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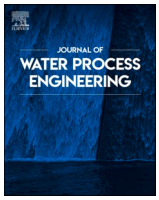

Assessment of molecularly imprinted polymers for selective removal of diclofenac from wastewater by laboratory and pilot-scale adsorption tests

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ABSTRACT

This study investigated the potential of Molecularly Imprinted Polymers (MIPs) to integrate schemes for wastewater reuse and to serve as effective adsorbent for the removal of a target emerging contaminant (i.e., diclofenac – DCF), after or within pilot scale anaerobic biological treatments. Batch tests were performed to evaluate the effect on DCF removal during anaerobic biological processes by enriching activated sludge of an Upflow Anaerobic Sludge Blanket (UASB) reactor (TSS =19.6 g/L), and an Anaerobic Membrane Bioreactor (AnMBR) (TSS = 120 mg/L) reactors with MIPs (3 mg/L). Therefore, tertiary treatments were investigated by columns adsorption tests that were performed first at lab scale using DCF (15 mg/L) solution in deionized water, and then in-site by treating the anaerobic permeate effluent from the AnMBR at pilot scale level (DCF 500 μg/L). Clogging or blockage of the column bed was not observed during these field tests, where the saturation process of MIPs was slower compared to laboratory tests that used deionized water. In addition, the empirical Thomas Model, Yoon-Nelson Model, Dose-Response Model and Adam Bohart Model showed very good fittings with the experimental data obtained during experiments performed with both synthetic water and anaerobic effluents showing their suitability for the description of breakthrough curves. Finally, it was observed that after regeneration the MIPs can be efficiently reused since adsorption capacity is sufficiently preserved.

1. Introduction

Eco-innovative and sustainable treatment trains for wastewater treatment for fertigation purposes includes anaerobic membrane bioreactors [1–3] for its capability to obtain a solid free effluent and allow soluble nutrients to be applied to soil. However, removal of emerging contaminants (ECs) by these innovative biological systems is limited, and, therefore, there is a need of integration or combination of novel solutions to anaerobic treatments to enhance the elimination of relevant ECs. These are a group of natural and synthetic chemicals, and biological agents that are not or poorly regulated. The concentration of ECs in natural water and wastewater ranges from ng/L to μg/L, which is relatively small as compared to other pollutants present in water and wastewater. However, ECs still represent a great threat to the humans and ecosystem [4,5] and wastewater treatment plant (WWTP) effluents are considered hot spots for the transfer of these micro-contaminants into the environment [5–7]. Indeed, conventional wastewater treatment plants, often stabilization ponds and activated sludge systems, have not been designed to remove these recalcitrant organic micropollutants from water [8,9]. To solve this issue, in Europe, the regulation of ECs in municipal wastewater effluents is under discussion and it has recently been included in the proposal for a revised European Wastewater Treatment Directive 91/271/EC [10]. On the other hand, some European countries such as Switzerland (due to the implementation of a new Water Protection Act in 2016) and Germany (two federal states on voluntary basis) are already implementing advanced treatments to remove these emerging contaminants from wastewater effluents. Furthermore, in the frame of the new EU regulation 741/2020 on minimum requirements for water reuse [11], standard limits for ECs in reclaimed water may be established if a performed risk assessment highlights possible adverse impacts on human health and the environment. In this scientific and regulatory challenging context, within the

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PRIMA European project FIT4REUSE (SaFe and sustaInable soluTions FOR the integRatEd USE of non-conventional water resources in the Mediterranean agricultural sector) a combination of solutions was proposed to integrate anaerobic treatment for irrigation and fertigation. Particularly, innovative adsorption materials such as molecularly imprinted polymers (MIPs) were tested in combination with anaerobic biological systems to improve the removal of ECs from treated wastewater. These non-conventional adsorption materials, synthesized in the presence of target templates with the formation of molecular recognition sites, can be excellent selective adsorbents [12] and can represent a valid tool to remove one or more specific target molecules in wastewater or surface water [13].

To date, adsorption tests on MIPs have only been performed to evaluate their effectiveness on selectively retaining target pharmaceutical compounds from water during a solid phase extraction (SPE) procedure with the aim to increase the quality of liquid chromatography analyses by reducing signal suppression due to undesired matrix effects [14–16]. Particularly, the very good results on selective retention of target contaminants, along with the reusability of the material by easy and efficient adsorption/regeneration cycles have suggested possible applications of these materials for real water/wastewater treatments [14,15,17,18].

In this study, Molecularly Imprinted Polymers (MIPs) were synthesized and tested with Anaerobic Membrane Bioreactor (AnMBR) effluent to remove diclofenac (DCF), which was used as a representative target compound due to its possible harmful effects on several aquatic species at very low concentrations $\leq$1 μg/L [19]. Particularly, several experimental tests were performed to evaluate DCF adsorption by packed bed columns with MIPs, which were integrated at pilot scale with an AnMBR. Moreover, the applicability of several mathematical models (i.e., Adams-Bohart model, Thomas model, Yoon-Nelson model, Modified Dose-Response model and, Clark model), which are commonly used for description of the breakthrough curve in Granular Activated Carbon (GAC) filters [20,21], was evaluated in the adsorption columns packed with MIPs. Indeed, those models are useful to characterize the polymers properties and also to support the design of possible future scale up solutions. Finally, batch tests were performed by enriching activated sludge from AnMBR with MIPs to evaluate the enhancement of DCF removal during these anaerobic biological processes.

2. Material and methods

2.1. Materials, tested waters, and pilot system

Description of chemicals and reagents used in this study is reported in Supplementary Material along with indication of physical-chemical properties of DCF (Text S1 and Table S1).

All experiments were accomplished in deionized (DI) water and wastewater spiked with selected concentrations of diclofenac (DCF). DI water was utilized to perform experiments at laboratory scale, whereas the wastewater effluent from the pilot system that included an Up flow anaerobic sludge blanket (UASB) reactor combined with an Anaerobic Membrane Bioreactor (AnMBR) was utilized to feed the adsorption columns packed by MIPs, which were operated at pilot scale. Brief description of the UASB-AnMBR pilot plant is reported in Supplementary Material Section (Text S2).

The pilot system is located in real environment at the municipal WWTP of Falconara Marittima (Ancona, Italy), which has a design treatment capacity of 80,000 population equivalent (PE) at an average dry weather flow rate of 18,000 m^3/d. The Falconara Marittima WWTP is in a coastal area and since it is a hotspot for infiltrations from groundwater and marine intrusions, low-loading wastewater occurs in the WWTP influent. Following preliminary treatment (screening, degritting and oil removal), pretreated influent from Falconara WWTP was sent to the pilot-scale based dynamic filter, UASB, AnMBR and MIPs systems. Typical water quality parameters of the wastewater influent to the MIP columns are reported in Supplementary Material (Table S2).

2.2. Synthesis of MIPs

MIPs were synthesized using DCF in acid form (DCF-H) by radical polymerization adapting the protocol reported by Samah et al. [22]. DCF-H was obtained by dissolving DCF sodium salt in water (7 mg per mL) and acidifying the solution with 1 M HCl. The final solution was stirred for 10 min using a magnetic stir bar and filtered through 0.45 μm paper filter to remove precipitated salts. MIP synthesis was performed by dissolving 1 mmol DCF-H as template and 4 mmol methacrylic acid (MAA) as monomer in 30 mL of acetonitrile. Hence, 20 mmol of ethylene glycol dimethyl acrylate (EGDMA) and 0.12 mmol of 2,2′-azobisisobutyronitrile (AIBN) were added to create and promote the polymer matrix around the template molecules. The solution was purged with nitrogen for 10 min to remove oxygen, and then heated at 60 °C for 24 h with a Arex Digital plate (VELP). The obtained monolith polymer was recovered and washed several times with methanol/acetic acid (9/1, *v*/v) mixture through sonication and centrifugation (Hemerle model Z-380) to remove the DCF used as template. A final washing step with 50 mL of methanol for two cycles was performed and the polymer was centrifugated at 6000 rpm for 10 min. Afterwards, the polymer was dried at 40 °C overnight, then grounded and sieved to have 20–100 μm particles. Non-Imprinted Polymers (NIPs) were synthesized in the same way without using the target molecule during the pre-polymerization step. NIPs were used as a control to evaluate the adsorption performance of the obtained polymers.

2.3. Regeneration of MIPs

In order to test the reusability of the synthetized materials, 7.7 g of MIP that already adsorbed DCF were washed by flushing the packed column first with 500 mL of methanol/acetic acid solution (9:1, *v*/v) and then with DI water to remove residuals of solvent [17]. Hence, regenerated MIPs were reused for the adsorption of DCF in the next cycle. The adsorption abilities of the regenerated MIPs were compared with the abilities of non-regenerated ones.

2.4. Batch adsorption experiments

The batch adsorption experiments were carried out in several vials of 5 mL under continuous shaking conditions (240 rpm) at room temperature (20 ± 1 °C). For equilibrium batch experiments, synthetized MIPs or NIPs (10 mg) were added to 4 mL of aqueous solution spiked with different DCF concentrations (25–600 mg/L) at pH 7. At the end of the batch experiments, liquid samples were withdrawn and filtered by 0.45 μm polytetrafluoroethylene (PTFE) syringe filter (Whatman, Clifton-NJ) before analyzing the residual concentration. By preliminary adsorption kinetic tests, it was observed that equilibrium conditions were reached in relatively short time and in <5 min for both MIP and NIP (Fig. S3). Langmuir and Freundlich isotherm models [23,24], whose fundamentals equations are reported in Text S3 (Supplementary Material), were employed to fit the experimental data and they provided essential information regarding adsorption mechanisms [25]. The coefficient of determination (R^2) was used to assess the goodness of fit.

Moreover, further batch tests were performed to evaluate the enhancement of DCF removal during biological processes by enriching activated sludge with MIPs emulating the practice of addition of powdered activated carbon to biological processes [26]. Hence, mixed liquor samples were collected from the UASB reactor (denoted as mixed liquor 1) and from the AnMBR tank (denoted as mixed liquor 2) along with a permeate sample. Total suspended solids and volatile solids content in the three different samples as well as the measured pH are reported in Table 1.

To evaluate DCF adsorption in these three different matrices, 1.5 g of MIPs were added to 0.5 L of each sample spiked with 25 mg/L of DCF.

Table 1
Total suspended solids, total volatile solids and pH values measured in mixed liquors collected from the UASB reactor, from the AnMBR tank and in the permeate.

Parameter/sample	Mixed liquor 1	Mixed liquor 2	Permeate
TSS (mg/L)	19,600	120	0
TVS (mg/L)	11,368	69.9	0
pH	8.23	8.19	7.5

The obtained solutions were slightly stirred to keep all materials suspended but avoiding introduction of air. Hence, at different time intervals ranging from 0 to 20 h (i.e., typical hydraulic retention time in biological reactors), different aliquots (3 mL each) were collected and filtered at 0.45 μm to evaluate DCF concentration in the liquid phase by UV absorbance measurements. Experiments were conducted in the dark to avoid photodegradation effects and at room temperature (20 °C).

2.5. Packed-bed column experiments

Packed-bed column experiments were conducted both at laboratory and pilot scale. During laboratory experiments, MIPs were placed in columns of 1.6 cm inner diameter with bed heights of 15 cm. A 15 mg/L (C_0) DCF solution was pumped upward at flow rate of 1.00 mL/min controlled by a peristaltic pump (Gilson, Minipuls 3). Consequently, the resulted empty bed contact time (EBCT) was around 30 min. The adsorption properties of different mixtures of sand and MIPs were tested to reduce the amount of the synthetic polymer, while controlling the hydraulic of the process (i.e., increasing the permeability of the sorbent while reducing the pressure in the column). Indeed, MIPs have very low pore sizes, and it may result in frequent clogging of adsorbent material and needs of backwash. Particularly, the adsorption bed was constituted by 33 % MIP and 67 % sand in the first test (Lab 1), 75 % MIP and 25 % sand in the second test (Lab 2), and 100 % MIP in the third test (Lab 3). The described adsorption beds were packed between sand layers to fill the whole volume of the column and operate the system under pressure avoiding the formation of preferential flow channels. Finally, MIPs utilized in the Lab 3 test were regenerated according to the procedure previously explained and tested again in a fourth column lab test to estimate the reusability of the synthetized polymer (Lab 4). Samples from the outlet were collected at regular intervals and the concentration of DCF in the effluent was measured immediately. The pH, temperature and conductivity in the effluent were regularly monitored. The concentration of DCF in inlet solution was also checked during the experiment to monitor any change. Details of the performed laboratory tests are reported in Table 2.

Pilot-scale adsorption experiments were conducted using the effluent of the UASB+AnMBR pilot system located at Falconara WWTP. The MIPs column was equipped with i) a storage tanks of 200 L to collect the permeate coming from the AnMBR; ii) a piston pump; iii) two porous stones as filter support placed at the top and the bottom of the column to prevent the washout of the fine particles; iv) two valves placed at the two sides of the column, two brass threaded fittings to block the porous stones, and v) a pressure gauge (Fig. S1). The transparent PVC column used in the experiment had an internal diameter of 3.4 cm and a total volume 0.45 L. The MIP column was fed in up flow direction with a wastewater flowrate of around 0.5 L/h, and DCF was spiked (around 500 μg/L) in the storage tank that collected the AnMBR effluent. MIPs column effluent was continuously collected by an automatic sampler able to withdraw 0.5 L of sample per hour. Even in this case mixtures of MIPs and sand (Pilot 1) or MIPs alone (Pilot 2) were used to create the adsorption bed as shown in Table 4. Sand was used as a filler, in the upper and lower part of the column, to standardize the front of the flow and reduce the effects of preferential channels. Illustrations related to the MIP column configurations are reported in Fig. S2.

The breakthrough curves were obtained by plotting the DCF normalized concentration (C/C_0) as a function of time (t, min). Moreover, the saturation time (t_s) was established when the effluent concentration exceeded 85 % of inlet concentration [27], and the breakthrough time (t_b) was referred to the time at which the outlet concentration reaches 5 % of the inlet concentration ($C/C_0 = 0.05$) [21]. Several mathematical models (i.e., Adams-Bohart model, Thomas model, Yoon-Nelson model, Dose-Response model and, Clark model) were applied to the experimental data to predict the breakthrough curves and to determine column kinetic parameters [28,29]. More details regarding breakthrough curve modelling are provided in Text S4 (Supplementary Material). The goodness of model fitting was evaluated using the coefficient of determination (R^2).

2.6. Analytical methods

Analysis of DCF at high concentrations in DI water, such those used during batch adsorption tests, were performed by an UV-VIS Synergy HT spectrophotometer (Biotek) measuring the UV absorbance at 276 nm as reported in the literature [30,47]. Around 0.2 mL of samples were needed for each analysis. On the contrary, analysis of DCF at μg/L level in wastewater were performed by High Performance Liquid Chromatography (HPLC - Agilent Infinity 1260 series) with diode array detection [31,32]. The used analytical procedure is briefly described in Supplementary Material (Text S5).

The characterization of MIP and NIP polymers was performed by SEM analysis with the Philips XL20 scanning electron microscope (SEM) with tungsten filament and 10 KV voltage. The Brunauer-Emmett-Teller (BET) area and porosity of the synthetized MIPs were obtained by a Tristar II Plus (Micrometrics) device.

Analyses of conventional water quality parameters (e.g., COD, conductivity, pH, TSS, etc) were performed according to standard methods [33].

3. Results and discussion

3.1. MIPs characterization

SEM characterization was carried out to analyze the surface morphology of the synthetized MIPs and NIPs [34,35]. Particularly, the surface analysis (Fig. 1) showed that both MIPs and NIPs had irregular and cross-linked particles agglomerates. However, NIPs surface resulted more homogeneous, but with a scarcer porosity structure. Indeed, the use of acetonitrile as solvent during the synthesis enhances the formation of the porous structure of the MIPs thanks to an effective diffusion of the template through the framework of the material [36,37].

Table 2
Operational variables for packed-bed column experiments conducted at laboratory scale and at pilot scale.

Test ID	Bed composition	MIP mass (g)	Bed height (cm)	flow rate (mL/min)	C_0 (mg/L)	EBCT (min)	Regeneration
Lab 1	33 % MIP 67 % sand	2.11	15	1.00	15	30	No
Lab 2	75 % MIP 25 % sand	4.75	15	1.00	15	30	No
Lab 3	100 % MIP	7.70	15	1.00	15	30	No
Lab 4	100 % MIP	7.70	15	1.00	15	30	Yes
Pilot 1	33 % MIP 67 % sand	15.09	25	0.5	500	26.5	No
Pilot 2	100 % MIP	49.48	25	0.5	500	26.5	No

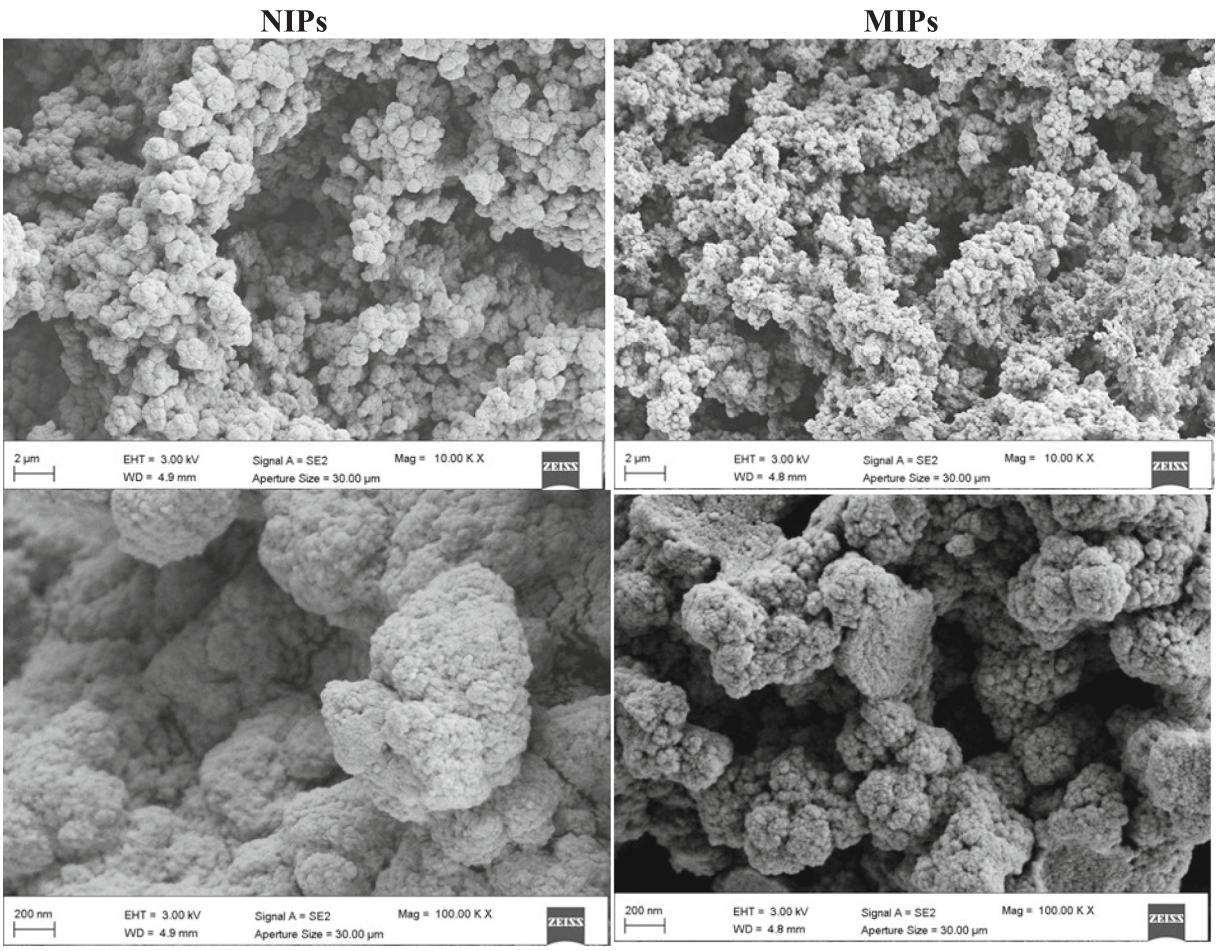

Fig. 1. SEM images of synthetized NIPs (left) and MIPs (right), at 10 KX (top) and 100KX (bottom) of magnification, respectively.

Gas adsorption volumetric analysis highlighted for both polymers a type II isotherm (Fig. S4) with a BET specific surface area (SSA) of 51.25 and 111.11 m^2/g for NIPs and MIPs, respectively. In accordance with SSA results, MIPs showed a higher cumulative pore volume (0.039 cm^3/g) than NIPs (0.005 cm^3/g). Finally, the average pore size was 47 Å for MIPs and 35 Å for NIPs. All these results are in agreement with previous work that used acetonitrile as solvent during the synthesis of these kind of imprinted polymers [35,38].

3.2. Comparison of DCF adsorption by MIPs and NIPs in batch experiments

The batch experiments were carried out to evaluate the increased adsorption capacity and affinity of synthetized MIPs towards DCF in water compared to NIPs. Experimental data and related Langmuir and Freundlich fittings are shown in Fig. 2. Meanwhile, isotherms parameters and the coefficients of determination obtained by fitting the experimental data with the selected isotherm models are reported in Table 3. Overall, Langmuir model exhibited a better fit to the experimental data compared to Freundlich model, and it was particularly true in the case of NIPs data (Table 3). The maximum adsorption capacity (q_m) obtained by the Langmuir model and the Freundlich capacity coefficient (K_F) were higher for MIPs than for NIPs confirming the higher adsorption affinity of MIPs towards DCF. In addition, values of the adsorption constants $0 < K_L < 1$ in the Langmuir model and $1/n < 1$ in the Freundlich model, for both MIPs and NIPs, are indicative of the occurrence of very favorable adsorption processes [39–42].

The imprinting factor (IF) characterizes MIP binding capacity over that for non-imprinted polymer, and it is the simplest estimation of the

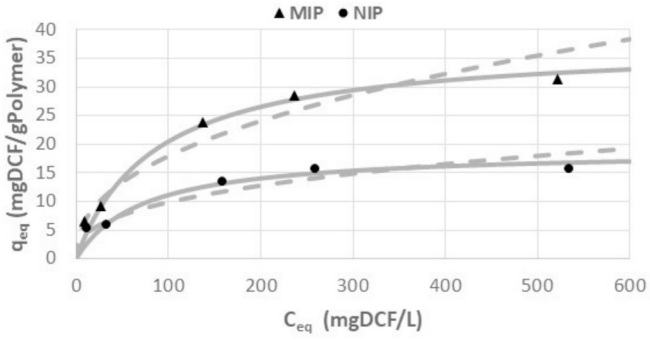

Fig. 2. DCF adsorption isotherms: MIPs (Triangle) and NIPs (circle) in DI water and related Freundlich (dotted line) and Langmuir (continuous line) fitting.

Table 3
Isotherm fitting parameters calculated for DCF adsorption on MIPs and NIPs.

Polymers	Langmuir			Freundlich		
	K_L (L/mg)	$q_{m.}$ (mgDCF/gMIPs)	R^2 -	K_F (mg/g)* (L/mg)	1/n a.u.	R^2 -
MIPs	0.0119	37.7	0.9994	2.55	0.371	0.9868
NIPs	0.0142	19.0	0.9961	1.79	0.424	0.9038

imprinting effect. Its calculation is based on the ratio between the adsorbed DCF by MIP ($q_{e\ MIP}$) over that for non-imprinted polymer ($q_{e\ NIP}$) under equilibrium conditions [43]. As shown in Table 4, the IF increased at higher DCF concentration in water, and it was always >1 highlighting the higher adsorption capacity of MIPs compared to NIPs. Obtained IF values in this study were similar to IF calculated in previous publications [15,35].

3.3. Use of MIPs to remove diclofenac in addition to anaerobic mixed liquors

Addition of adsorbent such as powdered activated carbon (PAC) to activated sludge has been tested in several full-scale plants and demonstrated its capability to enhance non-selective removal of toxic contaminants such as heavy metals and hydrocarbons [48]. However, selective adsorption in combination with biological processes is still an open challenge, that was addressed in this study. In general, adsorption of pharmaceuticals on activated aerobic or anaerobic sludge depends on the lipophilicity and acidity of the compound as well as the ambient conditions such as pH, ionic strength, temperature and the presence of complexing agents, and the properties of the sludge. Particularly, characteristics of sludge types differ greatly. For example, pH of the primary sludge is in general lower, and fat and grease content are higher than that of activated or digested sludge [19]. On the other side, it was shown that DCF can only be slightly adsorbed in sludge [44] (DCF Log K_{ow} = 4.51). Furthermore, its biodegradation during biological processes has been reported as negligible [45]. Particularly, previous studies have observed higher adsorption of DCF to primary (5–15 %) than to secondary sludge (<5 %) [44,46].

In this work, the addition of MIPs (3 g/L) to different mixed liquor types was tested to evaluate the enhancement of DCF adsorption during anaerobic biological processes emulating the practice of addition of powdered activated carbon to biological processes. The three tested samples had a very different content of flocs of sludge as shown in Table 1. Particularly, the permeate (the control experiment) had not solids content, whereas mixed liquor 1 from the UASB reactor had a much higher TSS concentration (TSS = 19,600 mg/L) compared to mixed liquor 2 (TSS = 120 mg/L) collected in the AnMBR tank. However, the TVS/TSS ratio was similar in both mixed liquor 1 and mixed liquor 2 samples (around 58 %). In all the performed experiments a plateau for DCF adsorption was observed after 6 h reaction (Fig. 3). In these conditions, when no MIPs were added to the testing solutions, DCF adsorbed in mixed liquor 1 sample was the highest (i.e., DCF removal >30 %), a DCF removal <20 % was observed in mixed liquor 2 sample, whereas no DCF was removed in the permeate. On the contrary, addition of MIPs to the permeate resulted in ca. 40 % DCF removal, whereas no significant differences in DCF adsorption were observed when MIPs were added to the other two testing solutions, with only a slight increase in the adsorption in mixed liquor 2, (Fig. 3). The presence of a high TSS concentration, especially in the case of mixed liquor 1, may cause a complete embedding of MIPs in the sludge thus overriding their adsorption contribution.

Table 4
Imprinting factor of MIP particles calculated for different concentrations of DCF in DI water.

DCF in DI water (mg/L)	$q_{e\ MIP}$ (mg/g)	$q_{e\ NIP}$ (mg/g)	IF
25.03	6.52	5.23	1.25
49.62	9.12	5.98	1.53
195.90	23.73	13.38	1.77
307.68	28.48	15.72	1.81
600.44	31.31	15.72	1.99

q_e = amount of adsorbate per mass unit of adsorbent absorbed at the equilibrium

Fig. 3. DCF removal during batch tests in three different matrices performed with MIPs (triangles) and without MIPs (circle). Mixed liquor 1 had TSS = 19,600 mg/L, Mixed Liquor 2 had TSS = 120 mg/L, permeate did not have solids content. DCF concentration in the three matrices was 25 mg/L.

3.4. DCF adsorption as tertiary treatment in packed-bed column

Fig. 4 shows the results of the laboratory tests conducted with DCF solution (15 mg/L in DI water) pumped through packed columns filled with different percentages of sand and MIPs. The experimental results are provided as breakthrough curves (DCF normalized concentration (C/C_0) versus operating time (t, min)). Five models were applied to fit the experimental data and to determine the column kinetic parameters, which are reported in Table 5. The empirical Thomas Model, Yoon-Nelson Model, Modified Dose-Response Model (useful to model the entire breakthrough curve) and the Adam Bohart Model (proposed for the description of the initial part of the breakthrough curve) showed very good fittings with the experimental data in all performed laboratory tests ($R^2 > 0.94$ in Lab 1, Lab 2 and Lab 4 tests and $R^2 > 0.84$ in Lab 3 test) suggesting their suitability for design, scale-up and optimization purposes. On the contrary, lower R^2 values were obtained when using Clark Model. Generally, the coefficient values of those models vary depending on some operative parameters such as the initial concentration, the flow rate, the bed height, mass of the adsorbent material and the temperature. Furthermore, the Thomas model and the Modified Dose-Response model allow the calculation of the adsorption capacity at the equilibrium (mg/g), which is a critical indicator of column performance (Text S4). In Fig. 4 the fitting curves obtained by the Thomas model are reported.

The influence of different MIP content in the adsorption bed was evaluated by accomplishing experimental tests with column beds filled with different percentages of sand and MIP, but with same EBCT (30 min). The comparison of breakthrough curves in Fig. 4 shows that the time needed to reach the breakthrough point and the saturation plateau increased significantly with the increasing of the MIP mass in the bed column. Indeed, it can be observed that the breakthrough curve referred to the column with the lowest MIP mass (2.11 g – Lab 1) is much faster than the one of the columns with 100 % MIP (7.7 g – Lab 3 and Lab 4), whereas the slope of breakthrough curves was similar for all the laboratory tests (i.e., Lab 1, Lab 2, Lab 3, Lab 4), Particularly, the breakthrough curves of Lab 3 and Lab 4 tests were very similar, and in both tests the breakthrough point was reached at comparable time (Fig. 4). Higher maximum adsorption capacities (q_{eb}), determined by the Thomas Model or the Modified Dose-Response model, were found for Lab 3 and Lab 4 tests compared to the other two operated with a lower mass of MIPs. (Table 5). Lab 3 and Lab 4 tests, which contains the same amount of MIPs, were operated with different materials: virgin material for Lab 3 test and regenerated MIPs for Lab 4 test. Hence, this result suggests that after regeneration MIPs can be efficiently reused as their adsorption capacity is sufficiently preserved.

Similar experiments were repeated at pilot scale and using a real wastewater, which was the permeate of the AnMBR located at Falconara WWTP. Even in this case, column beds were filled with different percentages of sand and MIP to evaluate the influence of different MIP content in the adsorption process and to monitor the hydraulic conditions of the system, including clogging of adsorbent material and

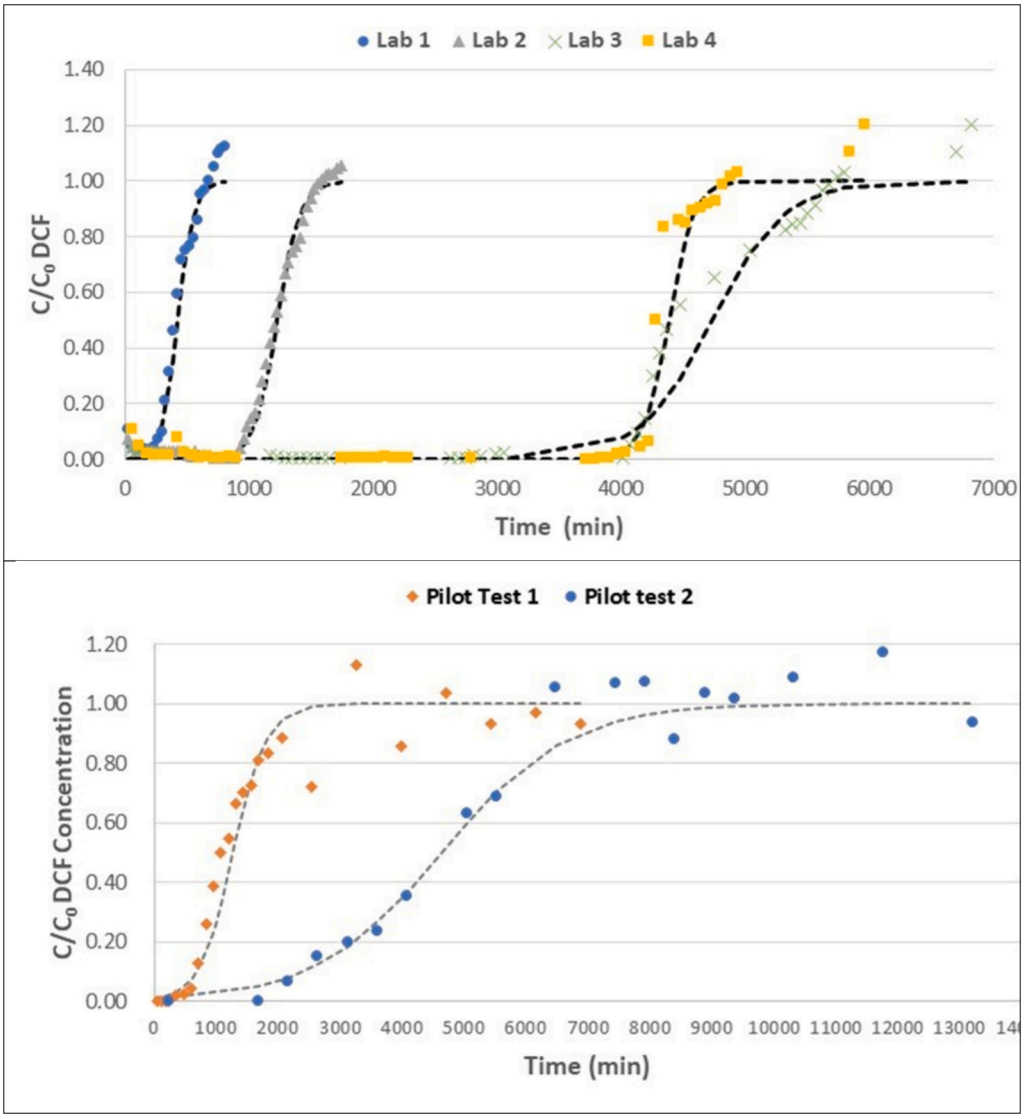

Fig. 4. Top: Breakthrough curves of DCF for laboratory tests with their fitting with Thomas model (black dotted lines). Lab 1 (MIPs 33 % - sand 67 %), Lab 2 (MIPs 75 % - sand 25 %), Lab 3 (MIPs 100 %), Lab 4 (MIPs 100 % and regenerated). EBCT = 30 min and C_0 = 15 mg/L in all tests. **Bottom:** Breakthrough curves of DCF for Pilot Tests 1 and Pilot Test 2 with fitting of Thomas model (grey dotted lines). EBCT = 26.5 min and C_0 = 500 μg/L in all tests.

Table 5
Breakthrough models and kinetic parameters from fixed-bed column experiments conducted at laboratory scale.

Model	Parameters		Lab 1	Lab 2	Lab 3	Lab 4
Experimental conditions	DCF (C_0)	mg/L	15.079	15.602	15.550	15.550
	MIP mass	g	2.11	4.75	7.7000	7.7000
	MIP	(%)	33	75	100	100
	EBCT	min	30	30	30	30
Adam Bohart Model	K_{AB}	L/mg/min	0.00099	0.00068	0.00022	0.00063
	N_0	mg/L	214.26	635.37	2439.93	2259.53
	R^2	–	0.97664	0.96352	0.84605	0.94625
Yoon-Nelson Model	K_{YN}	min	0.01498	0.01061	0.00343	0.00972
	τ	min	428.54	1228.19	4732.34	4382.45
	R^2	–	0.97664	0.96352	0.84605	0.94625
Thomas Model	K_{TH}	L/mg/min	0.993	0.680	0.220	0.625
	q_{eq}	mg/g	3.056	4.213	8.927	8.910
	R^2	–	0.97664	0.96352	0.84605	0.94625
Modified Dose-Response Model	K_{mdr}	–	5.92335	12.64594	16.59709	41.37917
	q_{mdr}	mg/g	2.891	4.151	8.857	8.883
	R^2	–	0.97560	0.96721	0.85708	0.94999
Clark Model	A	–	1,827,901,434	1.2891E+17	1.90156E+19	5.09908E+60
	r	1/min	0.03893	0.02820	0.00836	0.03044
	n	–	5.536	5.536	5.536	5.536
	R^2	–	0.90095	0.85439	0.65835	0.90431

increase of pressure within the column. Indeed, since MIPs have very small size (see SEM images in Fig. 1), blockage of the column bed may be a relevant issue when treating real wastewater.

Results of the performed experiments are reported in Fig. 4, indicating that the DCF breakthrough was faster in the test Pilot 1 with lower MIP content (15 g) compared to the test Pilot 2 filled with 100 % MIP (50 g).

In pilot-scale experiments, the DCF concentration was much lower than in laboratory tests (0.500 μg/ L vs 15 mg/L). However, the time of breakthrough point for both the Pilot tests was similar to that of the lab tests performed with same percentage of MIP content and EBCT (i.e., Lab 1 and Lab 3 tests, respectively). On the other side, the slope of the breakthrough curve was less steep in pilot tests, where the saturation process of MIPs was much slower compared to laboratory tests conducted in DI water. This fact is probably related to the presence of several water constituents (both organic and inorganic) in the real wastewater, which may have interfered with the adsorption process.

The mathematical Thomas Model, Yoon-Nelson Model, Modified Dose-Response Model, and the Adam Bohart Model showed again very good fittings ($R^2 > 0.92$) with the experimental data, whereas lower R^2 values were obtained with the Clark Model fitting. As in the lab tests, the pilot scale results confirmed the models' suitability for design and prediction of adsorption processes that utilize MIP materials. The determined kinetic parameters and the R^2 values are reported in Table 6, while the fitting curves obtained by the Thomas model are displayed in Fig. 4. Comparable maximum adsorption capacities (q_{eb}) were suggested by the Thomas Model or by the Modified Dose-Response model for the two pilot tests. However, these values were lower than the adsorption capacities obtained during the laboratory tests. This result is likely due to the lower DCF concentration used in the inlet water to the pilot column than that used in the lab tests.

During the pilot experiments, the flow rate was kept constant and the pressure within the column was stable around 1 bar. Furthermore, interruptions of the process because of clogging problems were not observed in both the columns filled with a mix of sand and MIPs or only MIPs.

Table 6
Breakthrough models and kinetic parameters from fixed-bed column experiments conducted at pilot scale.

Model	Parameters		Pilot 1	Pilot 2
Experimental Conditions	DCF (C_0)	mg/L	0.650	0.496
	MIP mass	g	15.09	49.48
	MIP	(%)	33	100
	EBCT	min	26.5	26.5
Adam Bohart Model	K_{AB}	L/ mg/ min	0.00601	0.00197
	N_0	mg/L	30.710	86.62
	R^2	–	0.921	0.981
Yoon-Nelson Model	K_{YN}	1/ min	0.00421	0.00098
	τ	min	1276	4632
	R^2	–	0.921	0.982
Thomas Model	K_{TH}	L/ mg/ min	5.686	1.9788
	q_{eq}	mg/g	0.462	0.397
	R^2	–	0.921	0.982
Modified Dose-Response Model	K_{mdr}	–	3.788	3.544
	q_{mdr}	mg/g	0.419	0.391
	R^2	–	0.981	0.970
Clark Model	A	–	91,918,810	30,698,587
	R	1/ min	0.01099	0.00298
	n	–	5.535	5.535
	R^2	–	0.808	0.956

4. Conclusions

In this work, the use of MIPs was investigated to integrate AnMBR technology for the removal of DCF by adsorption. Batch tests at laboratory scale were performed to evaluate the increased adsorption of MIPs compared to non-imprinted polymers (NIPs). Moreover, pilot-scale experiments carried out in a real WWTP investigated the removal of DCF within a combination of MIPs technology and AnMBR treatment. Hence, the following conclusions can be drawn from this study:

- MIPs are characterized by a higher cumulative pore volume and by almost a double specific surface area if compared to NIPs as observed by SEM and BET analyses. Furthermore, Langmuir and Freundlich isotherms as well as the imprinting factor calculation confirmed that MIPs have a higher adsorption affinity towards DCF compared to NIPs.
- In the adsorption column tests, increased amounts of MIPs used to pack the columns did not cause interruptions of the process because of clogging issues both in laboratory and pilot-scale experiments. This fact allowed to improve the adsorption performance of the packed columns.
- Different mathematical models (i.e.; Thomas Model, Yoon-Nelson Model, Modified Dose-Response Model and the Adam Bohart Model) showed very good fittings ($R^2 > 0.9$) with the experimental data collected during both laboratory and pilot-scale column tests. This fact proves the suitability of those mathematical tools to predict adsorption processes when using MIP materials.
- After regeneration, MIPs preserved their adsorption capacity with a breakthrough curve very similar to that obtained using virgin material.

In a future perspective, the data acquired within this study can be used for the design of a sustainable scale up treatment, thanks to the possibility of MIPs regeneration. Furthermore, different MIPs synthesis could be performed in order to obtain more versatile polymers with cross-selectivity towards ECs for wastewater treatment and for its reuse.

CRediT authorship contribution statement

Marco Parlapiano: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Alessia Foglia:** Writing – review & editing, Project administration, Investigation. **Massimiliano Sgroi:** Writing – original draft, Visualization, Supervision, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Michela Pisani:** Writing – review & editing, Supervision. **Paola Astolfi:** Writing – review & editing, Supervision. **Marica Mezzelani:** Writing – review & editing, Formal analysis. **Stefania Gorbi:** Writing – review & editing, Supervision. **Çağrı Akyol:** Writing – review & editing. **Anna Laura Eusebi:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Francesco Fatone:** Writing – review & editing, Supervision, Resources, 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

The data that has been used is confidential.

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Appendix A. Supplementary data

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