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Constructed wetlands as nature-based solutions in managing per-and poly-fluoroalkyl substances (PFAS): Evidence, mechanisms, and modelling

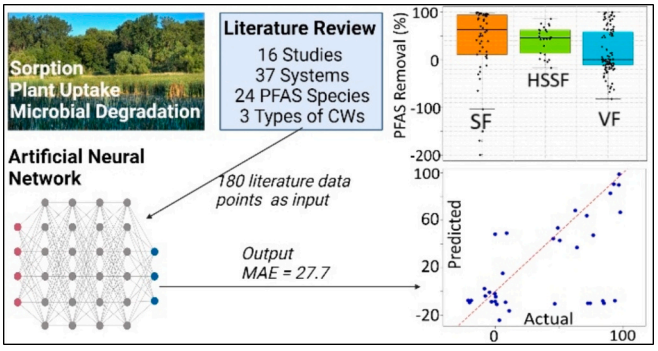
Pinelopi Savvidou, Gabriela Dotro, Pablo Campo, Frederic Coulon, Tao Lyu *

School of Water, Energy and Environment, Cranfield University, College Road, Cranfield, Bedfordshire MK43 0AL, United Kingdom

HIGHLIGHTS

- Constructed wetlands (CWs) as nature-based solutions are promising to remove PFAS.
- Surface flow CWs perform the highest PFAS removal with median value of 63.8 %.
- Current dataset cannot support numerical analysis of PFAS removal pathways.
- Machine learning models outperform mechanistic empirical models for PFAS removal.
- Long-term monitoring of full-scale CWs is crucial to improve PFAS removal evidence.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and poly-fluoroalkyl substances (PFAS) have emerged as newly regulated micropollutants, characterised by extreme recalcitrance and environmental toxicity. Constructed wetlands (CWs), as a nature-based solution, have gained widespread application in sustainable water and wastewater treatment and offer multiple environmental and societal benefits. Despite CWs potential, knowledge gaps persist in their PFAS removal capacities, associated mechanisms, and modelling of PFAS fate. This study carried out a systematic literature review, supplemented by unpublished experimental data, demonstrating the promise of CWs for PFAS removal from the influents of varying sources and characteristics. Median removal performances of 64, 46, and 0 % were observed in five free water surface (FWS), four horizontal subsurface flow (HF), and 18 vertical flow (VF) wetlands, respectively. PFAS adsorption by the substrate or plant root/rhizosphere was deemed as a key removal mechanism. Nevertheless, the available dataset resulted unsuitable for a quantitative analysis. Data-driven models, including multiple regression models and machine learning-based Artificial Neural Networks (ANN), were employed to predict PFAS removal. These models showed better predictive performance compared to various mechanistic models, which include two adsorption isotherms. The results affirmed that artificial intelligence is an efficient tool for modelling the removal of emerging contaminants with limited knowledge of chemical properties. In summary, this study consolidated evidence supporting the use of CWs for mitigating new legacy PFAS contaminants. Further research, especially long-term monitoring of full-scale CWs treating real wastewater, is crucial to obtain additional data for model development and validation.

* Corresponding author.
E-mail address: t.lyu@cranfield.ac.uk (T. Lyu).

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) constitute a group of aliphatic compounds on which hydrogen substituents have been replaced (totally or partially) with fluorine atoms (Buck et al., 2011). Owing to their exceptional thermal stability and hydrophobic/lipophobic properties, PFAS have found widespread applications in diverse sectors including aqueous film-forming foams (Leeson et al., 2021) and household items such as food packaging, waterproof fabrics, and non-stick cookware (Dewapriya et al., 2023). Unfortunately, this extensive utilisation since the 1940s has resulted in significant global environmental contamination, affecting both terrestrial (Johnson, 2022) and aquatic environments including groundwater, surface water, and coastal waters (Podder et al., 2021; Wei et al., 2018). Exposure to PFAS and their accumulation in the human body have been associated with various adverse health effects, such as immunotoxicity, neurotoxicity, and pancreatic tumours (Fenton et al., 2021; Panieri et al., 2022). Consequently, tighter regulations have been introduced to tackle PFAS contamination worldwide: the US Federal Government limited in 2023 PFOA and PFOS concentrations in drinking water to <4 ng/L (US EPA, 2023) and the European Union adopted a total PFAS concentration < 0.5 μg/L in 2021 (EU, 2021).

Several treatment technologies have been explored to mitigate PFAS contamination such as granular activated carbon (GAC) (Belkouteb et al., 2020), ion exchange resins (Woodard et al., 2017), membrane processes (Lee et al., 2022), chemical oxidation (López-Vázquez et al., 2024), and incineration (Liu et al., 2023). However, the development of cost-effective approaches capable of efficiently reducing PFAS concentrations to ppt levels or facilitating PFAS mineralization remains a critical gap. The challenge lies in addressing the stability of the carbon-fluorine (C—F) bond, which demands substantial energy (526 kJ/mol) for breakdown (Wang and Liu, 2020). While debates persist concerning the feasibility of microbes capable of transforming PFAS into innocuous products (Berhanu et al., 2023; Zhang et al., 2022), an innovative development emerged with the work of Huang and Jaffé (2019), who reported the successful bioremediation of PFAS by microbial communities containing *Acidimicrobium* sp. strain A6 (Huang et al., 2022). There are other studies reporting biodegradation of PFAS through various bacterial species that have the ability to defluorinated the contaminant such as *Gordonia* sp. strain NB4-1Y and *Pseudomonads* sp. (LaFond et al., 2023; Berhanu et al., 2023). These studies offer valuable insights into exploring a potentially cost-effective approach for PFAS removal.

As a nature-based solution (NBS), constructed wetlands (CWs) have been widely used for water and wastewater treatment while simultaneously offering environmental, economic, and societal benefits. When compared with conventional treatments, studies have shown that CWs can exhibit similar or, at times, better performance during the treatment of micropollutants including pharmaceuticals and personal care products (Hijosa-Valsero et al., 2010; Li et al., 2014). The efficacy is attributed to synergies between substrate sorption, biodegradation, and phytoremediation processes (Wagner et al., 2023). Studies have indicated a reduction in PFAS concentrations in contaminated water after passing through both natural and constructed wetlands (Arslan and Gamal El-Din, 2021). Recently, efforts have focused on enhancing PFAS removal with the use of innovative wetland substrates (Kang et al., 2023; Ma et al., 2023; Yu et al., 2023). Nevertheless, the information is sparse and difficult to compare, highlighting a need for a systematic review to synthesise current state-of-the-art using CWs for PFAS risk mitigation and the understanding of potential removal mechanisms and pathways to inform future designs.

The modelling of pollutant removal is fundamental for predicting and designing water/wastewater treatment infrastructure, including CWs. While conventional CW designs primarily focus on organic matter and nutrient removal (Dotro et al., 2017), the evolving landscape of stringent discharge regulations has led to increased efforts in micropollutant modelling. Previous studies have reported several empirical or mechanistic models, such as sorption isotherms and compound degradation (Sima and Jaffé, 2021), mainly based on chemical properties of compounds. However, specific efforts dedicated to PFAS removal modelling remain limited. Data-driven models, including multiple regression and machine learning models, have demonstrated advantages in simulating the removal of compounds with mostly unknown properties (Yaqub et al., 2022). Although promising, the application of these models to simulate PFAS remediation within the context of CWs remains unexplored.

To address these knowledge gaps, this study aims to consolidate existing evidence, unravel underpinning mechanisms, and apply advanced models to support future CW implementation for the removal of emerging PFAS contaminants. A comprehensive literature review, supplemented by unpublished experimental data, was first conducted to showcase the PFAS removal performance and mechanisms in different types of CWs. Subsequently, the potential impacts of operational factors on PFAS removal were analysed. To enhance applicability and predictive capacity, the development and validation of both empirical and data-driven models were carried out. Furthermore, future research needs and challenges were identified to facilitate future research and implementations.

2. Methods

2.1. Dataset collection

A systematic literature review was conducted using the following databases: Web of Science, Scopus, and Google Scholar. Selected keywords included “constructed wetlands” and/or “nature-based solutions” and/or “treatment wetlands”, and “per and polyfluorinated compounds” or “PFAS” or “forever chemicals” (TITLE-ABS-KEY). Eight searches were conducted for each database totalling to 24 searches and resulting in 138 hits. After the removal of duplicate results, 40 publications were identified (Fig. S1, supplementary material). A set of inclusion and exclusion criteria was established to select publications discussing PFAS in constructed wetlands and exploring their removal pathways. A thorough screening of titles and abstracts resulted in 37 relevant publications. These were further refined to include studies presenting removal efficiency values or influent and effluent concentrations, resulting in a final list of 16 studies.

In addition to the systematic review, data were collected from three outdoor pilot scale vertical flow (VF) wetlands treating real wastewater at Cranfield University (UK). One VF wetland (6.25 m^2) filled with electroconductive media was commissioned in 2020 to treat the primary effluent from Cranfield sewage works with the hydraulic loading rate (HLR) of 0.16 m/d. The other two VF wetlands (1m^2 each) were built in 2022 to treat the raw sewage. Both systems were operated under French treatment wetland conditions, with an HLR of 0.37 m/d for 3 days and followed by 7 days of rest. In June 2023, three sampling campaigns were conducted across all three systems for PFOA and PFOS analysis. Triplicate samples were collected for both influent and effluent waters of the VF systems. Samples were analysed with a SCIEX LC interfaced to Qtrap Mass Spectrometer with an electrospray ionisation source (Framingham, MA, USA). The details of the system construction, operation, PFAS sampling, and PFAS analysis can be found in Text S1 (supplementary material).

2.2. PFAS removal calculations

The influent/effluent concentrations of individual PFAS substances were extracted from the literature and summarised in Table S1. Some literature reported the percentage removal of PFAS (%), for those studies without reporting removal extents, the percentage removal of PFAS was calculated with Eq. (1). To account for the bias caused by the wetland size and HLR on the removal performance, the mass load removal (μg/

m^2/d) was also calculated based on Eq. (2).

$$Removal\ Efficiency\ (\%) = \frac{Concentration_{influent} - Concentration_{effluent}}{Concentration_{influent}} * 100 \quad (1)$$

$$Mass\ Load\ \left(\mu g/m^2/d\right) = \frac{Concentration_{influent} - Concentration_{effluent}}{1000 * Hydraulic\ Loading\ Rate} \quad (2)$$

Further data was processed with R Studio (R v. 4.1.2) to explore the statistical significance of parameters affecting the removal of PFAS. A backward stepwise regression procedure was considered where independent descriptors were removed to improve the fit of the model. Also, a correlation analysis was performed for pairwise comparisons of parameters to identify any correlated features indicating a positive or negative relationship with the removal of PFAS.

2.3. Modelling

For modelling purposes, the extracted variables (descriptors) from the retrieved studies and Cranfield University's testing were the following: influent and effluent concentration, removal efficiency, PFAS species, experimental period, substrate, vegetation, CW type, scale, wastewater type, flow rate, HLR, HRT, and CW size. All these descriptors were included in the backward stepwise regression (Eq. (3)). The values were set as 0, 1, or 2 for unplanned, single culture and hybrid, respectively. Similarly, the value was set to 1 for synthetic wastewater, 2 for spiked wastewater, and 3 for pure wastewater. Finally, the values describing CW size were 1 for lab scale, 2 for pilot scale, and 3 for full-scale systems. The independent descriptors found to be statistically significant ($\alpha \leq 0.05$) were extracted and used as input parameters in the multiple linear regression, multiple polynomial regression, and artificial neural network (ANN).

$$\begin{aligned} PFAS\ Removal\ (\%) = {} & a*HLR + b*HRT + c*Flow\ rate + d*Experimental\ period + e*Substrate + f*PFAS\ Species + g*Vegetation + h*wastewater\ type \\ & + i*constructed\ wetland\ type + j*Scale + k*Influent\ concentration + l*effluent\ concentration + m_0 \end{aligned} \quad (3)$$

where a, b, c, d, e, f, g, h, I, j, k, l, m_0 were empirical constants.

2.3.1. Multiple linear and polynomial regression

Multiple linear regression makes predictions using more than one explanatory variable generating a multivariate model between one dependent variable (y_i) and multiple independent variables ($x_1 \ldots x_n$) (Bingham and Fry, 2010). Following backward stepwise regression five independent variables were introduced to the multiple linear (Eq. (4)) and 2nd-degree polynomial regression using the following equations (Eq. (5)).

$$\begin{aligned} PFAS\ Removal\ (\%) = {} & \alpha_1 * HLR + \alpha_2 * HRT + \alpha_3 * Flow\ rate \\ & + \alpha_4 * Experimental\ period + \alpha_5 * Substrate + m_1 \end{aligned} \quad (4)$$

where α_{1-5} β_{1-10}, are m_{1-2} represent the coefficients associated with each regression and each term, and e is the error term.

2.3.2. Artificial Neural Network (ANN) model

The multi-layer perception (MLP) type of ANN, similar to what has been used by other studies (Lyu et al., 2018) was implemented. The configuration of a typical MLP consists of a single input layer, one computational layer (hidden), and a single output layer (producing one variable: predicted removal). The hidden nodes in the hidden layers use the Rectified Linear Activation Unit (ReLU) functions (Eq. (6)). ReLU introduces non-linearity to the model; training the model in complex patterns of the dataset (Brunton and Kutz, 2019; Chollet, 2021).

$$ReLU\ (x) = \begin{cases} x\ if\ x > 0 \\ 0\ if\ x \leq 0 \end{cases} \quad (6)$$

In this ANN, the entire neural network is connected (Fig. S2). This means each node in one layer connects to every node in the next layer. The output c of each neuron is:

$$c = \varphi\left(\sum_i w_i a_i + b\right) \quad (7)$$

where a_i denotes input values and w_i the respective weights of each neuron, b is the error of the neuron and φ represents the activation function. More information can be found under the supplementary material.

For all three models, the input data were randomly split into two subsets (4:1 ratio), with the larger subset used for training and the smaller subset used for validation. Thus, 144 and 36 data points were used to train and validate each model, respectively. The mean absolute error (MAE), mean square error (MSE), and root mean square error (RMSE) (Eqs. S1-S3, Modelling Method) were used to evaluate the precision of all three models during model validation in the present study.

3. Evidence of constructed wetlands for PFAS mitigation

3.1. Current state of PFAS research in CWs

The growing concern regarding PFAS contamination has accelerated significant research efforts, expanding into the area of CWs for water and wastewater treatment. A comprehensive literature examination found 16 research articles, along with a recent study at Cranfield University, UK. These studies documented the monitoring of 37 individual CW systems (Table 1 and Table S2) which showed different CW sizes namely, laboratory scale (0.008–1 m^2, 24 system), pilot scale (1–6.25

$$\begin{aligned} PFAS\ Removal\ (\%) = {} & \beta_1 * HLR + \beta_2 * HLR^2 + \beta_3 * HRT + \beta_4 * HRT^2 + \beta_5 * Flow\ Rate + \beta_6 * Flow\ Rate^2 + \beta_7 * Experimental\ Period + \beta_8 * Experimental\ Period^2 \\ & + \beta_9 * Substrate + \beta_{10} * Substrate^2 + m_2 + e \end{aligned} \quad (5)$$

Table 1
Details of the 16 studies retrieved from the systematic literature review and a recent study at Cranfield University, UK.

Type of CWs	Scale	Size (m^2)	Number of studied PFAS	Influent (ng/L)	Removal efficiency[a] (%)	Number of Systems	Wastewater Matrix	Monitoring period/ system's age	Country	References
Surface flow/ Free water surface flow (FWS) wetlands	Full-Scale	–	12	0.19–11,550	Negative - 27 %	1	Industrial and Domestic	1 day/ n.a.	China	Wang et al. (2019)
	Full-Scale	311 (km^2)	8	0–12	Negative - 67 %	1	Stormwater Runoff	1 day/n.a.	United States	Zhang et al. (2021)
	Lab-Scale	0.0452	12	1000	33.6 % - 88.9 %	3	Synthetic	14 days/2 months	China	Li et al. (2021)
	Lab-Scale	–	8	180–4,300,000	–	3	Stormwater Runoff	3 months/2 weeks	United States	Zhang et al. (2020)
	Lab-Scale	–	2	200–30,000	–	4	Stormwater Runoff	28 days/2 weeks	Australia	Awad et al. (2022)
Horizontal subsurface flow (HF) wetlands	Lab-Scale	1	2	50,000	70–85 %	2	Synthetic	25 days/44 days	China	Yu et al. (2023)
	Pilot-Scale	3	4	4220–81,650	<50 %	1	Groundwater	12 months/ n. a.	Italy	Ferrario et al. (2022)
Vertical flow (VF) wetlands	Pilot-Scale	0.2544	92	2–1665	1.2 % - 7.7 %	4	Landfill Leachate	32 days/n.a.	United States	Lott et al. (2023)
	Lab-Scale	0.0283	2	6500–9300	>96 %	3	Rainwater	5 months/n.a.	China	Ji et al. (2023)
	Lab-scale	0.0491	2	50,000	>50 %	3	Synthetic	225 days /n.a.	China	Ma et al. (2023)
	Lab-scale	0.0491	2	50,000	>90 %	3	Synthetic	100 days/n.a.		Kang et al. (2023)
	Lab-scale	0.0079	1	100,000–1,000,000	49.69–73.63 %	2	Synthetic	210 days/3 months	China	Xiao et al. (2023)
	Pilot-Scale	0.4661	1		61–89 % (soil) and 5–30 % (plant uptake)	1	Domestic	42 days/ n.a.	China	Qiao et al. (2021)
	Pilot-Scale	1.0 & 6.25	2	6.39–1135	Negative – 6.6 %	3	Domestic	3 months/ 2 years	United Kingdom	Cranfield University 2023
Hybrid wetlands	Full-Scale	10,000	18	0.07–208.6	61 %	1	Landfill Leachate	11 months /6 years	Singapore	Yin et al. (2017)[b]
	Full-Scale	–	23	25,900–56,600	21 %	1	Industrial	1 day/ n.a.	China	Chen et al. (2020)
	Lab-Scale	–	1	10,000	–	1	Landfill Leachate	150 days/ n.a.	Singapore	Yin et al. (2019)

[a] The removal of individual PFAS compound can be found in Table S1 (supplementary material).
[b] Individual HF system was extracted for the comparison study.

m^2, 9 system), and full scale (0.01–311 km^2, 4 system). For those studies lacking a scale classification, the sizes of 1 and 10 m^2 were used as thresholds to define lab-scale (< 1 m^2), pilot-scale (1–10 m^2), and full-scale (> 10 m^2). Full-scale wetland investigations were conducted in China (Chen et al., 2020; Wang et al., 2019), the United States (Zhang et al., 2021), and Singapore (Yin et al., 2019, 2017); all of them were mature systems with operational records ranging up to 6 years. The monitoring of these systems, however, has been short and involved limited sampling campaigns mainly due to high analytical costs associated with PFAS. Current efforts lasting up to one year primarily focus on lab-scale and pilot-scale systems, which treated either clean tap water or wastewater spiked with PFAS (10 μg/L) (Yin et al., 2019). In this study, individual cells in hybrid CWs (Table 1), which measured inlet and outlet concentrations, were considered as separate systems for comparison between different CW types (Section 3.2).

Within the current research scope of this review, retrieved studies have targeted the removal of 32 types of PFAS, categorised into four groups: perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), perfluoroalkane sulfonamides (FASAs), and fluorotelomers (Table S3). Perfluorooctanoic acid (PFOA) and

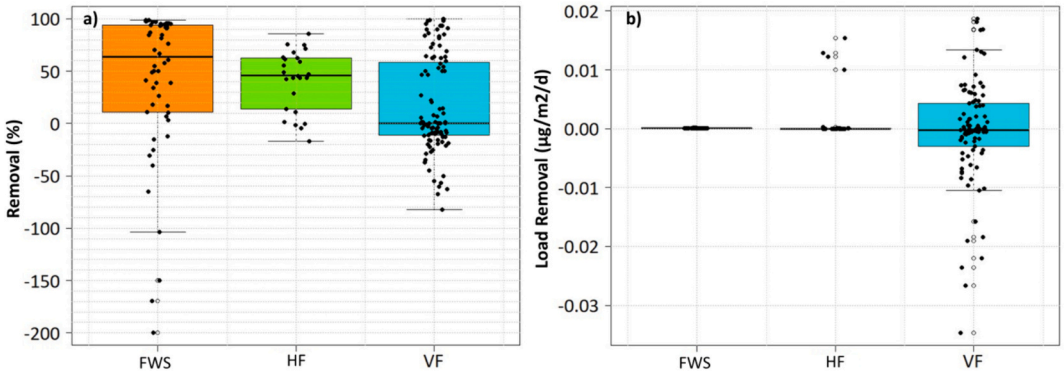

Fig. 1. Percentage removal (a) and load removal (b) of PFAS in free water surface (FWS), horizontal subsurface flow (HF), and vertical flow (VF) wetlands. The lines and dots in the box plots represent the median value and individual reported value in the summarised studies (Table S1).

perfluorooctane sulfonate (PFOS) are the most regulated PFAS, hence, making them the most studied compounds in 27 and 26 CW systems, respectively. Four studies focused on evaluating removal capabilities and therefore were included in reviewing removal mechanisms (Section 4) of PFAS through microbial/sediment adsorption (Yin et al., 2019), plant uptake (Awad et al., 2022), and microbial degradation (Zhang et al., 2020).

3.2. Performances of PFAS removal in different types of CWs

Regardless of influent wastewater types and system scale, the median percentage removal extents in three different CW types ranked as follows (Fig. 1a): 64 % free water surface (FWS), 46 % horizontal subsurface flow (HF), and 0 % vertical flow (VF). While FWS wetlands emerge as the most promising CW for PFAS removal, this configuration concurrently shows the larger variances and negative removals down to −200 %. Such variances can be attributed to how full-scale systems are monitored as compared to the well-controlled lab-scale systems (i.e., HF and VF). For instance, sampling campaigns at full-scale usually involve the collection of a limited number of grab samples that might not accurately reflect the actual system performance as hydraulic retention times (HRTs) are not considered. Additionally, PFAS desorption from sediments could contribute to the observed negative removal because of long-term operation periods. Notably, the median load removal (Fig. 1b) remains comparable (between −0.035 to 0.018 μg/m^2/d) across all three CW types, with VF wetlands displaying the highest variance potentially influenced by the adsorption capabilities of diverse substrates. The load removal was significantly lower than those measured for persistent pharmaceuticals (e.g., Ofloxacin and Sulfadiazine, 4 μg/m^2/d) (Ilyas et al., 2020), demonstrating the recalcitrance of the PFAS 'forever chemicals'. Overall, the results demonstrated that CWs can safeguard receiving waters by removing PFAS from the influents of varying sources and characteristics.

3.2.1. Free water surface and horizontal subsurface flow wetlands

Few studies reported influent and effluent PFAS concentrations for FWS (five) and HF (four) wetlands (Table S1). Notably, the only reported values for full-scale CWs were conducted in two FWS and one HF

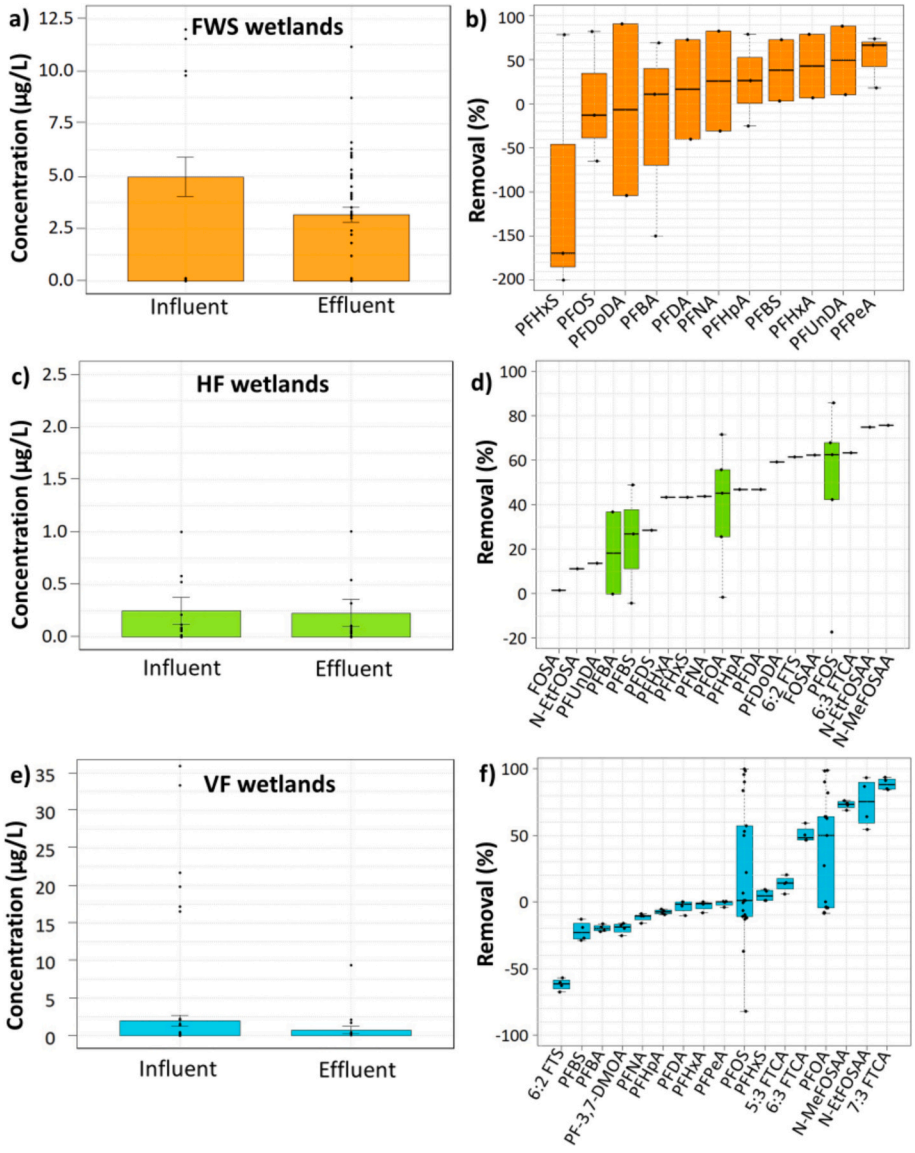

Fig. 2. PFAS concentration range of influent and effluent in free water surface (FWS, a), horizontal subsurface flow (HF, c), and vertical flow (VF, e) wetlands. The percentage removal of individual PFAS compounds in FWS (b), HF (d), and VF (f) wetlands. The lines and dots in the box plots represent the median value and individual reported value. Note: three studies were excluded due to high spiked concentrations in VF (Xiao et al., 2023; Kang et al., 2023, and Ma et al., 2023) and one study in HF (Yu et al., 2023).

systems. Measured influent PFAS concentrations (regardless of PFAS species) ranged from 0.52 to 12 μg/L in FWS wetlands, and effluent concentrations ranged from 0.17 ng/L to 11.17 μg/L (Fig. 2a) reflecting the environmentally relevant PFAS levels. Some lab-scale studies used PFAS fortified influents so that the highest value was 50 μg/L in HF wetland reported by Yu et al. (2023). Excluding this study, influent PFAS concentrations in HF wetlands ranged between 0.00007 and 2.7 μg/L; similar values were observed in effluents (0.00005 to 2.7 μg/L) (Fig. 2c).

Most values for full-scale systems treating raw wastewater (landfill leachate and industrial effluents) fell at the level of ng/L, reaching as low as 0.05 ng/L (Yin et al., 2017). For lab-scale experiments, the removal varied between 34 and 99 % (Li et al., 2021). By contrast, the PFAS removals in full-scale systems ranged from −200 to 67 % (Wang et al., 2019; Zhang et al., 2021). A total of 11 and 19 PFAS species were monitored and examined for FWS and HF wetlands, respectively (Figs. 2b and d). Although the overall percentage removal of PFAS varied widely in both CW types, from −200 to −99 % in FWS wetlands and from −17 % and 89 % in HF wetlands, the FWS wetlands achieved higher removal capabilities for PFAS compared to HF wetlands. Moreover, long-chain PFAS (e.g. telomers) exhibited higher removal than short-chain PFAS (e.g. PFBS, PFBA) as reported by Wang et al. (2019). Fluorotelomers tend to break down during treatment producing short-chain PFAS as transformation products. This leads to the perception that CWs can remove telomers. From this study, it is not possible to conclude whether carboxylic acids or sulfonic acids are better removed since there is only one measurement available (PFDS, PFHxA, PFHxS, PFNA, PFDA, PFHpA in Fig. 3d). For FWS wetlands, most PFAS species have a median removal between 10 and 49 % irrespective of their hydrophilic functional group.

3.2.2. *Vertical flow wetlands*

In VF wetlands, influent concentrations derived from seven studies involving 19 systems ranged from 2 ng/L to 1 mg/L, reaching as low as 0.9 ng/L in the effluent (Fig. 2e). The wide range of influent PFAS concentrations (0.002–1000 μg/L) from three studies was excluded in Fig. 2e. Despite more studies conducted in VF wetlands, none were implemented at full-scale. The reported 18 PFAS in VF wetlands (Fig. 2f) showed no clear pattern, making it challenging to discern whether short-chain PFAS (e.g., PFSAs or PFCAs) exhibit better removal over longer-chain PFAS (e.g., FOSAs and telomers). This ambiguity could be attributed to the varying media used in the different studies which potentially hide differences for specific comparisons based on one type of media. Nevertheless, N-EtFOSAA and N-MeFOSAA effected higher removal rates than PFOA and PFOS. Similarly, telomers containing carboxylic acid (5:3 FTCA, 6:3 FTCA, 7:3 FTCA) reached significant removals in VF systems compared to those containing a sulfonic acid (6:2 FTS). However, such observation does not imply a preferential mineralization of PFCAs over PFSAs, as telomers break down into shorter-chain PFAS during treatment (Yin et al., 2019).

Seven VF studies involved ten different substrates or mixtures shown in Fig. 3a. The use of GAC or mixtures with gravel exhibited the highest percentage removal of PFAS (>95 %). This superior performance can be attributed to the adsorption capabilities of GAC, a material widely used in drinking water treatment for PFAS mitigation (Belkouteb et al., 2020). Other media materials or amendments such as magnetite and quartz sand, improve organics and nutrient removal (Ma et al., 2023) and better PFAS treatment (between 72 and 99 % removal extent) when compared to CWs equipped with conventional gravel and sand (between −50 and 99 %). An innovative electroconductive material was reported to accelerate the removal of nutrients (Ramírez-Vargas et al., 2019) and pharmaceuticals (Pun et al., 2019). However, the median removal of PFOS in such systems ranged from −37 to 1.2 %. These systems were designed to treat real domestic wastewater containing a high variety of PFAS concentrations in the influent, Moreover, the results were obtained from only three one-day grab sampling events. Longer-term monitoring is important to establish robust conclusions for this innovative electroconductive material. Moreover, the particle size of the medium in CWs may affect the removal of PFAS as this parameter dictates the number of

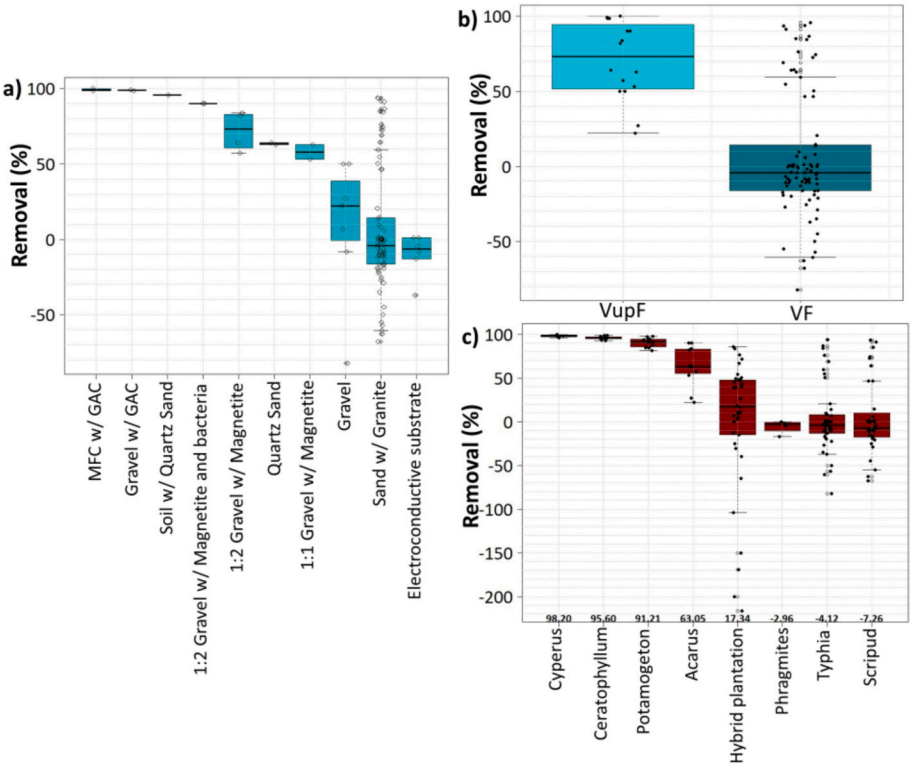

Fig. 3. The percentage removal of PFAS in (a) different combinations of substrates in VF systems, (b) upflow and downflow VF systems, and (c) types of plantation. The lines and dots in the box plots represent the median value and individual reported value in the summarised studies.

available sites for adsorption. Additionally, the medium porosity also controls air/O_2 transfer as well as the growth of attached biofilms, which might contribute to the biodegradation of pollutants. However, the current available VF systems contained a similar particle size, which did not enable the assessment of the impact of media porosity on PFAS removal.

Beyond traditional down-flow VF, up-flow schemes in VF wetlands were investigated. Up-flow systems exhibited significantly higher median PFAS removal (73 %) compared to down-flow systems (Fig. 3b). Under up-flow operation, the systems were saturated, allowing for prolonged contact time between influent water and media/microorganisms, potentially enhancing PFAS removal. While promising, up-flow VF is not widely adopted in practice due to the high energy requirements for pumping water through. The systems will mainly show an anaerobic/anoxic environment that limits organic and ammonia removal (Ji et al., 2023; Ma et al., 2023). Additionally, solids predominantly accumulate at the bottom of these CWs, posing additional challenges for maintenance as compared to traditional down-flow VF wetlands that only require surface sludge cleaning.

4. Impacting factors and PFAS removal mechanisms

4.1. The impacts of operational conditions

An examination of operational conditions including flow rate, HRT, HLR, experimental period, type of vegetation, wetland type, influent concentration, wetland scale, wastewater type and substrate type, was conducted through pairwise correlation analysis to assess their impacts on PFAS removal (Fig. 4a). Results indicated that wastewater type (cor. Coefficient = −0.93), CW scale (cor. Coefficient = −0.85), and hydraulic loading rate (HLR, cor. Coefficient = −0.60) exhibited the highest negative correlations with PFAS removal, while hydraulic retention time (HRT, cor. Coefficient = 0.49) and CW type (cor. Coefficient = 0.60) showed positive correlations.

Fig. 4b shows high variability in PFAS removal in raw (non-spiked wastewater) an expected outcome given the fluctuations of influent PFAS concentrations in real wastewater compared to fortified synthetic matrices. PFAS removal was higher when using clean water (e.g. tap water) as a base compared to spiking in real wastewater (e.g. domestic sewage). The result aligns with the knowledge that wastewater, comprising a complex matrix with diverse pollutants and fluorotelomers, affects the removal of target compounds (Lenka et al., 2021).

A similar trend can be found when considering the impacts of CW scales, i.e. lab (<1 m^2), pilot (1–6.25 m^2), and full (0.01–311 km^2) scales (Fig. 4c). Full-scale FWS systems exhibited higher variability, and in some instances, higher negative removal values compared to lab and pilot-scale experiments. These results indicated the challenges and highlighted the crucial importance of monitoring full-scale systems, as small-scale studies using synthetic wastewater influent may offer unreliable insights for real-world applications. In conventional wastewater treatment within CWs, high HLR and low HRT typically result in lower removal performance for BOD, ammonia (Ghosh and Gopal, 2010), and certain organic micropollutants (Ávila et al., 2014). However, it appears that the size of wetland does not significantly impact the removal of PFAS (Fig. S3). Concerning PFAS removal, statistically insignificant negative (Fig. 4d, $R^2 = 0.07$) and positive (Fig. 4e, $R^2 = 0.4$) correlations were found between HLR/HRT and PFAS removal, respectively. This finding suggests a distinct removal mechanism compared to other pollutants, hinting that the biological treatment process might not be the primary contributor. Further insights into potential pathways will be explored in the following sections.

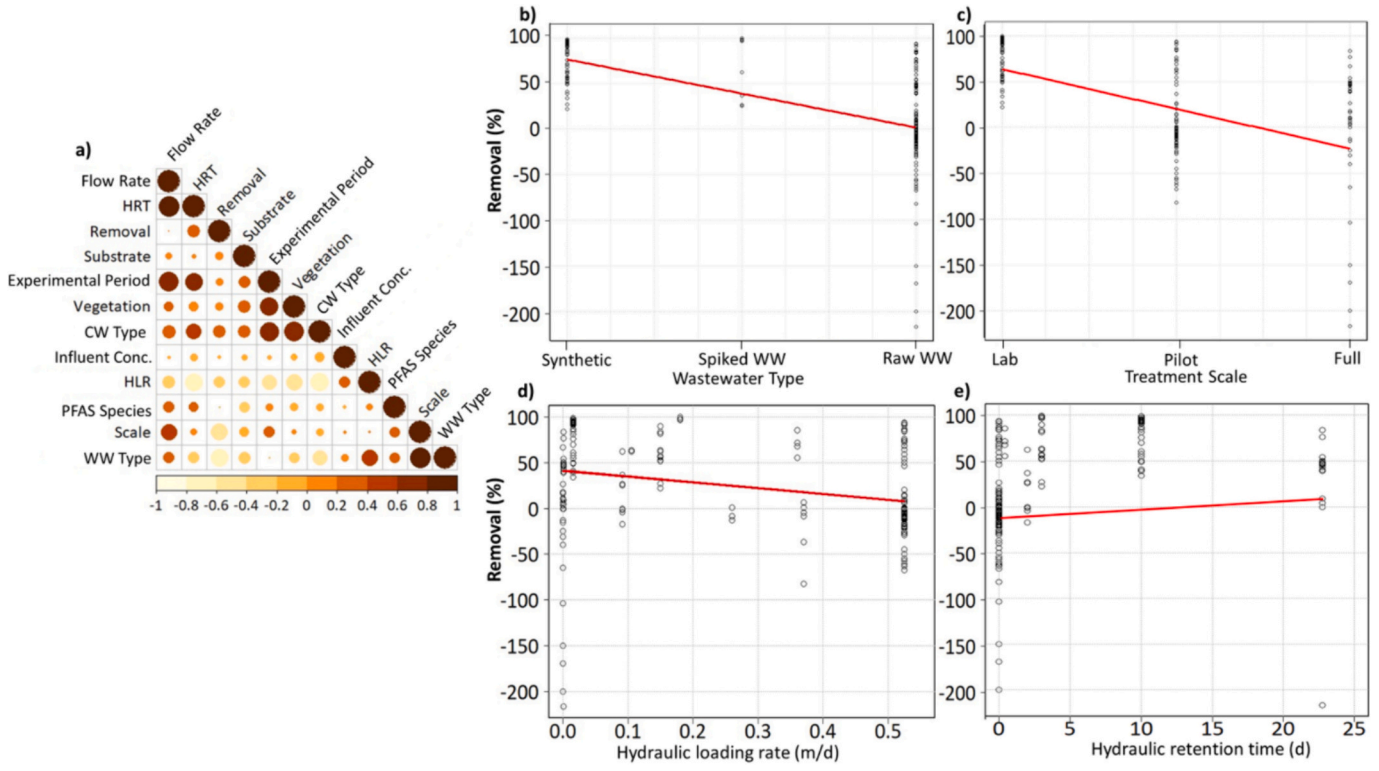

Fig. 4. Correlation plot (a) visualising the pairwise correlation coefficients between 12 operational and experimental parameters. Dark red indicates positively correlated variables (values between 0 and 1), whereas yellow indicates negatively correlated variables (values between −1 and 0). The bigger the size of the circles, the more intense is the correlation between the two variables (close to extremes −1 and 1). Negative correlation of PFAS removal with (b) wastewater type (−0.93), (c) wetland scale (−0.85), and (d) hydraulic loading rate (−0.60). Positive correlation (e) of PFAS removal with hydraulic retention time (0.49).

4.2. Substrate sorption

Previous studies generally agree on the crucial role of substrate adsorption in the removal of PFAS, which may facilitate subsequent phyto- and biological remediation processes. In contrast to conventional wetland gravel media, the mixture of magnetite iron mineral and GAC has demonstrated a remarkable increase in PFAS removal (Fig. 3a) (Ji et al., 2023; Kang et al., 2023; Ma et al., 2023). The enhancement is primarily ascribed to the improved hydrophobic interactions between PFAS compounds and the electrode layers of GAC (Ji et al., 2023). Moreover, the particle size of GAC is also important with larger particles contributing to slower adsorption rates due to prolonged intra-particle diffusion of PFAS anions. Therefore, substrates characterised by large mesopores, and a higher specific surface area are generally anticipated to enhance PFAS adsorption. Beyond the substrate itself, the organic matter content in the sediment has been identified as a contributing factor to the efficacy of PFAS adsorption (Sima and Jaffé, 2021). Additionally, PFAS removal is dependent on the pH levels, with acidic conditions typically favouring the process (Lei et al., 2023). On the other hand, substrates enriched with minerals have been shown to increase plant tolerance to the toxic effects of PFAS and enhance pollutant removal. For example, increasing the content of Fe (III) promotes the formation of PFAS ligand complexes, thereby facilitating removal through the ligand-to-metal charge transfer mechanism (Ma et al., 2023; Sun et al., 2021).

4.3. Phytoremediation

Wetland plants play a dual role in the removal of pollutants by directly contributing to pollutant uptake and indirectly stimulating microbial communities and activity through the release of root exudates and oxygen (Malyan et al., 2021). Previous studies have proved the efficacy of phytoremediation processes in CWs for the removal of macropollutants, pesticides, and metals (Gray and Sedlak, 2005; Weis and Weis, 2004; Zhang et al., 2010). It was estimated that a hybrid plantation would exhibit superior removal compared to monocultures due to the variety of plants present, contributing to an increased microbial community that could potentially enhance PFAS removal. This hypothesis was not supported by the available dataset (Fig. 3c), possibly because the results were not derived from comparable studies.

Distinct plant species exhibit varying levels of PFAS uptake. For instance, *E. crassipes*, characterised by a high root surface area and protein content, accumulated a significantly higher amount of PFOS (6–1186 mg/kg) compared to *C. alternifolius* (9–162 mg/kg) when exposed to PFOS-contaminated water at concentrations ranging from 1 μg/L to 10 mg/L (Qiao et al., 2021). Compared to emergent macrophytes, Li et al. (2021) suggested that FWS systems with submerged macrophytes such as *C. demersum* may be advantageous for PFAS elimination from water. Qiao et al. (2021) stated two primary mechanisms of plant adsorption involving either PFAS absorption to root surface tissue or transpiration. Surface tissue absorbance dominates plant uptake, particularly for long-chain PFAS. Conversely, short-chain PFAS translocate more readily from roots to shoots than long-chain counterparts (Sima and Jaffé, 2021), suggesting that aboveground plant harvest may enhance short-chain PFAS removal from CWs. However, the challenge of plant and substrate disposal persists, necessitating thermal treatment for the complete mineralization of adsorbed and bioaccumulated PFAS (Gagliano et al., 2020).

4.4. Microbial biodegradation

Owing to the inherent stability of their chemical structures, volatilization and photocatalytic processes may yield low removal efficiencies when treating PFAS (Garg et al., 2021; Sima and Jaffé, 2021). A similar limitation applies to the potential contribution of microbial communities, as biodegradation is unlikely due to the strength of the C—F bond. However, Huang and Jaffé (2019) first reported the capability of the wetland microbe, *Acidimicrobium bacterium A6*, to effectively detoxify PFAS contaminants. Moreover, various fungal and bacterial strains have been isolated and proven capable of PFAS degradation. Nevertheless, concerns persist regarding the potential for slow and incomplete mineralization of PFAS (Berhanu et al., 2023). More importantly, the indigenous microbes in CWs exhibit limited ability for PFAS biodegradation. To address this limitation, the introduction of microorganisms capable of degrading specific contaminants has shown promise in enhancing the biodegradation of various emerging pollutants like antibiotics (Choi et al., 2016). Extending this approach to PFAS, the introduction of defluorination microorganisms adept at utilising methane and hydrogen as electron donors could facilitate the breakdown of the challenging C—F bond resulting in PFAS biodegradation (Huang and Jaffé, 2019). However, further investigations are essential to thoroughly evaluate the effectiveness of this strategy (Ji et al., 2020).

5. PFAS removal modelling: mechanistic and machine learning models

5.1. Mechanistic models (K_{oc} simulation and empirical models)

Mechanistic models derived from chemical properties and associated removal pathways, including adsorption processes (Sima and Jaffé, 2021), have been used for predicting the removal of various organic contaminants such as pesticides and pharmaceuticals (Gatidou et al., 2017; Ilyas et al., 2021). Despite several attempts to include PFAS in these models (Gefell et al., 2022; Rafiei and Nejadhashemi, 2023), no studies have been conducted on PFAS removal in CWs for wastewater treatment.

5.1.1. K_{oc} simulation

The sorption process of organic micropollutants is mainly explained in terms of organic carbon partition coefficient values (LogK_{oc}). Vymazal and Březinová (2015) applied a rough simulation by correlating LogK_{oc} values of 87 pesticides with their removal extents. This work found a clear correlation ($R^2 = 0.162$) between removal and LogK_{oc} and highlighted the substantial adsorption of pesticides to soil particles in CWs. However, the PFAS family comprises over 5000 compounds and presents a challenge as K_{oc} values are unknown for most of them. We managed to obtain the K_{oc} values for 23 PFAS from the studied 32 compounds (Table S3). Unfortunately, the simulation result was poor ($R^2 = 0.02$, Fig. 5a). This discrepancy is partly due to the considerable variance in PFAS removal performances and the incomplete data for many PFAS compounds, with Koc values derived from estimates rather than experimental measurements. Therefore, the subsequent empirical model simulations focused exclusively on the extensively studied compounds PFOA and PFOS, leveraging the most available data and known chemical properties.

5.1.2. Linear isotherm model

Sorption isotherms have proven effective in evaluating the sorption in CW of pollutants such as phosphorus and ammonia (Cui et al., 2008; Wen-Ling et al., 2011). For these compounds, the linear isotherm model (Eq. (8)) (Sima and Jaffé, 2021), which represents the partitioning/sorption of a compound between the liquid and solid phases is directly proportional.

$$S_e = K_d{}^{*}C_w \tag{8}$$

where K_d is the distribution coefficient (mL/g), S_e is the pollutant concentration in the solids at equilibrium (μg/g), and C_w is the pollutant concentration in the water phase at equilibrium (μg/mL).

Currently, there is very little information on PFAS sorption in CWs. In carbon-rich materials, Fabregat-Palau et al. (2022) reported the positive influence of material aromaticity on K_d, indicating that sites with

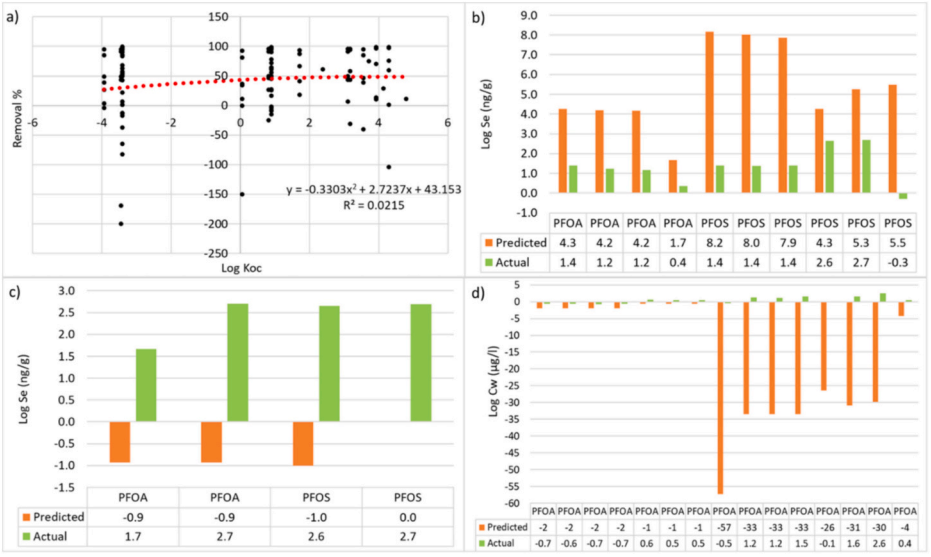

Fig. 5. (a) Relationship between LogK_{oc} and removal of PFAS. Removal derived from literature data discussed in Sections 3 & 4, $n = 109$. (b) Linear isotherm: LogS_e (ng/g) for predicted and actual values, number of studies = 4 and $n = 7$. (c) Non-linear isotherm (Freundlich Isotherm): LogS_e (ng/g) for predicted and actual values, number of studies = 2 and $n = 4$. (d) Degradation pseudo-first-order degradation: LogC_w of predicted and actual effluent concentrations of PFOA, $n = 17$, and number of studies = 9.

π-electron-rich regions are important for PFAS sorption. External validation of the linear model, with $R^2 = 0.9$, applied to these carbon-rich materials obtained an RMSE of 0.53 for predicting K_d. In the current study, theoretical linear isotherm K_d values were compiled from the literature (Ahrens et al., 2011; Xiao et al., 2017; Zareitalabad et al., 2013) and used for model implementation. As S_e values were not consistently reported in all studies, predicted values for 4 PFOA and 6 PFOS actual values were calculated with Eq. (8); detailed calculations are provided in Table S4. The results in Fig. 5b indicated a percentage difference higher than 100 between predicted and actual S_e values, with an average RMSE over 6×10^6, which suggests the inadequacy of the linear isotherm model for predicting PFAS removal.

5.1.3. Non-Linear (Freundlich) Isotherm

In predicting the adsorption of hydrophobic compounds, non-linear models like the Freundlich and Langmuir Isotherms have been more commonly used (Ahrens et al., 2011; Fabregat-Palau et al., 2022; Higgins and Luthy, 2006). The preference to use a non-linear sorption isotherm for PFAS arises from the intricate sorbet-sorbent interactions, such as electrostatic repulsion (Yu et al., 2009). Therefore, the Freundlich Isotherm (Eq. (9)) was used to simulate PFAS removal in CWs (Sima and Jaffé, 2021).

$$S_e = K_F * C_w^N \quad (9)$$

where K_F and N are Freundlich constants. Higgins and Luthy (2006) showed that the sorption of PFAS is nonlinear since K_d values seem to decrease with increasing concentration. Similar to the linear isotherm, information was derived from literature for K_F and N (Table S5).

Utilising the available dataset, LogS_e (ng/g) was plotted for predicted and actual concentrations in the substrate at equilibrium for two studies (Fig. 5c). Unfortunately, the non-linear isotherm also yielded a poor simulation of PFOA and PFOS concentrations, with an average RMSE of 76. Hence, despite adsorption being acknowledged as a primary PFAS removal mechanism, conventional isotherm models (both linear and non-linear) prove inadequate in accurately predicting their removal. The discrepancies in this instance can be attributed to the absence of experimental values for isotherm constants and the small sample size.

5.1.4. Pseudo-first-order degradation model

Biodegradation kinetics have extensively applied in CWs for simulating the removal of various micropollutants(Krone-Davis et al., 2013; Lv et al., 2016). Despite the challenge of demonstrating the biodegradability of PFAS in CWs, we applied the pseudo-first-order kinetics (Eq. (10)) to predict the PFAS degradation. The k values, unfortunately, were only available for PFOA and were derived from 1 publication, with k equal to 0.015 h^{-1} (Xiao et al., 2023). The model was applied across 17 systems (Table S6), and again, with RMSE ranging from 0.04 up to 74 when comparing predicted and actual PFAS removals (Fig. 5d).

$$C_w = C_{w0} * e^{-kt} \quad (10)$$

where C_{w0} is the initial concentration in the aqueous phase (µg/L) and k is the rate constant. The rate constant k is dependent on the compound's properties and abiotic factors (i.e., temperature, pH, redox capacity).

Other mechanistic models, such as the plant uptake model, have been developed to simulate the removal of organic micropollutants in CWs or phytoremediation processes (Mohammed and Babatunde, 2017). However, given the lack of chemical properties information on PFAS and the limited studies available for this review, it is not possible to apply a plant uptake model for PFOA and PFOS.

5.2. Data-driven and machine-learning models

Since there is no need for imputing values of chemical properties, data-driven models were employed to predict PFAS removal in CWs as a way of avoiding inconsistencies inherent in empirical models. Data-driven models have been effectively used for simulating the removal of pesticides, total nitrogen, and total phosphorus (Akratos et al., 2009a; Kumar and Zhao, 2011; Lyu et al., 2018; Ugya and Meguellati, 2022). A common approach involves applying multiple regression on a dataset of measured parameters. Another method gaining attention recently is the use of machine learning tools, including Artificial Neural Networks (ANN) and Self-Organization Maps. To our knowledge, this study is the first to apply these data-driven models to PFAS treatment processes in CWs.

The identified variables (Section 2.3) were first used in a thorough analysis using a backward stepwise regression to identify the principal variables affecting removal. The significant variables identified,

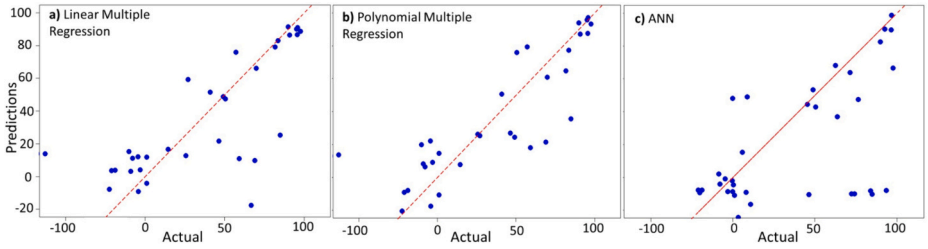

Fig. 6. The comparison of predicted and Actual values for (a) Multiple Linear Regression model (RMSE = 65.55, MSE = 4296.8, R^2 = 0.5989) (b) Multiple Polynomial (2nd degree) Regression (RMSE = 62.6 and MSE = 3918.5, R^2 = 0.65), and (c) Artificial Neural Network (ANN) model (RMSE = 39.03 and MSE = 1528.4, R^2 = 0.11).

including HLR, HRT, flow rate, experimental period, and substrate types, were extracted and employed in linear multiple regression, polynomial multiple regression, and the ANN models as input parameters.

All three data-driven models provided much better results (Fig. 6), demonstrating the remarkable alignment between predicted and actual PFAS removal in diverse CWs when compared to mechanistic models (Fig. 5). The linear multiple regression model proved to be the least reliable (Fig. 6a) with MAE = 35.4, followed by the 2nd-degree polynomial (MAE = 34.8, Fig. 6b), while the ANN exhibited the highest accuracy (MAE = 27.27, Fig. 6c). Although the MAE is lower for ANN, the goodness of fit (R^2) of ANN is less robust in comparison to the 2nd degree polynomial regression. These results showed the advantage of data-driven models for predicting PFAS removal, leveraging their independence from input chemical properties and relying on predictions based on measured values. However, it should be noted that the current dataset size (180 data points describing 24 compounds) for the ANN model development was relatively small in the context of data modelling in artificial intelligence. This is a common challenge when adapting data-driven models to simulate/predict results in other relevant environmental studies. However, the same approaches have been used to evaluate the removal of phosphorus (Akratos et al., 2009a) and total nitrogen (Akratos et al., 2009b) in treatment wetlands, proving more accurate predictions in comparison to mechanistic models. The current attempts demonstrated insight into the feasibility of using data-driven models and underly the need for further study and collaborative research to obtain more data towards more reliable data-driven modelling.

5.3. *Perspectives on future model development*

Increasing studies have been made in water sciences to advance our understanding of PFAS fate during treatment. However, the complicated structure of PFAS featuring both hydrophilic and lipophilic groups poses a challenge for accurate modelling. A recent study by Xu et al. (2022) introduced a spatial fate model based on convection and diffusion kinetics, with a focus on water diffusion and sediment adsorption processes. This model can predict the distribution of PFAS in water-sediment interfaces, particularly highlighting their accumulation in soils. Such insights significantly contribute to unravelling the fate and transport mechanisms of these contaminants. However, CWs represent more complex systems than traditional biological treatments, like the activated sludge process. In addition to the main removal pathways, e.g. sorption and biodegradation, any fate model for CWs must include various phytoremediation processes. Understanding these processes necessitates knowledge about PFAS concentrations in plant roots and shoots, transpiration capacities, and lipid content.

A promising avenue for predicting concentrations in the effluent, roots, shoots, and removal efficiencies is the utilisation of data-driven models, which have been demonstrated in this study. By establishing relationships among measured values, these models offer a comprehensive view. Additionally, a hybrid approach involving both data-driven and empirical models, such as ANN, can be employed. For instance, Akratos et al. (2009b) successfully developed an equation for TN removal using ANN. Similar expressions could be derived for PFAS removal through an enhanced development of ANN, supported by more data points from full-scale system monitoring.

6. Conclusions

Among the 37 investigated CWs, FWS wetlands performed as the most promising systems for PFAS removal, exhibiting a median percentage removal of 63.8 % surpassing HF and VF systems. However, FWS displayed the highest variances in percentage removal, partly attributed to being primarily full-scale systems dealing with influent PFAS fluctuations. The removal of PFAS was found to be negatively correlated with wastewater type, wetland scale, and HLR, and positively correlated with HRT. Adsorption processes were claimed to be the key removal pathway for PFAS in CWs, however, quantitative analysis was not possible due to data limitations and a lack of knowledge regarding PFAS chemical properties. Mechanistic models failed in predicting PFAS removal, while data-driven models, particularly the machine-learning-based Artificial Neural Network (ANN), demonstrated superior simulation results. Further research should focus on expanding measured values of PFAS in CWs, enabling data-driven models to offer more accurate predictions and enhancing the understanding of underlying mechanisms. Ultimately, a synergistic approach employing both empirical and data-driven models holds promise as a predictive tool and contributes to future system design.

CRediT authorship contribution statement

Pinelopi Savvidou: Writing – original draft, Validation, Formal analysis, Conceptualization. **Gabriela Dotro:** Writing – review & editing, Supervision. **Pablo Campo:** Writing – review & editing. **Frederic Coulon:** Writing – review & editing. **Tao Lyu:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data available within the article and its supplementary materials

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.173237.

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