Carbon and ammonia removal in the activated sludge reactor were not significantly affected by the presence of PFOA and PFOS. The pseudo-second order kinetic model and the Freundlich isotherm provided the best fitting of the experimental data.

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1. Introduction

PerFluoroAlkyl Substances (PFASs) represent a class of industrial compounds largely employed in the last fifty years, due to their high chemical and thermal stability, hydrophobicity and lipophobicity. The extensive application of PFASs (from plastic polymers to textile fibers and cosmetics industry) has resulted in their environmental ubiquity and worldwide presence in groundwater and sewage as well as in the human body (Ahrens et al., 2011; Castiglioni et al., 2015). Among PFASs, Perfluorooctane sulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA) are the mostly investigated compounds because of their higher persistence and bioaccumulation capacity in the trophic chain (Castiglioni et al., 2015). Furthermore, scientific research confirmed the endocrine disrupting properties of PFOS and the carcinogenic effect of PFOA, as well as their toxicity to animals and human beings (Persistent Organic Pollutants Review Committee Twelfth Meeting, 2016; United Nations, 2006; White

et al., 2011). As a consequence, in Directive 2013/39/EU Environmental Quality Standard (EQS) on PFOS in surface water and biota were fixed; besides, more restricted limit concentrations on PFASs in drinking water were also proposed by the European Community (The European Parliament and the Council of the European Union, 2018).

Through the sewage network, PFOS and PFOA enter the Wastewater Treatment Plants (WWTPs). Since these compounds possess a high stability versus biological and chemical degradation, the processes here implemented for the removal of carbon and nutrient compounds are unable to achieve also significant reduction of PFOA and PFOS concentrations. Furthermore, potential transformations of precursor compounds to PFOA and PFOS during the same processes may lead to an increase of their concentrations (Pan et al., 2016). Therefore, the WWTPs become one of the main sources of release into the environment through the effluent and sludge disposal. As highlighted in several studies, physical-chemical properties of these compounds play a relevant role in the removal processes and make its understanding to be more complicated (Buck et al., 2011; Dalahmeh et al., 2019). The molecular structure of PFOA and PFOS is characterized by hydrophobic strong

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carbon–fluorine bond chain and hydrophilic functional groups, which give them a surfactant property. Similarly to many pollutants such as heavy metals and some organics, also for PFOA and PFOS an important mechanism of removal seems to be their adsorption onto sludge flocs (Quirantes et al., 2017; Vilardi et al., 2017). Therefore, the waste sludge represents the main mass flow coming out from the treatment plant, with concentrations found to be in the range <5–190 ng/g for PFOA and 13–702 ng/g for PFOS (Pan et al., 2016; Yu et al., 2009).

The number of reports examining the biodegradation and biotransformation of PFOS and PFOA by aerobic and anaerobic microbial populations is very limited (Grassi et al., 2013). Furthermore, results found in the scientific literature about the biodegradability of PFOS and PFOA are somehow conflicting (Arvaniti and Stasinakis, 2015). For instance, it was reported that PFOS can be decomposed up to 67 % by a specific microorganism present in activated sludge (Kwon et al., 2014). By contrast, other authors concluded that PFOS is microbiologically inert under aerobic conditions (Avendaño et al., 2015). The same authors of the first paper replied that, under the experimental conditions applied in their study, PFOS decomposed to some unknown products due to microbial activity (Kwon et al., 2015). Parsons et al. (2008), after analysing the foregoing literature, affirmed that PFOA is considered biologically inactive under all the examined conditions. Processes other than biodegradation and adsorption are reported to determine PFASs removal from the system, although their specific contribution has not been fully assessed yet (Liou et al., 2010).

Despite the high relevance and interest, few and often contradictory are the information available in the scientific literature about the removal and transformation mechanisms involving PFOA and PFOS in the activated sludge reactor, which represents the main stage of wastewater treatment. Therefore, additional understanding is strongly required.

The aim of the present study was to improve the knowledge about the fate and behaviour of PFOS and PFOA in the activated sludge reactor of a WWTP. Therefore, a series of experimental tests was performed to understand the role of biodegradation, adsorption and other processes. Furthermore, it was also searched if the presence of PFOA and PFOS in the activated sludge reactor can inhibit the nitrification and organic carbon removal efficiency. Finally, it was evaluated the amount of the adsorbed contaminants that is released from the sludge. The novelty of the present experimental work with respect to most of the studies found in the scientific literature is represented by the attempt to analyse all the aspects related to the presence and behaviour of PFOS and PFOA in the activated sludge reactor of the WWTP.

2. Materials and methods

2.1. Chemicals and sludge

Standard solutions of the isomers together as total of PFOA and PFOS were purchased from *Ultra Scientific Italia S.r.l.*, each one at a concentration of 200 µg/mL in methanol. This solution was then diluted in methanol (at 99 %, w/v) to achieve the concentrations required for the batch tests. Perfluorooctane Sulfonate sodium salt (13C8, 99 %) was the isotopically labelled compound used as internal standard (IS); it was purchased from Cambridge Isotope Laboratories, Inc. at a concentration of 50 µg/mL. Main characteristics of PFOA and PFOS are reported in Table S.M.1 (Supplementary Materials).

The activated sludge (8000 mg/L Total Solids (TS)) used for the tests was collected from the return loop of the secondary settlement tank of a full-scale WWTP treating domestic sewage, and then stored at T = 4 °C for less than a week until its use.

Nitrogen and phosphorous solutions were made by dissolving ammonium chloride (NH₄Cl) and sodium dihydrogenphosphate (NaH₂PO₄) salts, respectively, into deionized water (MilliQ water). Organic carbon substrate was supplied only through the methanol contained in the standard solutions of PFOA and PFOS. The micro-nutrient solution was prepared according to OECD n. 209 (Oecd, 2010), that was by dissolving into 1 L deionized water the following components: 0.7 g NaCl, 0.4 g CaCl₂·2H₂O, 0.2 g MgSO₄·7H₂O. All solutions were stored at T = 4 °C.

2.2. Experimental set up

The following three series of experimental tests were carried out: (1) Activated sludge tests, (2) Sterilized sludge tests, (3) Leaching tests. Details of each series are reported below.

2.2.1. Activated sludge tests

Removal processes from the liquid phase and potential inhibition of biomass activity in the activated sludge reactors were investigated through a series of batch tests using the same experimental setup as outlined in previous works by the same research group (Boni et al., 2018; Chiavola et al., 2019).

The experiments were carried out at the following initial contaminant concentration inside the flasks of each PFOA and PFOS: 200, 500, 1000, and 4000 ng/L. These values were chosen as they fall within the common range of concentrations found in domestic and industrial wastewater (Bijlsma et al., 2014; Causanilles et al., 2017; Mackul'ak et al., 2016; Nefau et al., 2013; Senta et al., 2013).

The tests were designed with the aim to simulate conditions and processes occurring in a real biological reactor. To this purpose, the activated sludge was mixed with the PFOA and PFOS solutions at the selected concentrations together with a solution containing carbon, nitrogen, phosphorous and micronutrients in order to simulate the main wastewater components entering the biological reactor of a WWTP. The initial concentrations inside the reactors were set as follows: 3000 mg/L TS, 300 mg/L Chemical Oxygen Demand (COD), (provided only through the methanol of PFOA and PFOS standard solutions), 30 mg/L NH₃-N, 6 mg/L P and micronutrients (according to OECD n. 209). These concentrations allowed to achieve a C:N:P ratio inside the reactors equal to 100:10:2, considered suitable for the microbial activity.

A 600 mL glass flask (500 mL operating volume) was used to conduct the experiments. Each test was repeated in duplicates, and the results obtained were averaged. Each flask was placed in a jar tester to provide mechanical stirring in order to maintain the content under completely mixed conditions; aeration was provided for all the duration of the tests, with the aim to fix the dissolved oxygen concentration (DO) at approximately 6 mg/L O₂. Through the addition of NaOH 30 % (w/v), pH value was kept between 7.2–8.0 which is considered the optimal range for nitrification (Metcalf and Eddy, 2013). The flasks were covered with aluminium foils to avoid photo-degradation phenomena and temperature was maintained within the range T = 22 ± 2 °C. Prior to the addition of the PFOA and PFOS solution and nutrients, the activated sludge was kept under completely mixed and aerated conditions for 24 h in order to bring the biomass into the endogenous respiration state. Tests were started (t = 0) when the Oxygen Uptake Rate measurements were at about 0.1 mg/L·min. At this time, PFOA, PFOS and nutrient solutions were added to the flasks. The overall duration of each test was fixed at t = 24 h based on previous tests which showed that this was the time needed for COD removal and nitrification processes to reach the equilibrium conditions. After the start, samples were collected from the flasks at t = 3, 6 and 24 h, in order to determine the kinetics of the removal process from the liquid phase. PFOA and PFOS concentrations were measured in the liquid phase after sample filtration at 0.2 µm pore size. Nitrification and COD removal were also

monitored during the tests by measuring the following parameters at the same contact times: COD, $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and TS. At the beginning and the end of each test, PFOA and PFOS concentrations were also measured in the sludge phase of the same samples.

The experimental data were fitted using the zero, first, second, saturation, pseudo-first, pseudo-second order kinetics, intraparticle diffusion (IDM) and Elovich models (Erhayem et al., 2015; Plazinski et al., 2013; Saad et al., 2017). The best fitting model was considered that one providing the highest value of the correlation coefficient (R^2) between experimental and modelled data, based on the linear form of the equation of each model.

A further test was run as a control (Blank, B), using the same operating conditions and composition except for the absence of PFOA and PFOS in the feed solution.

The potential inhibition effect due to PFOA and PFOS on the biomass activity was evaluated by following the Activated Sludge, Respiration Inhibition Test, Carbon and Ammonium Oxidation OECD 209 method (Oecd, 2010). This method allows to determine how different concentrations of a tested compound may affect microorganisms activity based on the Oxygen Uptake Rate (OUR) measurements at $t=3$ h during the test. The Specific OUR (SOUR) was calculated by normalizing the OUR to the average value between the initial and final total solids contents in the flask. The effect on the biomass activity of each tested concentration was finally expressed as a percentage inhibition, I%, as described in the OECD procedure.

2.2.2. Sterilized sludge tests

The second series of experimental tests was carried out with the aim to simulate the processes other than biological occurring in the reactor. To this purpose, they were conducted maintaining in the flasks the same composition of the mixed liquor as in the Activated sludge tests, whereas a sterilized sludge was used instead of active biomass (3000 mg/L TS; initials contaminant concentration inside the flasks 200, 500, 1000, and 4000 ng/L of each PFOA and PFOS; 7.2–8.0 pH; sampling times $t=0, 3, 6$ and 24 h). Furthermore, the tests were conducted in the absence of aeration. Sterilization was obtained by maintaining the sludge inside an autoclave at a temperature $T=120^\circ\text{C}$ for 30 min. Sludge inactivation was considered successful if DO value never decreased throughout the duration of the tests (Ying and Droste, 2015).

Equilibrium tests were performed using the sterilized sludge with the aim to identify the isotherm model of PFOA and PFOS adsorption onto the sludge. The experimental set-up was maintained the same as above, whereas concentrations of PFOA and PFOS were fixed at 1000 ng/L each one, which was considered representative of the average value of the range tested in the present study. Five different dosages of sterilized sludge were added to the flasks: 1, 2, 3, 4 and 5 g/L TS. At the beginning ($t=0$) and at the end of the tests ($t=24$ h), concentrations of TS, PFOA and PFOS in the liquid and sludge phases were measured. pH was maintained within the 7.2–8.0 range, as in the activated sludge tests, through the addition of NaOH 30 % (w/v). The following isotherm models were applied to the experimental data of the equilibrium tests: Langmuir, Freundlich, Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich (DRK), Tempkin and Harkins–Jura (Erhayem et al., 2015; Foo and Hameed, 2010; Saad et al., 2017; Shanavas et al., 2011). The best fitting model was considered that one providing the highest value of the correlation coefficient (R^2) between the experimental and modelled data, based on the linear form of the model equation.

2.2.3. Leaching tests

The release of contaminants adsorbed on the sludge is considered one of the main mechanisms potentially responsible of environmental risks. In order to evaluate the potential release of

PFOA and PFOS adsorbed on the sludge, leaching tests according to standard UNI EN 12457-2 procedure were performed. The sludge samples were collected at the end of the equilibrium tests conducted at 4 and 5 g/L TS. Prior to the use, they were centrifuged at 4000 rpm for 10 min, in order to eliminate the supernatant. The leaching agent used for the test was deionized water in accordance to the standard procedure (UNI EN 12457-2). A proper volume of leaching agent (33 mL and 41 mL for the tests performed at 4 and 5 g/L TS, respectively) was added to the sludge in order to obtain a liquid/solid ratio $L/S=10$ L/kg. The content of the flasks was maintained under mixed conditions using a magnetic stirrer, for $t=24$ h. At the end of the tests, PFOA and PFOS concentrations in the liquid phase were measured and the mass of contaminants leached by the sludge was determined, as required by the UNI EN 12457-2 procedure.

2.3. Analytical methods

Concentrations of the following parameters were measured according to APHA methods (Eaton et al., 2005): COD, $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, and TS. pH, temperature and dissolved oxygen (DO) were measured using standard probes. The quantitative analysis of PFOA and PFOS in the liquid and sludge phases was performed by means of the High-Performance Liquid Chromatography coupled to tandem Mass Spectrometry (HPLC–MS/MS). The EPA method 537 was followed, amended so as to be suitable for wastewater analyses (Kwon et al., 2014). All the parameters were measured twice for each contact time during the experimental tests and the results obtained averaged.

For calibration and quantification, the internal standard (IS) approach was followed. The liquid sample pre-treatment consisted only of a filtration step by using a $0.2\ \mu\text{m}$ membrane filter of regenerated cellulose. Before the injection in the HPLC–MS/MS system, 800 μL of supernatant was spiked with 10 μL of IS for the analytes quantification. The instrumental conditions applied are reported below:

- 1) HPLC: Perkin Elmer Series 2000 equipped with chromatography column Phenomenex Kinetex $2.6\ \mu\text{m}$ F5 100A, 100×2.1 mm and security-guard column. Mobile phase A: 95 % LC–MS water and 5 % LC–MS methanol with ammonium acetate 20 mM. Mobile phase B: 100 % LC–MS methanol with ammonium acetate 20 mM. The gradient elution conditions were from 60 % A and 40 % B to 10 % A and 90 % B in 9 min. The injected volume was 50 μL , the temperature was 40°C and the flow rate equal to 0.25 mL/min.
- 2) Mass spectrometer: Applied Biosystem – API 2000 LC–MS–MS System. The applied HPLC–MS/MS parameters are reported in Table S.M.2.

The overall response time for each liquid sample was below 20 min.

Each contaminant was quantified by MRM (Multiple Reaction Monitoring ratio) using the two most abundant precursor/product ion transitions of the two analytes and the IS.

The solid sample pre-treatment was carried out by following the Ultra-Sound assisted Extraction (USE) procedure: 50 mL of wastewater samples were centrifuged at 4000 rpm for 15 min in order to separate sludge from supernatant; 10 mL of 50 % methanol and 50 % MilliQ water were added to centrifuged solids. The samples underwent the USE for 15 min at 30°C ; then, they were filtered at a $0.2\ \mu\text{m}$ using a membrane filter, spiked with the IS and injected in the HPLC–MS/MS system, as described above for the liquid phase. The USE extraction method was selected since recent scientific studies and previous tests by the same authors showed to be superior to

Table 1

Validation parameters of the analytical method for PFOA and PFOS detection (UPLC-MS/MS) in the liquid and sludge phases for the transitions used for the quantification: MRPL_w= minimum required performance limit for liquid samples; MRPL_m= minimum required performance limit for sludge samples; Rep_w= repeatability in water; Rep_m= repeatability in experimental matrix; R²= calibration curves linearity; REC_L= recovery from liquid samples; REC_S= recovery from sludge samples.

Compound	MRPL _w ng/L	MRPL _m ng/g	Rep _w %	Rep _m %	R ²	REC _L %	REC _S %
PFOA	20	>6.7	5	2	0.999	100	30
PFOS	10	>3.3	19	14	0.998	101	34

the Accelerated Solvent Extraction (ASE) (Álvarez-Ruiz et al., 2015; Boix et al., 2016; Chiavola et al., 2019; Gago-Ferrero et al., 2015).

The analytical method was validated based on the criteria of the 2002/657/EC Commission Decision (Decision, 2002/657/EC). The validation parameters were defined and calculated as follows:

- Minimum required performance limit (MRPL), determined as the concentration which gives a signal/noise ratio ≥ 10 ; the test was performed on n. 6 replicates using MilliQ water (MRPL_w) and the experimental matrix (MRPL_m);
- Repeatability (Rep), calculated as the relative standard deviation percentage (RSD%) on the measured concentration of n. 6 injections; the samples were made by spiking 68 µg/L PFOA and PFOS and 10 µL of IS in MilliQ water (Rep_w) and the experimental matrix (Rep_m);
- Linearity, expressed as R² of the calibration curves;
- Recovery from the liquid (REC_L) and sludge (REC_S) phase, obtained by spiking 68 µg/L PFOA and PFOS and 10 µL of IS in the experimental matrix sample without sludge and with sludge, respectively; the test was carried out using glass flasks; it was performed in triplicate and the results compared with the initial concentration; the REC values were also used to correct the concentrations, in both liquid and sludge phases, of the experimental samples in order to discard all the errors; Recovery was calculated based on the mass balance, as follows:

$$REC_S [\%] = \frac{M_{sludge}}{M_{spiked} - M_{liquid}} \cdot 100 \quad (1)$$

$$REC_L [\%] = \frac{M_{liquid}}{M_{spiked}} \cdot 100 \quad (2)$$

where M_{spiked}, M_{sludge} and M_{liquid} represent the mass of PFOA and PFOS that was spiked, measured in the sludge and measured in the liquid, respectively.

Results of the validation phase are reported in Table 1.

2.4. Mass balances

Experimental data from the Activated sludge tests and Sterilized sludge tests were analysed by following the mass balance approach, as reported by previous studies (Jelic et al., 2011; Pan et al., 2016). Percentage mass proportions of each contaminant in the liquid and sludge phases (Liquid [%] and Sludge [%], respectively), were calculated at the end of the tests (t = 24 h) with respect to the mass added at the beginning (t = 0). The difference between the mass found in the liquid and sludge phases was referred to as “loss” (Loss [%]) and ascribed to a series of processes and transformations not identified. Calculations were performed as follows:

$$Liquid [\%] = \frac{M_L}{M_T} \cdot 100 \quad (3)$$

$$Sludge [\%] = \frac{M_S}{M_T} \cdot 100 \quad (4)$$

$$Loss [\%] = \frac{M_T - M_S - M_L}{M_T} \cdot 100 \quad (5)$$

where M_L and M_S stand for the mass of contaminant found in the liquid and sludge phases, respectively, at the end of the tests, whereas M_T indicates the mass added to the tests at the beginning. All the values of PFOA and PFOS concentration used for the mass balance calculations were already corrected by the recovery values obtained from the analytical method validation. As a result, the mass not detected due to the analytical method was excluded from the “loss” and considered to represent the effect of the transformation processes.

The leaching potential of the sludge was calculated as follows:

$$Leached\ mass [\%] = \frac{M_l}{M_0} \cdot 100 \quad (6)$$

where M_l is the mass of contaminant measured in the liquid phase at the end of the Leaching tests (t = 24 h) and M₀ is the mass of contaminant found on the sludge at the end of the Equilibrium tests, which was also the beginning of the Leaching tests.

3. Results and discussions

3.1. Activated sludge tests

3.1.1. Removal from the liquid phase

Fig. 1a and b depict the time profiles of PFOA and PFOS concentration in the liquid phase, respectively, measured in the Activated sludge tests, for the different initial concentrations (C₀): 200 ng/L, 500 ng/L, 1000 ng/L and 4000 ng/L of each compound.

The figures show for PFOA a continuous decrease of the concentration in the liquid solution throughout the tests can be observed at all the initial concentrations. More in details, the main removal took place in the first 3 h, whereas afterwards it continued at a slower rate. At the end of the tests, total PFOA removal accounted, as average, for 59 %, 68 %, 63 % and 68 % at 200 ng/L, 500 ng/L, 1000 ng/L and 4000 ng/L, respectively. Therefore, it can be highlighted an increasing trend with the concentrations.

In the case of PFOS, shown in Fig. 1b, main reduction occurred rapidly at the beginning of the tests for all the concentrations. The PFOS removal observed in the following hours was very low, and at the end of the tests it reached 66 %, 85 %, 90 % and 96 %, as average, at 200 ng/L, 500 ng/L, 1000 ng/L and 4000 ng/L, respectively. Therefore, it is confirmed an increasing trend with the concentrations also in the case of PFOS. However, the removals values were always higher than those measured for PFOA.

These results do not fully agree with most of the scientific studies, where negative or much lower removal were referred (<30 %). The difference has to be ascribed to the fact that these studies were mainly carried out at full scale WWTPs with a real wastewater having a more complex composition and containing other compounds; furthermore, more processes take place in the biological reactor which may interfere with the removal of PFOA and PFOS. For instance, it is known that municipal wastewaters contain also precursors, e.g. fluorotelomer alcohols, perfluoroalkyl phosphates, fluorotelomer sulfonates and other compounds not completely identified, which are being transformed into PFOA and PFOS during the processes taking place in the WWTPs (Arvaniti and Stasinakis, 2015; Pan et al., 2016). Furthermore, PFOA and PFOS are subjected to processes which may give rise to by-products (Arvaniti and Stasinakis, 2015; Becker et al., 2010; Dauchy et al., 2017; Loganathan et al., 2007; Xiao, 2017; Zhang et al., 2013b). By contrast, in order to obtain a better understanding of the processes, the current study was conducted in laboratory under controlled conditions; besides, the feeding solution of the tests was a syn-

Fig. 1. Time-profiles of (a) PFOA and (b) PFOS concentrations in the Activated sludge tests (error bars indicate the standard deviation).

thetic wastewater containing only selected compounds, that were PFOA, PFOS and nutrients.

3.1.2. Mass balances

Based on the residual concentrations measured at the end of the Activated sludge tests in the liquid and the sludge phases, it was possible to carry out a mass balance on the contaminants. The results obtained are shown in Fig. 2.

Normalized mass in the liquid and sludge phases and the loss were computed with respect to the mass of each contaminant initially added to the tests. The loss represents the fraction of contaminant that could not be found neither in the liquid nor in the sludge phase at the end of the tests. It was computed as the difference between the fractions measured in solution and on the sludge. This loss of PFOA and PFOS from the system cannot be completely attributed to the uncertainty of the analytical method of detection: indeed, concentrations used in the mass balances were previously corrected based on the recovery percentage determined in the method validation.

The mass of PFOA found in the liquid phase ranged from 32 % to 41 %, at decreasing concentration. An inverse trend was observed for the mass remaining on the sludge, which increased from 42 % to 48 % with the concentration. The total loss was accounted to be from 17 % to 24 %.

Arvaniti et al. (2014), using the same solid concentration as in the present study, found a similar mass percentage adsorbed on the secondary sludge (about 50 %). Pan et al. (2016) observed a similar mass loss, below 25 %, in a real scale WWTPs study; however, the residual concentration in the effluent was much higher, i.e. about 75 % of the initial load, likely due to the presence of precursors in the real wastewater which gave rise to transformation processes increasing the final concentrations. The different percentages reported with respect to the present work are likely due to the fact that most of the previous studies were carried out at full-scale, whereas in this case the behaviour of PFOA and PFOS was

investigated in the activated sludge reactor at laboratory scale, in absence of precursor compounds.

Considering that PFOA is reported not to be biodegradable, these results seem to indicate that adsorption was the main responsible of the removal from the liquid phase. However, the uptake capacity of the sludge was unable to determine the complete mass transfer from the liquid solution.

The liquid-solid partition coefficient (k_d), calculated as follows at each concentration, confirmed this result:

$$k_d[\text{L/kg}] = C_s/C_l \quad (7)$$

where C_s and C_l represent the concentrations in the solid phase (ng/kg) and in the liquid phase (ng/L) (Stasinakis et al., 2013). Values of k_d , listed in Table 2, resulted to be in the range 345–466 L/kg, and confirm the moderate sorption potential of the sludge (Tran et al., 2018). These results are in agreement with other studies as shown in Table S.M.1 (Zareitalabad et al., 2013).

In the case of PFOS, the main fraction found at the end of the tests (up to 63 %) was that adsorbed on the sludge. The residual mass in the liquid phase decreased proportionally at increasing concentration: it varied from 34 % in the test at 200 ng/L up to 4 % for 4000 ng/L. The PFOS mass loss showed exactly an opposite trend. Since biodegradation is reported to be very low for this contaminant, adsorption was considered to be the main removal mechanism (Kwon et al., 2014).

It is likely that during the tests there was a mass transfer from the liquid to the sludge phase or to the interface, since molecules of PFOA and PFOS are partly hydrophilic and partly hydrophobic; however, processes other than adsorption and biodegradation were likely responsible for the definitive leaving of the compounds from the system (referred to as loss). Biodegradation was excluded from the responsible processes because no reliable evidence of biodegradability of PFOA and PFOS under aerobic conditions was reported in the scientific literature (Parsons et al., 2008; Tjanowiczro et al., 2018). Indeed, although microorganisms can remove non-fluorinated functional groups, they are unable to suc-

Table 2

Results of the Activated sludge tests: removal efficiency (R); experimental adsorption capacity ($q_{e,exp}$); liquid-solid partition coefficient (k_d); pseudo-second order kinetic model parameters (R^2 , $q_{e,calc}$, k_2').

	Unit	PFOA				PFOS			
C_0	ng/L	200	500	1000	4000	200	500	1000	4000
R	%	59	68	63	68	66	85	90	96
k_d	L/kg	344.71	465.72	401.82	431.02	946.64	1946.23	3143.71	4681.54
$q_{e,exp}$	ng/g	49.04	143.33	265.41	1150.86	54.76	181.50	384.27	1636.88
R^2		0.98	1.00	0.99	1.00	1.00	1.00	1.00	1.00
$q_{e,calc}$	ng/g	52.04	145.91	275.43	1215.52	54.89	182.28	385.34	1640.86
k_2'	g/ng·h	0.01	0.01	0.003	0.001	0.23	0.03	0.03	0.01

cessfully attack and remove PFASs fluorine substituents to achieve mineralization of perfluorinated molecules (Parsons et al., 2008). For this reason, the strength of the carbon–fluorine bond is generally considered the main factor that limits biodegradability of PFASs.

To explain the loss, it must be also taken into account that volatilization from water cannot be considered as a relevant mobility mechanism for PFOA and PFOS due to the low values of the Henry's constant (H) and the vapour pressure (p_v) as highlighted in Table S.M.1 (Johansson et al., 2017). Values of the water solubility of PFOA and PFOS are relatively high (3.4 g/L for PFOA and 0.52 g/L for PFOS), due to the presence of the two hydrophilic functional groups (Zhang et al., 2013). However, the compounds have also hydrophobic properties related to the C–F long chains; this turns out to be more relevant for PFOS, and suggests that the hydrophobic interaction represents a key mechanism in the sorption process (Zhou et al., 2010). Furthermore, being $pK_a < 0$, they exist in a dissociated form at the typical pH of aquatic systems, which means as positively charged cation and negatively charged anion, carboxylate or sulfonate, indicating that they are strong acids (Smith et al., 2016). Another reason of mass loss might be considered their irreversible adsorption to glass (Martin et al., 2004; Ferrey et al., 2012; Zhang et al., 2013a). However, this loss contribution has been already taken into account in the tests used for the definition of the recovery percentage of the two compounds in the analytical method validation. These tests were performed using glass flasks in the presence of all the elements which were also contained in the experimental reactors. Due to the high polarity of PFASs molecules, a specific test involving only water, glass and contaminants was considered not reliable and maybe misleading, since in that case PFASs would have had high affinity with the only available phase other than water.

3.1.3. Kinetic models

Time-profiles concentrations measured in the Activated sludge tests were best fitted by the pseudo-second order kinetic model at all the tested concentrations and for both contaminants, since it provided the highest value of R^2 with respect to the other models. Table S.M.3 summarizes the results obtained by the application of all the selected kinetic models.

The linear form of the pseudo-second kinetic model is described by the follow equation:

$$\frac{t}{q(t)} = \frac{1}{k_2' \cdot q_e^2} + \frac{t}{q_e} \quad (8)$$

where $q(t)$ and q_e stand for the adsorption capacity at time t and at equilibrium ($t = 24$ h), respectively, whereas k_2' is the pseudo-second order kinetic constant (Plazinski et al., 2013).

The parameters values found for the best model are shown in Table 2, where $q_{e,exp}$ and $q_{e,calc}$ stand for the equilibrium adsorption capacity experimentally calculated and predicted by the model, respectively. It can be noted that values of $q_{e,exp}$ and $q_{e,calc}$ do not differ appreciably for all the tested concentrations (for example at 200 ng/L, they were 49 ng/g and 52 ng/g, respectively): this con-

firms the good quality of the kinetic results fitting. Similar results for PFASs were also found by other authors (Zhou et al., 2010).

3.1.4. Nitrogen and COD removal processes

During the Activated sludge tests, ammonia, nitrates, nitrites and COD concentrations were also monitored in order to evaluate if the presence of PFOA and PFOS can affect the biomass activity.

Fig. 3a shows ammonia and nitrate nitrogen concentrations measured with time at the different initial concentrations of PFOA and PFOS, and in the absence of these contaminants (Blank tests, B). It can be noted that ammonia was continuously converted into nitrate at all the tested concentrations of PFOA and PFOS, with removal efficiency of about 100 % measured at the end. Furthermore, the difference with the blank tests in the rate of conversion was negligible. Nitrite concentration (not here shown) was always under the detection limits. These results indicate that complete nitrification was taking place without any inhibition by PFOA and PFOS.

Fig. 3b shows carbon removal with time in the presence and in the absence (Blank test, B) of PFOA and PFOS. Reduction of COD occurred continuously at a similar rate as that observed in the Blank test. COD oxidation reached final values above 80 % for all the concentrations, which were comparable with those measured in the absence of PFOA and PFOS (Blank test). Therefore, it can be deemed that these contaminants do not affect the main biological processes taking place in the activated sludge reactor.

3.1.5. Respirometric tests

To further investigate the potential inhibition, respirometric tests were also conducted by following a standard procedure (OECD n. 206). These tests allowed to determine the inhibition index of the biomass activity at $t = 3$ h contact time for all the concentrations. The values found for this index resulted to be always zero, except at the highest concentration (4000 ng/L) when the index was calculated to be equal to 14 %.

Based on these results, it can be assessed that PFOA and PFOS are capable of negatively affecting biomass activity only at the highest load; however, the inhibition still remains quite low.

3.2. Sterilized sludge tests

3.2.1. Mass balances

Fig. 4 shows the results obtained at the end of the Sterilized sludge tests in terms of mass of PFOA and PFOS measured in the liquid and sludge phases and the total loss. The fraction of PFOA found in the liquid phase varied from 46 % to 65 % as the initial concentrations decreased from 4000 ng/L to 200 ng/L, respectively. This trend is similar to that observed in the Activated sludge tests; however, now the residual concentrations are always higher. The mass adsorbed on the sludge slightly decreased at the higher concentration, as observed in the Activated sludge tests. By contrast, trend of loss was different, with an important decrease with the concentrations (from 21 % to 1 % at 4000 ng/L and 200 ng/L, respectively).

Fig. 2. Normalized mass of PFOA and PFOS remaining in the liquid and sludge phases and the loss measured at the end of the Activated sludge tests.

Fig. 3. Time-profiles of ammonia and nitrate concentrations (a) and COD concentration (b) in the Activated sludge tests (error bars indicate the standard deviation).

These results confirm that adsorption was the main responsible of PFOA removal.

At the higher concentrations (4000 ng/L and 2000 ng/L), the mass loss of PFOA due to processes other than biological and adsorption was comparable in the Activated and Sterilized sludge tests, whereas it decreased significantly at the lower concentrations in the presence of inactive biomass (Figs. 2 and 4). This seems to indicate that these other processes were likely mediated by activated sludge bacteria when they were not inhibited.

As far as PFOS is concerned, at the end of the Sterilized sludge tests the residual mass was found mainly adsorbed on the sludge, with values ranging from 65 % at 200 ng/L up to 90 % at 4000 ng/L. It is confirmed the high tendency of PFOS to be adsorbed onto the sludge. The mass remaining in the liquid phase showed the same profiles as observed in the Activated sludge tests, with an increase at lower concentrations. The amount accounted as loss was very low (few percentages) and much smaller than that measured in the presence of active biomass. It is noteworthy that both PFOA and PFOS showed a higher loss in the presence of biomass activity,

Fig. 4. Normalized mass of PFOA and PFOS in the liquid and sludge phases and the loss measured at the end of the Sterilized sludge tests.

Fig. 5. Experimental data and Freundlich isotherm modelling of the Equilibrium tests.

highlighting some role of the biological processes or the effect of an active biosorption of microorganisms, as also highlighted by Zhou et al. (2010).

3.2.2. Equilibrium tests

In accordance with other studies, the adsorption process of both PFOA and PFOS was better represented by the Freundlich model, which provided the higher value of the R^2 between the experimental and modelled data (Arvaniti and Stasinakis, 2015; Hu et al., 2017; Zareitalabad et al., 2013; Zhang et al., 2013a). Supplementary Materials show the results of the application of the other isotherm models.

Fig. 5 shows the experimental data and the fitting obtained by the application of the linear form of the Freundlich equation, which is reported below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where K_F is the Freundlich adsorption coefficient and n is the Freundlich exponent (Quirantes et al., 2017).

The Freundlich model usually applies to heterogeneous surface energy systems (non-uniform distribution of sorption heat), when more than one sorption mechanism is exhibited. This hypothesis seems to fit the double behaviour of the molecules having a hydrophilic head group and a hydrophobic perfluorinated chain, such as PFOA and PFOS. Values found of the Freundlich model parameters are reported in Fig. 5. The maximum adsorption capacity, $q_{\max}$, can be extrapolated posing $C = C_0$, where C_0 is the initial concentration of the contaminant in solution (Eskandarpour et al., 2008). In the present case, being $C_0 = 1000$ ng/L, it resulted to be $q_{\max} = 1004$ ng/g for PFOA and 6624 ng/g for PFOS.

Values of K_F , which represents the adsorption capacity, was higher for PFOS than PFOA (5.66 ng/g and 0.01 ng/g, respectively); this confirms the stronger sorption potential of PFOS on the sludge, as also reported by previous studies (Zhou et al., 2010). PFOA was mainly found distributed between the aqueous and the sludge phases, while PFOS showed higher accumulation on the sludge. This different behaviour is also due to the shorter chain ($C < 8$) of the PFOA molecule, while PFOS has a longer chain ($C \geq 8$) (Pan et al., 2016).

The magnitude of the value of $1/n$ is a measure of the adsorption intensity or the surface heterogeneity, becoming more heterogeneous as its value approaches zero. When $1/n$ assumes a value above unity, the adsorption is described to be cooperative: this means that adsorbate already present on the surface of the adsorbent material, facilitates the adsorption of others molecules from the solution, due to the steric interaction and the interaction between the same compounds in solution (Liu, 2015). In the present case, $1/n$ was found to be equal to 1.63 and 1.02 for PFOA and PFOS, respectively, thus indicating the cooperative nature of the adsorption process. These values are comparable to those reported by Zhang et al., (2013) which found $1/n = 0.88$ –1.22 and $1/n = 0.78$ –1.09 for PFOS and PFOA, respectively.

3.3. Leaching tests

A further series of tests was carried out with the aim to evaluate the stability of the adsorption process of the contaminants on the sludge; this would allow to determine the eventual risk associated to the reuse/disposal of the sludge loaded by PFOA and PFOS in the biological reactor and then wasted by the WWTP. The Leaching tests were performed on the sludge collected at the end of the Equilibrium tests carried out at the initial concentration of 1000 ng/L PFOA and 1000 ng/L PFOS, at two different solid contents. The released mass of PFOA at the end of the Leaching tests was found to be 1.2 % and 0.6 % (mass/mass) at 4 g/L TS and 5 g/L TS, respectively, with respect to the load present on the sludge at the beginning of the tests. For PFOA, the released mass was equal to 0.3 % and 0.2 %, at 4 g/L TS and 5 g/L TS, respectively. These results highlight that these contaminants, once transferred on the sludge, remain strongly adsorbed and cannot be leached out under the conditions of the standard tests. Therefore, disposal of waste sludge does not pose a serious risk due to leaching processes.

4. Conclusions

The present paper allowed to obtain a better understanding of the fate and processes occurring to PFOA and PFOS in the activated sludge reactor of a WWTP. Results of the experimental activity highlighted that PFOA and PFOS are removed from the liquid phase with efficiency ranging from 59 % to 68 % and from 66 % to 96 %, respectively, for initial concentrations from 200 ng/L to 4000 ng/L, respectively; this gives rise to a residual mass left over in the liquid phase ranging from 41 % to 32 % and from 34 % to 4 %, respectively, for the same concentrations. The mass removed from the liquid phase is partly found adsorbed onto the sludge and partly lost from the system due to processes other than adsorption and biodegradation, which are likely mediated by the microbial activity. The adsorbed mass on the activated sludge was measured to be 43–48% and approximately 60 % for PFOA and PFOS, respectively, at concentrations from 200 ng/L to 4000 ng/L. PFOS showed a sorption potential on the sludge higher than PFOA.

The presence of PFOA and PFOS even at the highest concentration (4000 ng/L) does not exert a significant effect on the microbial activity and the nitrification and carbon removal in the biological reactor.

These results have been obtained under laboratory controlled conditions, and therefore need to be confirmed under real operating conditions. However, they still represent the first step to assess the best strategies to adopt for the management of these pollutants in the WWTP. Particularly, since PFOA has been demonstrated to remain distributed between the liquid and the sludge phases at the end of the secondary treatment, the risk assessment on the final effluent should be carried out to evaluate the potential adverse effects on the environment and the human health when it is discharged or reused. Based on this evaluation, it can be deemed the need to add an additional treatment in the WWTP for a more advanced removal. About the PFOS, it was demonstrated that it remains mainly concentrated in the sludge phase, from which it can be released to a very low extent. Therefore, adsorbed compounds on the sludge should not represent a source of risk; however, specific studies on this issue are also required.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.psep.2019.11.003>.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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