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Rapid and high-throughput analysis of PAHs and pesticides adsorbed on microplastics using SPME-MS through a microfluidic open interface coupled to liquid electron ionization mass spectrometry

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ABSTRACT

Microplastics (MPs) are pervasive contaminants in aquatic environments, capable of adsorbing and transporting hazardous chemicals such as polycyclic aromatic hydrocarbons (PAHs) and pesticides. Understanding these adsorption processes is crucial for evaluating their ecological and health risks. In this study, a green analytical approach with a high-throughput, solid-phase microextraction coupled with a microfluidic open interface and liquid electron ionization mass spectrometry (SPME-MOI-LEI-MS), was applied to investigate the kinetics and thermodynamics of PAHs and pesticides adsorption on low-density polyethylene (LDPE) and polypropylene (PP) microplastics. Method optimization and validation demonstrated intraday RSD values below 15% and limits of quantification below 10 μg/L. Results revealed that PAHs adsorb predominantly through non-polar interactions, with adsorption efficiency correlating with analyte hydrophobicity. For pesticides, adsorption patterns were more diverse, reflecting differences in molecular structure and physicochemical properties. Notably, chlorpyrifos exhibited high affinity for LDPE (95% recovery), raising concern due to its toxicity. Competition experiments further highlighted how strongly adsorbing molecules can inhibit the uptake of weaker ones as adsorption capacity at the equilibrium of atrazine, metalaxyl, dichlorvos and alachlor increases in absence of chlorpyrifos.

1. Introduction

Pollution has been a chronic and escalating global problem for decades, with its severity exacerbated over time by growing industrialization, urbanization, and unsustainable human practices. Aquatic habitats are increasingly contaminated by a variety of pollutants, including microplastics (MPs), pesticides, antibiotics, and industrial and agricultural waste. The contaminants in question are of particular concern as they pose a dual threat to human health and biodiversity. Furthermore, these contaminants interact with one another, with the potential to generate more harmful and persistent chemicals. Such interactions have the potential to give rise to novel classes of contaminants, thereby exacerbating both health and environmental concerns. It has been demonstrated that MPs have the capacity to adsorb a variety of environmental contaminants, including polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, organochlorine pesticides, polybrominated diphenyl ethers, alkylphenols, bisphenol A, and metals [1]. These contaminated MPs are ingested by marine organisms [2], potentially transferring toxins up the food chain through bioaccumulation and biomagnification, posing risks to marine life and humans [3]. The combined threat of MPs and sorbed contaminants requires urgent attention. MPs have become the focus of study due to their potential toxic impact on aquatic ecosystems and have already been detected in surface water [4], bottom sediments [5], and the water column [6], with contamination reported across diverse natural environments, including rivers [7], estuaries [4], the open ocean [8], and the deep sea. Previous studies indicate that microplastics transport pollutants (heavy metals, organics, antibiotics), influence their mobility, and harm ecosystems [9,10]. The most frequently detected MPs in the aquatic environment are polyethylene (PE), polystyrene (PS), polypropylene (PP), polyamide (PA), and polyvinyl chloride (PVC) [11], having differences in morphological characters, adsorption capacities

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and affinity to pollutants [12]. Each polymer type contains different additives. MPs, pesticides and PAHs are three classes of widespread contaminants with proposed negative impacts to aquatic ecosystems. PAHs are persistent, hydrophobic organic compounds formed during the incomplete combustion of fossil fuels, biomass, and other organic materials [13], ubiquitously present across multiple environmental media and known to pose significant risks to marine ecosystems through various pathways, including oil spills, industrial discharges, urban runoff, and atmospheric deposition. Industrial activities such as fossil fuel combustion, petroleum refining, and chemical manufacturing release PAHs into the air and water [14], while urban runoff transports these pollutants from roads and urban areas into aquatic systems [15] and atmospheric deposition further contributes through airborne particle settling onto ocean surfaces. Once in the marine environment, PAHs undergo various processes, including long-range transport via ocean currents, photodegradation, microbial and chemical transformation, sediment adsorption leading to long-term accumulation [16], and bioaccumulation in marine organisms, ultimately posing significant ecological risks. Pesticides are chemical or biological agents used to control pests, such as insects, weeds, fungi, and microorganisms, that threaten crops, livestock, and human health. While they are essential in agriculture and public health, their use often leads to environmental contamination and risks to non-target organisms. Due to their low utilization efficiency and poor biodegradability, pesticides frequently contaminate water and soil [17] and have been detected in surface waters worldwide [18–20]. The environmental pollution caused by pesticide utilization has attracted great concern [21]. When MPs carry pesticides, it leads to combined contamination, impacting water, sediments, and organisms, with potential long-term ecosystem damage [22, 23].

Green analytical techniques are crucial in modern chemistry, reducing environmental impact and enhancing safety by minimizing hazardous substances. It includes device miniaturization, waste reduction, and use of greener solvents and reagents [24,25]. An emerging class of analytical techniques to improve greenness and throughput is represented by solid-phase microextraction-mass spectrometry (SPME-MS) techniques based on micro-desorption. The green aspect of the SPME technique lies in its speed, minimal to no solvent use, reduced sample preparation, and low laboratory waste generation. As SPME is currently the extraction technique that possesses the highest greenness factor, its direct coupling with MS represents an ideal combination for optimizing most analytical methods [25–27]. SPME-MS techniques offer several advantages to avoid some issues faced with ambient MS techniques, such as sensitivity, selectivity, matrix effect and need for frequent cleaning and maintenance of MS instrument. This is achieved thanks to SPME clean up and enrichment, which allows to minimize interferences from the matrix during the analysis while keeping the sensitivity high. Many SPME-MS interfaces have been developed since 1996, allowing the coupling of SPME with different ion sources such as EI, ESI and MALDI, as well as ambient MS techniques such as DART and DESI [26].

Microfluidic open interface (MOI) was developed in 2018 and allows the static desorption of Bio-SPME fibers in small volumes of solvent prior injection in the ESI. Briefly, a syringe pump delivers the solvent used for the desorption and analysis. If the flow rate of the syringe pump is greater than the constant flow rate of the ESI (around 120 μL/min) the solvent goes to a microfluidic open port and is filled with the solvent. The flow rate of the syringe pump was set as equal to the ESI flow rate, the solvent in the microfluidic open port remains static, allowing the desorption of the SPME fiber. Afterwards, the syringe pump delivers a flow rate lower than the constant flow rate of the ESI, allowing the suction of the solvent in the desorption chamber and the injection of the analytes desorbed previously [28]. In this study, SPME-MS was realized by coupling a modified MOI with a Liquid Electron Ionization (LEI) interface for the conversion in gas phase of the liquid flow before the injection in the EI ion source [29–32]. LEI coupling to SPME-MOI enables the analysis of molecules with low polarity and not properly ionizable with ESI, also minimizing suppression of ionization efficiency due to the gas phase ionization under vacuum conditions in EI ion source, allowing often external calibration with negligible matrix effect [33]. This instrumental setup was used to achieve high throughput and greenness in monitoring adsorption kinetics and thermodynamics of some target PAHs and pesticides among the most occurring in Italian surface and ground waters [34] on MPs, allowing a better understanding of these phenomena and how MPs can transport and accumulate environmental pollutants.

2. Materials and methods

2.1. Chemicals

Pyrene, naphthalene, anthracene, 4-n-nonylphenol analytical standard grade were purchased from Supelco Inc. (Bellefonte, PA), atrazine, dichlorvos, clorfenvinfos, chlorpyrifos, alachlor, metalaxyl analytical standard grade were purchased from Sigma Aldrich. Ultrapure water was obtained with a Direct-Q 3 UV system from Millipore Corp. (Merck, Milan, Italy). HPLC-MS grade acetonitrile (ACN), methanol (MeOH) and isopropanol (iPrOH) were purchased from VWR (Milan, Italy). Hydrophilic-lipophilic balanced/polyacrylonitrile (HLB/PAN) and C18/PAN SPME fibers were prepared at the University of Waterloo, ON, Canada and assembled using nitinol wires (length 50 mm, diameter 200 μm) coated with a mixture of polyacrylonitrile (PAN) and C18 particles. Coating thickness and length were 20 μm and 10 mm, respectively. A detailed description of the fibers' manufacturing process is reported elsewhere [35]. LDPE and PP pellets with a diameter, respectively, of 5 mm and 4 mm were purchased from Goodfellow GmbH (Hamburg, Germany).

2.2. LEI-MS interface

An Agilent 1290 Infinity II HPLC system was coupled to an Agilent 7010 B QqQ triple quadrupole mass spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA) utilizing a LEI interface. The HPLC was used to pump ACN at 10 μL/min in the system without performing chromatographic separation, using an Agilent 3.5 μm Zorbax XDB C18 0.3 × 150 mm column to ensure a proper backpressure. A passive flow splitter (PFS) was used to reduce the flow to 500 nL/min. The PFS comprises a tee connection that receives a stainless-steel capillary from the MOI (0.175 mm I.D.; 1.59 mm O.D.), a fused silica capillary for the waste (40 μm I.D, 360 μm O.D.) and a fused silica capillary as inlet capillary connected successively to the vaporization microchannel (VMC) (30 μm I.D, 150 μm O.D.). The length of the waste and inlet capillaries was adjusted to achieve the desired flow rate, by measuring with a Sensirion Flowmeter and monitoring the MS vacuum parameters. The VMC and LEI interface setup is described in previous studies [29,30,36]. Briefly, a stainless-steel tee junction connects a fused silica inlet capillary of 150 μm O.D. and 30 μm I.D. that delivers the sample to the MS with a VMC made with a deactivated fused silica capillary of 700 μm O.D. and 500 μm I.D. with a cooling gap of approximately 5 cm in length between the hot zone of the MS and the tee junction. The inlet capillary is inserted into the larger capillary, with its tip positioned at the beginning of the hot zone. An Agilent 7890B Gas Chromatograph supplied Helium to the MS through the perpendicular junction of the tee, allowing solvent nebulization, avoiding sample backflow and maintaining stable MS conditions.

2.3. SPME-MOI interface

The configuration of the MOI interface used in this work is based on the design used in previous studies with some modifications (Figure S1) [31,32]. Solvent coming from HPLC at a 10 μL/min flow enters an automatic six-port valve at position 1, with the MOI chamber connected

at position 6 and the waste flow directed to position 2, while positions 3, 4, and 5 remain closed (Figure S1). In the 1–6 connection of the valve (injection position), ACN fills the MOI chamber before flowing to the PFS-LEI. When the valve switches to 1–2 connection (load position), the HPLC flow is directed to waste, keeping ACN static during desorption in the MOI chamber. The main difference between the previous connectivity and the new proposed configuration occurs in this step: the previous configuration used to keep static the flow in the MOI chamber but used to deliver constantly to the MS the solvent; the new configuration connects directly the MOI to the PFS and then afterwards to the LEI interface, for this reason during the desorption step the solvent does not arrive to the MS. This situation was evaluated and the presence of Helium flowing continuously keeps stable the MS conditions. As avoiding dead volume between the 6-port valve and MOI interface is not easy working at low flow rates, dead volume and analyte deposition were observed with the previous connectivity, affecting reproducibility and accuracy. For this reason, avoiding analyte flow in the 6-port valve was a practical solution to this limitation and improved the reproducibility and accuracy of the instrumental response. After the desorption of the SPME fiber, the valve was switched back to position 1–6 to inject the desorbed analytes into the mass spectrometer. The desorption volume around the fiber in the MOI chamber is approximately 2.5 μL to allow an effective analyte focusing.

2.4. SPME extraction condition

C18/PAN and HLB/PAN SPME fibers were used for the extraction of PAHs and pesticides. The fibers were cleaned in ACN/MeOH/iPrOH (1:1:1 v:v) for 10 min under 3000 rpm agitation using an orbital vortex, followed by 10 min of conditioning in 1 mL of H_2O/MeOH (1:1 v:v). Extraction was performed in 1 mL of fortified water at target PAH and pesticide concentrations, maintaining ACN constant at 1 % to improve anthracene solubility in PAH experiments. The equilibrium was achieved at 30 min for PAHs and 60 min for pesticides under 3000 rpm agitation. The SPME fiber was then desorbed in the MOI chamber for 1 min in ACN.

2.5. Kinetic adsorption experiment

The kinetic experiments were conducted in a 500 mL glass bowl by exposing 500 mL of water fortified with 50 μg/L PAHs and 80 μg/L pesticides to microplastic pellets 200 and 254 pellets of LDPE and PP, respectively, were used for their kinetic experiments, keeping the agitation at 1500 rpm. The different number of pellets was chosen to keep constant the total surface area [37]. Their masses were recorded prior to the experiment to calculate the adsorption capacity. The pseudo-first and pseudo-second order equations of Lagergren used to describe the kinetic of the process are reported in Eqs. (1)–4.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

$$\frac{dq_t}{dt} = k'_2(q_e - q_t)^2 \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k'_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

$$q_t = \frac{(C_0 - C_t) \times V_{sample}}{m_{MPs}} \tag{5}$$

Eqs. (1) and 2 describe the pseudo-first order kinetic model, with k_1 the first order kinetic constant; Eq. (2) is obtained after integration of Eq. (1), while Eqs. (3) and 4 describe the pseudo-second order kinetic model with k_2 the pseudo, with Eq. (4) obtained after integration and linearization of Eq. (3). Eq. (5) is the adsorption capacity at time t, with the capacity at the equilibrium described as q_e. The kinetic experiments were conducted by collecting 4 aliquots of 1 mL at specific time intervals (5, 15, 30 and 60 min for the short-term kinetics and 3, 6, 12, 24, 30 and 48 h for the long-term kinetics). SPME extraction was performed in 1 mL aliquots of water collected after adsorption time t and transferred in clean glass vials, so the SPME extraction occurs in absence of microplastic pellets. Aliquots of 1 mL of water were taken from the bottom of the bowl after turning off the magnetic stirrer and waiting 1 min to ensure that all pellets were on the surface. This approach allows for the collection over time, regardless of the SPME extraction equilibration time, simplifying monitoring within the first hour.

The quantification was performed monitoring the aqueous concentration over the time. The absorbed amount at time t of adsorption (q_t) is derived as the difference between the initial concentration and the concentration at time t, as reported in Eq. (5).

2.6. Method validation and optimization

The method validation was carried out according to the Eurachem guideline [38] for calibration and repeatability; whereas LOD and LOQ were calculated considering the signal-to-noise ratio (S/N).

Intra- and interday RSD % have been measured performing 10 replicates of extraction and analysis the first day and 5 more replicates each day for other 4 days. LOD and LOQ values have been determined considering S/N of 3 and 10, respectively. Calibration was performed using 5 points between the LOQ value and the concentration used in the kinetic experiments (50 and 80 μg/L for PAHs and pesticides, respectively). Method optimization was performed evaluating each parameter while keeping the others constant. The parameters considered are conditioning solvent, SPME fiber selection, extraction time, cleaning step and desorption time.

The validated method is intended to be applied for the analysis of different types of water samples (river, sea, waste). In some cases, for more complex real water samples, the matrix effect evaluation could be necessary.

2.7. Greennees evaluation

The greenness evaluation was done using four different indices namely Analytical GREEnness Metric Approach Software - AGREE [39], Analytical greenness metric for sample preparation - AGREEprep [40], Complementary green analytical procedure index - complexGAPI [41] and Click Analytical Chemistry Index - CACI [42] in comparison with two representative methodologies, which includes conventional QuEChERS method for water extraction with analysis LC coupled to quadrupole-linear ion trap tandem mass spectrometry (LC-QqLIT-MS/MS) [43] and one more similar to ours, based on direct immersion SPME with GC–MS/MS for pesticide analysis in water [44].

3. Results and discussion

3.1. SPME extraction optimization and validation

The extraction method for the fortified water samples was optimized by evaluating conditioning solvent, extraction time, fiber selection and cleaning step after the analysis. SPME fiber selection was performed comparing the extraction efficiency of C_{18}/PAN and HLB/PAN fibers. The two different extraction phases have shown similar extraction efficiency for pesticide analysis, while PAH extraction has shown different efficiencies depending on the analyte (Figures S2, S3). In particular, 4-n-nonylphenol showed better results with C_{18}/PAN SPME fibers; anthracene and pyrene had similar results with both fibers, but the naphthalene signal was significantly low. HLB/PAN fibers, on the contrary, showed a higher efficiency for naphthalene and a satisfactory efficiency for the other analytes, good enough to obtain acceptable LOD values for

all compounds. For the purpose of this study, HLB/PAN was a better choice as it was important to keep good LOD and LOQ values for all the analytes studied. Conditioning of SPME fibers is important for obtaining reproducible and optimal results. Methanol, methanol/water (1/1, V/V) and acetonitrile have been evaluated. As reported in Figure S4, methanol shows better results than acetonitrile, while between methanol and methanol/water mixture, the results were comparable. Methanol/water mixture was selected as conditioning solvent because it reduces the cost per analysis and improves the greenness. A cleaning step of 10 min in 1 mL of ACN/MeOH/IPA (1/1/1 V/V/V) after each analysis was included in the protocol because the desorption in the MOI chamber is not exhaustive as it's based on a micro-desorption, so it was important to remove the analytes from the SPME fiber prior the following extractions to avoid carry over. SPME extraction time profiles have shown an equilibrium at 30 min for the PAHs, while most of the studied pesticides reach the equilibrium at 60 min (Figure S5). Dichlorvos, contrarywise, reaches the equilibrium in 15 min because of a lower extraction efficiency than the other analytes; however, competition on the active sites and displacement effects were not observed up to 90 min, allowing to select 60 min as extraction time for the target pesticides [45]. After the optimization of the extraction conditions, the method validation was performed. Intra- and inter-day RSD % and linearity were evaluated. The results, reported in Table 1, show that intra-day RSD % is lower than 14 % while the inter-day RSD % is lower than 20 %. The linearity of the calibration was acceptable as R^2 values were higher than 0.9928.

3.2. Kinetic and thermodynamic adsorption experiments

The efficiency of the SPME-MOI-LEI-MS setup for monitoring the kinetic of adsorption has been evaluated initially performing an initial experiment in agreement with previous studies on PAHs adsorption on microplastics [37]. The comparison was performed evaluating the short-term kinetic constants obtained in the previous study with those obtained using this setup, performing an experiment in analogous conditions. LDPE adsorption has been chosen as candidate for the comparison as it shows the fastest kinetic of PAHs adsorption among the studied MPs pellets. The results have shown a good agreement with previously obtained results using Membrane Introduction Mass Spectrometry (MIMS). MIMS is an analytical system useful for real-time data collection; however, this technique has been validated for a narrower range of compounds compared to SPME. The pseudo-first order constants obtained in the first hour of adsorption of PAHs on LDPE surface in the previous study are the following: naphthalene $K_1 = 0.56\ h^{-1}$; anthracene $K_1 = 2.0\ h^{-1}$; pyrene $K_1 = 2.3\ h^{-1}$; 4-n-nonylphenol $K_1 = 0.14\ h^{-1}$ [37]. In this study, the experiments gave the following pseudo-first order constant in the first hour of adsorption of PAHs on LDPE surface: naphthalene $K_1 = 0.55 \pm 0.08\ h^{-1}$; anthracene $K_1 = 1.9 \pm 0.2\ h^{-1}$; pyrene $K_1 = 2.2 \pm 0.3\ h^{-1}$; 4-n-nonylphenol $K_1 = 0.14 \pm 0.05\ h^{-1}$. The results show a good repeatability and comparability with the data present in literature. Afterwards, long-term kinetics and their adsorption constant have been measured for the target PAHs and pesticides. PAHs adsorption on LDPE and PP is shown in Fig. 1.

LDPE adsorption rate is faster than PP. The overall kinetic trend is of second order (Figure S6). R^2 values showed a better fit for the experimental data with the theoretical model of second order rather than for the first order (Table 2). Even if LDPE films are known for having an important diffusion coefficient for PAHs [46], the high R^2 shows good agreement with the theoretical model used, based on exclusive adsorption of the pellets used in the time considered. Pyrene has higher adsorption kinetic constants and capacity than anthracene and naphthalene, showing a dependence on non-polarity and surface of the molecule on the interaction with LDPE and PP surface active sites. 4-n-nonylphenol, despite a higher Log P value, shows a significantly slower adsorption kinetic and lower Qe. As described by Zvekic et al. [37], 4-n-nonylphenol adsorption depends on H-bond formation with the MPs surface, showing higher adsorption capacity on photo-oxidized MPs. The high R^2 values show a very good agreement with the theoretical model. The agreement with the theoretical model is obtained through the use of MPs particles with a uniform surface and keeping the agitation constant. This also confirms the absence of competition for the active sites and steric hindrance around the active sites, factors that can cause a deviation from the first or second order kinetic model. Real exposures in water bodies can show deviation from the theoretical kinetic as MPs shape is irregular, competition for the active sites can occur, creating also steric hindrance around the active sites for the analytes.

The 6 pesticides studied have different structures and chemical properties, while the PAHs studied had similar structures but different number of aromatic rings. The results show that for LDPE adsorption, the analytes with higher Log P usually have higher Q_e values. Among them, chlorpyrifos shows a particularly high affinity with LDPE, reaching a high adsorbed amount at a high rate (Fig. 2).

The recovery (amount recovered by the adsorbent from the solution on adsorbent mass expressed as a percentage) of LDPE at the equilibrium is 95 %. The high capacity of adsorption of LDPE for chlorpyrifos is an important information and could be further monitored as it represents a possible threat for aquatic systems and human health as World Health Organization (WHO) classified it as a "moderately hazardous" pesticide (Class II). Clorfenvinfos also shows a high adsorption capacity, while the other four target pesticides have shown relatively low adsorption. As the initial test was performed on an aqueous mix of all six pesticides, the high adsorption of chlorpyrifos could create competition for the active sites of the microplastics. For this reason, a new test was performed excluding chlorpyrifos from the mix. The results of the two tests are shown in Fig. 3. In the presence of chlorpyrifos, metalaxyl reaches adsorption equilibrium in 15 min with a $Qe < 1$; in the absence of chlorpyrifos, metalaxyl reaches equilibrium in 30 min with a $Qe = 1.4$. This result also shows how the presence of a molecule with a stronger affinity can create competition for the active sites on the surface, limiting the adsorption of low-affinity substances resulting in displacement effects. A similar trend was also observed for atrazine, alachlor and dichlorvos. The Qe values obtained in absence of chlorpyrifos (thus, without competition for active sites) are reported in Table 2. While LDPE adsorbs more and faster PAHs than PP, the trend with pesticides shows some differences. While PAHs exhibit adsorption primarily driven by

Table 1
Figures of merit for method validation.

Analyte	Intra-day RSD %	Inter-day RSD %	LOD (μg/L)	LOQ (μg/L)	R^2	Calibration Line Equation
naphthalene	11 %	18 %	2	5	0.9984	$y = 792.22x + 2905.5$
anthracene	9 %	16 %	0.1	0.5	0.9984	$y = 11188x + 13{,}002$
pyrene	8 %	16 %	0.1	0.5	0.9969	$y = 19571x - 6287.7$
4-n-nonylphenol	13 %	19 %	1	5	0.9992	$y = 2785.4x + 2225$
chlorpyrifos	8 %	14 %	1	5	0.9978	$y = 598.49x + 1115$
clorfenvinfos	10 %	15 %	1	5	0.9993	$y = 1091.5x - 290.14$
atrazine	14 %	20 %	5	10	0.9990	$y = 31.596x + 731.55$
metalaxyl	12 %	17 %	2	5	0.9928	$y = 119.41x + 599.49$
dichlorvos	11 %	17 %	5	10	0.9956	$y = 66.414x - 25.015$
alachlor	13 %	16 %	2	5	0.9963	$y = 139.06x + 617.84$

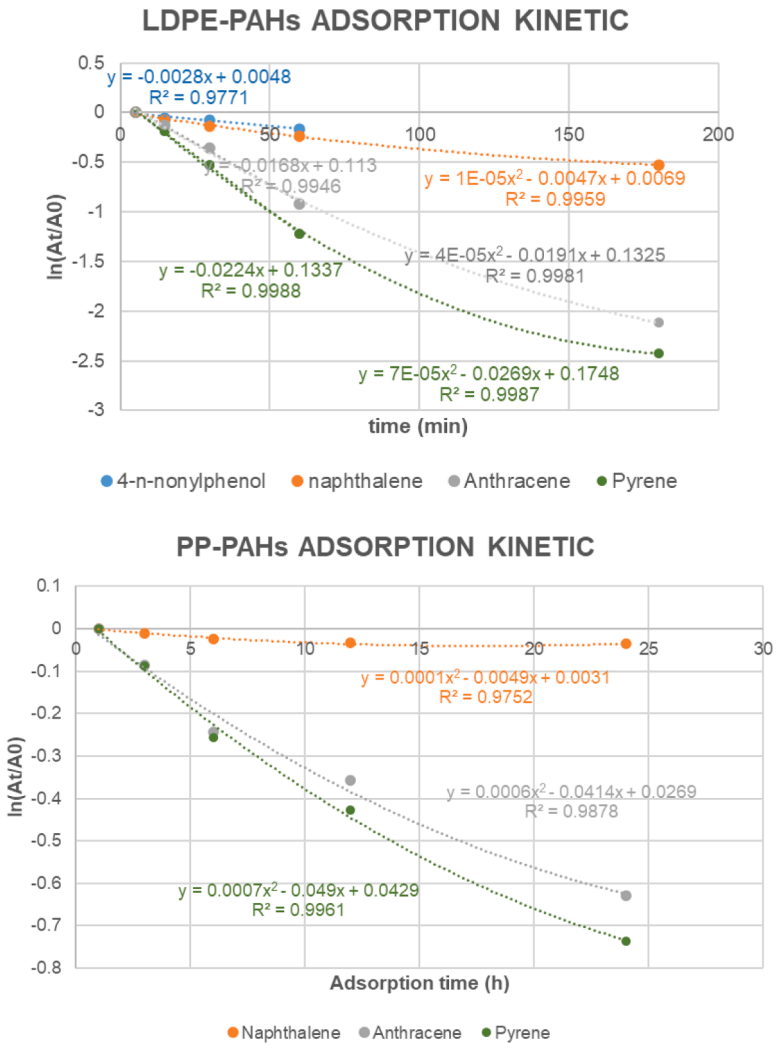

Fig. 1. PAHs adsorption on LDPE and PP pellets.

Table 2
LogP values, capacities at equilibrium (Qe), kinetic constants of second order (K_2) and R^2 for the second/first order kinetic model of PAHs and pesticides on LDPE and PP.

Analyte	LogP	Qe (LDPE) (μg/g)	K_2 (LDPE) (h^{-1})	R^2 (LDPE)	Qe (PP) (μg/g)	K_2 (PP) (h^{-1})	R^2 (PP)
naphthalene	3.3	2.3	0.5	0.9930	1.4	0.2	0.9930
anthracene	4.5	3.6	0.8	0.9984	2.1	0.3	0.9984
pyrene	4.9	3.8	1.1	0.9995	2.2	0.6	0.9995
4-n-nonylphenol	5.7	2.2	0.5	0.9965	<1	/	/
chlorpyrifos	5.0	6.0	2.9	0.9998	3.5	First order kinetic: 0.09	0.9928
clorfenvinfos	3.8	3.2	First order kinetic: 0.7	0.9896	1.0	0.4	0.9868
atrazine	2.6	1.2	2.4	0.9977	<1	/	/
metalaxyl	1.7	1.4	2.5	0.9983	1.4	First order kinetic: 0.04	0.9989
dichlorvos	1.4	1.7	0.5	0.9861	2.8	0.3	0.9904
alachlor	3.5	1.0	First order kinetic: 0.5	0.9926	<1	/	/

non-polar interactions, meaning adsorption efficiency increases with adsorbent non-polarity, the six pesticides studied differ in their structures and physicochemical properties. As a result, adsorption patterns vary for chlorpyrifos, atrazine, alachlor, and clorfenvinfos. LDPE and PP show trends similar to those observed for PAHs, with lower adsorption occurring as adsorbent hydrophobicity decreases. Interestingly, however, dichlorvos shows an increased adsorption capacity on PP than on LDPE. This may be due to specific structure-dependent interactions between dichlorvos and the adsorbent, which seem to play a dominant role despite dichlorvos having the lowest LogP value among the pesticides examined. In contrast, such an increase was not observed for metalaxyl, another analyte with a similarly low LogP value.

3.3. *Greenness evaluation*

The SPME-MOI-LEI MS method developed reveals good environmental performance across comprehensive greenness evaluations compared to established extraction-chromatography approaches. AGREE [39] assessment scores are 0.58 (SPME-MOI-LEI MS) (Fig. 4 A1), 0.51 (DI-SPME-GC–MS/MS) (Fig. 4 A2), and 0.42 (QuEChERS-LC-MS)

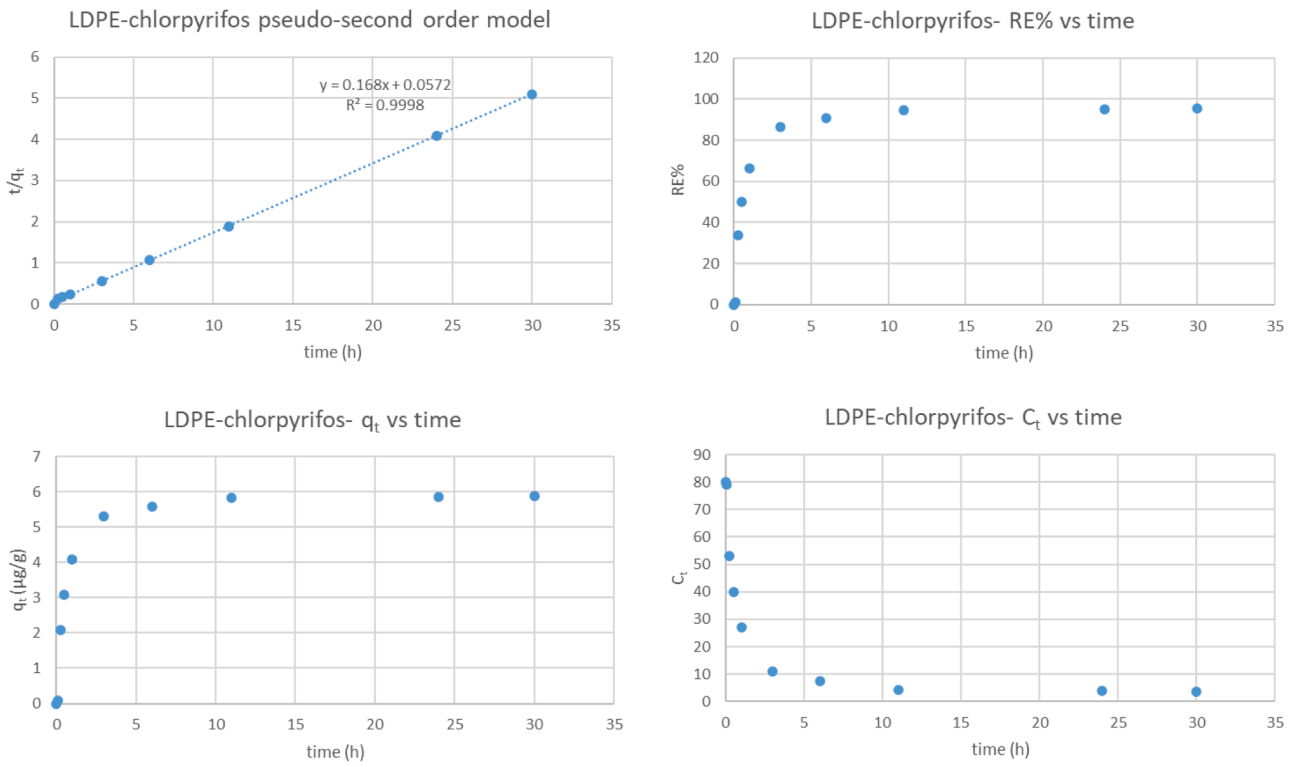

Fig. 2. Chlorpyrifos kinetic second order model and recovery (RE %), capacity at time t (Q_t) and concentration in solution at time t (C_t) plotted against adsorption time.

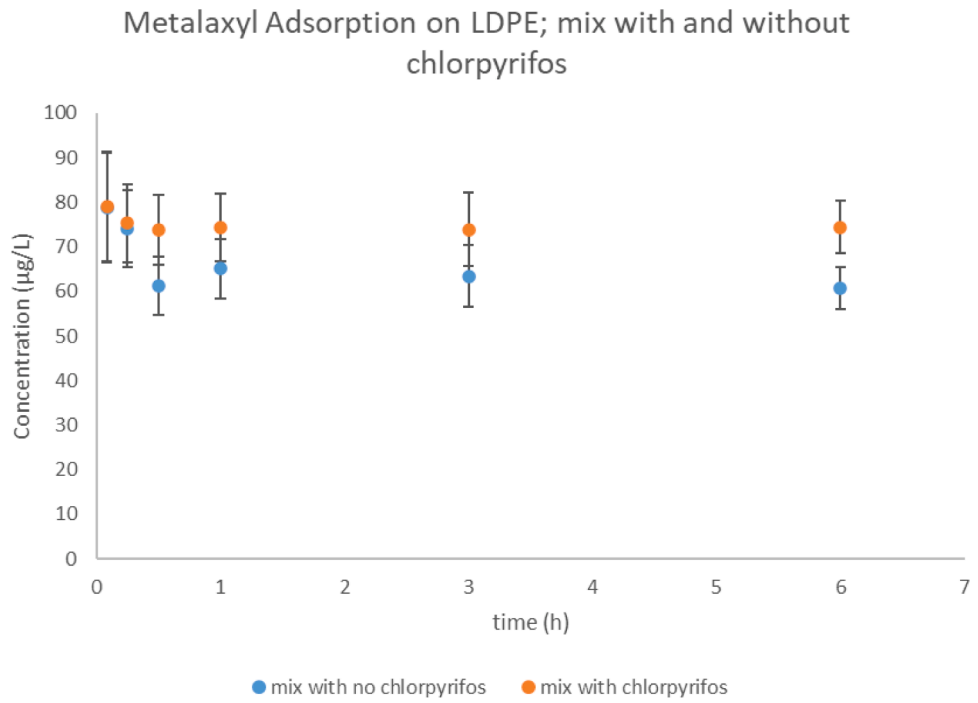

Fig. 3. Adsorption of metalaxyl on LDPE microplastics pellets in presence and absence of chlorpyrifos in the aqueous solution.

(Fig. 4 A3), with the SPME-MOI-LEI MS method showing high green segments across the twelve analytical principles, exhibiting predominantly green segments across twelve analytical principles; whereas, the conventional approach displayed extensive red coloring indicative of high solvent consumption and waste generation.

The AGREEprep index [40], which considers ten different greenness factors, is mainly focused on evaluating sample preparation greenness, revealed differences with scores of 0.51 (Fig. 4 B1), 0.47 (Fig. 4 B2), and 0.19 (Fig. 4 B3) for SPME-MOI-LEI MS, DI-SPME-GC–MS/MS, and QuEChERS-LC-MS methods, respectively, highlighting the environmental burden associated with complex multi-step QuEChERS extraction protocols.

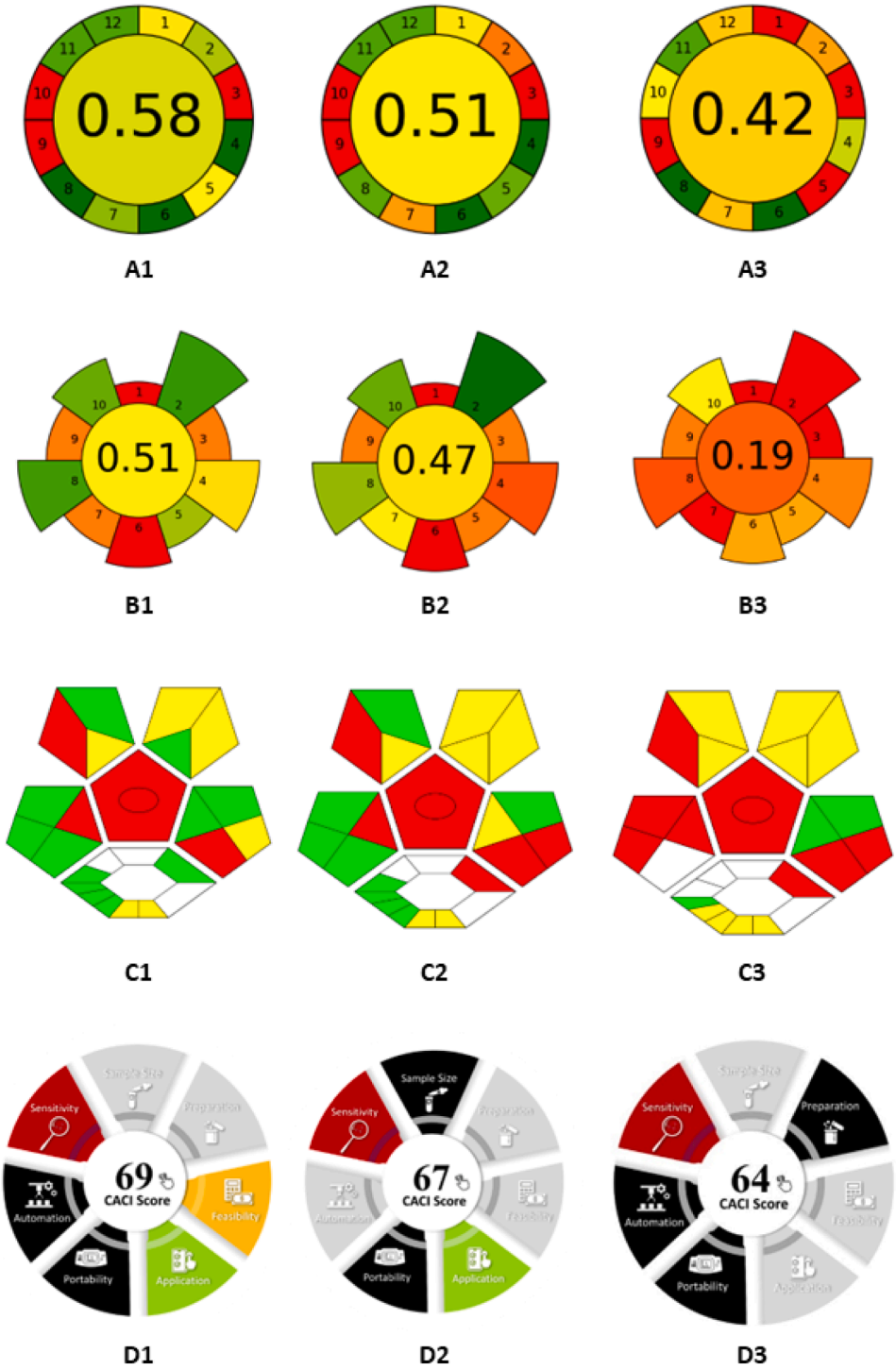

Fig. 4. AGREE (A), AGREEprep (B), ComplexGAPI (C) and CACI (D) greenness evaluation for SPME-MOI-LEI MS (1), DI-SPME-GC–MS/MS (2), QuEChERS-LC-MS (3) and SPME-MOI-LEI MS methods.

The ComplexGAPI software [41] is a modification of GAPI [47] which considers a wide range of parameters, including both pre-analysis and analysis, and focuses on instrumentation, energy consumption, waste generation, and reagent safety. The complex GAPI index in Fig. 4 C1, C2 and C3 shows that the SPME-MOI-LEI MS method resulted in better performance in sample processing stages through direct SPME fiber desorption via the MOI, eliminating complex sample preparation steps and associated chemical waste.

CACI index [42] emphasises small sample size, portability of instruments, analysis feasibility, and sensitivity. CACI scores 69 (SPME-MOI-LEI MS method) in Fig. 4 D1, 67 (DI-SPME-GC–MS/MS) in Fig. 4 D2, and 64 (QuEChERS-LC-MS) in Fig. 4 D3 account for the reduced chemical exposure, high sensitivity, and faster analysis of SPME-MOI-LEI MS method.

All four indices demonstrate that the SPME-MOI-LEI MS method provides a significant improvement in sustainable analytical practices through reduced chemical consumption and minimized waste generation while maintaining sensitivity and selectivity for PAH and pesticide determination in water.

4. Conclusions

This study proposes a green, fast and effective analytical method to monitor almost in real-time the concentration of the analytes during adsorption phenomena. SPME-MOI-LEI-MS allows a fast and accurate quantification of the analytes utilizing an ion source particularly suitable for PAHs analysis due to their volatility and low polarity. This instrumental setup minimizes matrix effect as ionization occurs in gas phase, allowing the simultaneous quantification of more analytes without internal standards. This study also proposes a new connectivity for the SPME-MOI-LEI interface solving carryover and improving linearity and reproducibility of the response. This study meant to provide initial information on the adsorption of PAHs and pesticides on microplastics, supporting future research on a wider range of pollutants such as pharmaceuticals and endocrine disrupting chemicals. Also, future research can consider more deeply some factors that can influence adsorption on MP surface, such as photo-oxidation, biofilms, salinity and pH. This article provides important information on the adsorption of chlorpyrifos on LDPE with recovery of 95 %, posing significant risk for aquatic environments. In addition, displacement effects caused by competition for the active sites of MPs was addressed for pesticides kinetic as metalaxyl, dichlorvos, alachlor and atrazine adsorption increases in absence of chlorpyrifos in pure water.

CRediT authorship contribution statement

Tommaso Grazioso: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Achu Kuriakose:** Writing – original draft, Formal analysis, Data curation, Conceptualization. **Genny Grasselli:** Writing – review & editing, Validation, Data curation. **Wei Zhou:** Writing – review & editing, Resources, Data curation. **Janusz Pawliszyn:** Writing – review & editing, Resources, Data curation. **Adriana Arigò:** Writing – review & editing, Supervision, Data curation. **Giorgio Famiglini:** Writing – review & editing, Supervision, Conceptualization. **Achille Cappiello:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare no conflicts of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.greeac.2025.100315.

Data availability

The data presented in this study are available on request from the corresponding author.

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