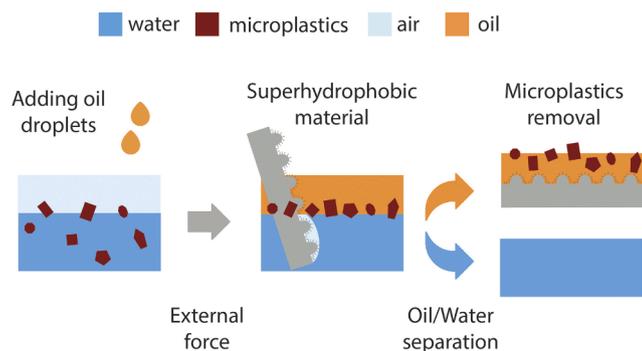


Superhydrophobic cotton fabrics for effective removal of high-density polyethylene and polypropylene microplastics: Insights from surface and colloidal analysis[☆]

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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Dodecanoic acid
Interface
Microplastics
Oil–water separation
PDMS
Polydimethylsiloxane
Superhydrophobic Surfaces

ABSTRACT

Hypothesis: The use of superhydrophobic materials to remove particulate pollutants such as microplastics is still in its infancy. In a previous study, we investigated the effectiveness of three different types of superhydrophobic materials - coatings, powdered materials, and meshes - for removing microplastics. In this study, we will explain the removal process by considering microplastics as colloids and taking into account their wetting properties as well as those of a superhydrophobic surface. The process will be explained through the interactions of electrostatic forces, van der Waals forces, and the DLVO theory.

Experiments: In order to replicate and verify the previous experimental findings on the removal of microplastics using superhydrophobic surfaces, we have modified non-woven cotton fabrics with polydimethylsiloxane. We then proceeded to remove high-density polyethylene and polypropylene microplastics from water by introducing oil at the microplastics-water interface, and we determined the removal efficiency of the modified cotton fabrics.

Findings: After achieving a superhydrophobic non-woven cotton fabric ($159 \pm 1^\circ$), we confirmed its effectiveness in removing high-density polyethylene and polypropylene microplastics from water with a removal efficiency of 99%. Our findings suggest that the binding energy of microplastics increases and the Hamaker constant becomes positive when they are present in oil instead of water, leading to their aggregation. As a result, electrostatic

[☆] The Corresponding Author gave a Young Investigator Perspective oral presentation at the 11th International Colloids Conference, 12-15 June 2022, Lisbon, Portugal.

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<https://doi.org/10.1016/j.jcis.2023.05.127>

Received 17 January 2023; Received in revised form 15 May 2023; Accepted 17 May 2023

Available online 22 May 2023

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interactions become negligible in the organic phase, and van der Waals interactions become more important. The use of the DLVO theory allowed us to confirm that solid pollutants can be easily removed from the oil using superhydrophobic materials.

1. Introduction

The global industrial revolution that occurred during the 19th century marked a major turning point in history, leading to the exponential growth in technology, processes and materials. The human population has also increased along with anthropogenic emissions of carbon dioxide resulting from rapid industrialization worldwide. These changes, caused by human activity, have given rise to a new geological epoch known as the Anthropocene [1,2]. Since the industrial revolution, the population, carbon dioxide emissions, ocean acidification, and energy consumption have all increased exponentially [3]. The mounting pressure exerted by humans on the environment has resulted in a range of environmental changes, including land degradation, climate change, and freshwater contamination [4]. These changes have led to numerous health effects, such as undernutrition, acute respiratory infections (from air pollution), and malaria, which are directly caused by environmental factors [5]. Unfortunately, this growth has been accompanied by the appearance of different types of pollutants such as a new variety of chemical compounds and materials, called emerging pollutants, appeared in the second half of the 20th century such as industrial additives, endocrine disruptors, drugs and microplastics, among others. Microplastics (MPs) have become a significant emerging pollutant in several ecosystems such as marine ones [6]. Although the plastics industry provides many functional and advantageous products, their waste and the improper disposal of their products are escalating plastic pollution worldwide [7]. Different types of products, like personal care products, contain MPs or their degradation leads to the formation of MPs. The challenge of plastic pollution has been recognized in seven of the Sustainable Development Goals from the 2030 Agenda of the United Nations that have been developed to conserve and sustainably use resources from oceans, seas and marine systems [8].

1.1. Microplastics

Microplastics are particulate matter with a size smaller than five millimeters in length with different compositions such as polyethylene (high/low density PE), polypropylene (PP) or polystyrene (PS) among others [9,10]. These solid pollutants can persist for hundreds of years due to their strong resistance to environmental stress while the amount of microplastics will reach up to 53 million metric tons [11,12]. MPs can enter the human body (by ingestion, inhalation or through the skin), causing cytotoxicity, disruption of the immune system or even neurotoxicity, among other adverse effects [13]. Additionally, metals and metalloids can be found on to the microplastic surface behaving as a pollutant vector [14,15]. As an example, 90% of the analyzed items obtained from the Mediterranean Sea were reported to correspond to artificial polymer materials such as straws, bottles and plastic pieces of different sizes, with the sources of these being recreational activities and poor waste management practices (38%) as well as sanitary and sewage items (7%) [16]. Nowadays, there are several technologies that are used to remove MPs in wastewater treatment plants, the most widely used being membrane separation processes, electrocoagulation, flocculation and air flotation [17,18]. Although these technologies are efficient in removing MPs, they are still inefficient in removing small-sized MPs that result from fragmentation through physical abrasion, biodegradation, chemical oxidation, ultraviolet radiation and photooxidation processes [19]. Despite the huge variety of technologies that have been used to remove MPs and the new methodologies that eliminate these persistent solid pollutants [20–23], the behavior of MPs in water and in mixtures with other fluids like oils has not been studied in depth and explained

from a physicochemical point of view. Therefore, considering MPs or nanoplastics (NPs) as colloids allows us to explain and contrast their properties during their separation from water. Herein, we report our recent findings of using three categories of superhydrophobic materials (coatings, powders and meshes) in the removal of MPs from water, taking advantage of the wetting properties of superwetttable surfaces and their relationship with those of MPs.

1.2. Superwettability

Superhydrophobic surfaces can be achieved with a wide variety of methods such as polymerization [24,25], electrodeposition [26,27] among others [28–31] in order to generate a hierarchical structure. Additionally, its surface free energy can be modified with fluorocompounds [32–37] or natural substances [38–41], where the compounds containing C-F bonds present lower surface free energy than those containing C-H bonds [42–47]. Superhydrophobic surfaces have water contact angles (WCA) higher than 150° and a contact angle hysteresis (CAH) lower than 10°. Additionally, they show self-cleaning properties when the sliding angle (SA) is lower than 10° and water droplets roll off the surfaces [48,49]. These surfaces present two different wetting states with high adhesive force and low adhesive force corresponding to the rose petal and the lotus leaf, respectively [50,51]. These properties can be explained considering three wetting models [52,53]. On one hand, Young's model defines the WCA (θ) as a relationship between the surface free energy of the phases present in the system: air, water and solid [54]. On the other hand, the Wenzel model considers the roughness of the solid surface to a homogeneous regime [55], while the Cassie–Baxter model defines a heterogeneous regime where the air is filling the cavities of the rough structure [56].

1.3. Microplastics as colloids

The MPs used in these experiments as well as those found in natural environments can be considered a dilute suspension of solid particles in aqueous media [60–63]. In fact, by utilizing the binding energy and the Derjaguin–Landau–Verwey–Overbeek theory, we were able to explain the removal of microplastics from water when in contact with superhydrophobic surfaces. This approach is a novel method in the field of microplastic removal and can be applied to better understand how other removal technologies may also work. By understanding the underlying mechanisms, it could be possible to develop more efficient and effective methods for removing microplastics from water beyond just superhydrophobic materials.

As previously described, according to Young's model, the wettability of a surface is defined by an intrinsic parameter of each compound, which is the surface free energy and the interactions of MPs at the interface are governed by the thermodynamics of adsorption. Thus, assuming that the MPs have a spherical shape, the binding energy (ΔE) of the solid pollutants is defined as follows (Eq. (1)):

$$\Delta E = \pi R_p^2 \gamma_{aw} (1 \pm \cos \theta_w)^2 \quad (1)$$

where γ_{aw} is the surface free energy of the air–water phase, θ_w the static WCA on the MP surface, and R_p the radius of the particulate matter (in this case, the MPs themselves). From the binding energy equation, it can be observed that as the MP size decreases, the wettability of the particles increases, resulting in a decrease in the binding energy that promotes the dispersibility of the MPs. In fact, this explains why these persistent solid pollutants are really difficult to remove from water.

Directly related to the wettability of MPs and the surface chemistry of the solid pollutants are the interactions between the MPs in an aqueous phase such as the electrostatic interactions as well as the van der Waals forces. The contribution of both factors is explained by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory that describes the stability and aggregation of colloids in a solution, which is typically water in the case of MPs. The global DLVO interaction is described as the summation of both contributions (Eq. (2)):

$$U_{DLVO} = U_{vdW} + U_{EDL} \quad (2)$$

Where the electrostatic interactions (UEDL) are related to the surface chemistry of microplastics such as the dissociation of functional groups at their surface while the van der Waals interactions (UvdW) are responsible of the attraction between the particles.

Alternatively, it has been shown that the separation of MPs can be carried out in the presence of different weak interactions between MPs using a removal agent, which, to date, has been PDMS. It has been reported that in addition to van der Waals forces, hydrogen bond interactions occur between the oxygen atom of PDMS and the hydrogen atom in the methyl group of PP-MP or the hydrogen atom of PE-MP [64]. Meanwhile, other types of MPs, such as PVC polymers containing chlorine atoms, may show an electronic effect because the lone pairs of electrons generate a negative density on the chlorine atom, improving the adsorption of PVC-MP on the PDMS surface due to the occurrence of electrostatic interactions as well as σ -p and p-p conjugations or π - π interactions [65].

2. Previous findings

Herein, we will show and revise our recent published articles about superhydrophobic/superoleophilic materials that can effectively remove MPs from water by taking advantage of their wetting properties. Superhydrophobic materials can completely remove MPs from water with efficiencies close to 100%, also avoiding the breakdown of the polymeric micropollutants. We will discuss three different types of materials (coatings, metallic powders and meshes) that have been used

to effectively remove MPs from water, taking into account their wetting properties and considering them as colloids (Fig. 1).

2.1. Coatings

To produce a superhydrophobic coating (WCA of $154 \pm 2^\circ$, an SA of $2 \pm 1^\circ$ and a CAH of 1°), aluminum (UNS A91070) was first anodized (60 min) before performing a liquid-phase deposition with dodecanoic acid to confer superhydrophobicity [66]. The removal of PP-MPs was carried out after the addition of an organic solvent and followed with stirring the system. While PP-MPs migrated from the aqueous phase to the organic one, the anodized surface was placed in contact with the solution and instantly removed all pollutants revealing an efficiency after three steps of 99% revealing (Fig. 2). In a technique analogous to the one used in anodization, a different coating was designed to fulfil this purpose. A composite superhydrophobic coating with excellent durability made of zinc laureate and TiO_2 particles was prepared and showed a WCA of $153 \pm 1^\circ$, a CAH of $1 \pm 1^\circ$ and an SA of $1 \pm 1^\circ$ [67]. As before, the MPs migrated to the oil after stirring and the coating was then moved across the solution to capture the oil and the MPs with an efficiency of 99%.

2.2. Powdered materials

Superhydrophobic (WCA = 154°) and superoleophilic (OCA = 0°) nanostructured metallic powder iron was used to remove oils from water, stabilized oil-in-water emulsions as well as HDPE-MPs showing efficiencies of 100% [68]. At the same time, a superhydrophobic magnetic CuFeCo powdered alloy was prepared (WCA of 162 ± 1 and a CAH of 1 ± 1) and used for oil/water separation as well as the removal of MPs from an aqueous solution. [69]. The capturing process of the microplastics with superhydrophobic powdered materials depends on the superwettability properties and the ability of the metallic particles to surround the microplastics. Under stirring, microplastics were displaced from the aqueous phase to the organic one because their oleophilicity. Then, the powdered materials surrounded the pollutants and under the

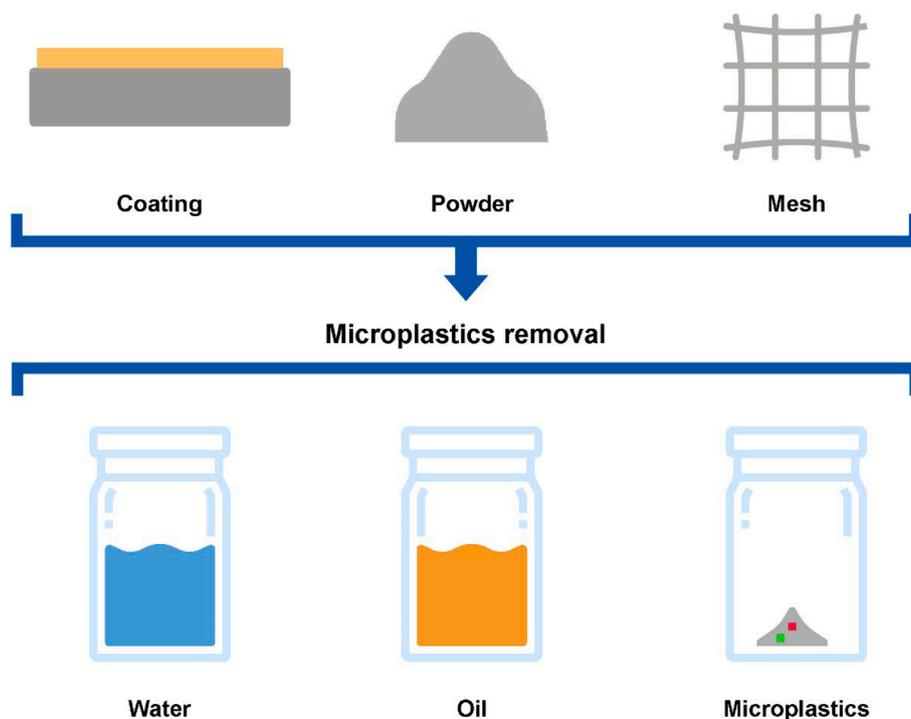


Fig. 1. Schematic of the three superhydrophobic materials (coatings, metallic powder and meshes) that have been used to remove solid pollutants, leading to three separated phases: water, oil and MPs.

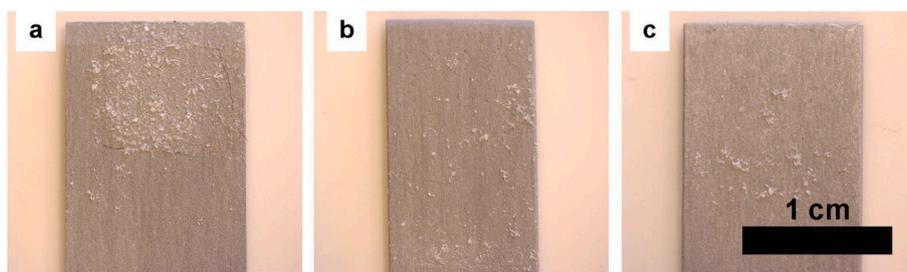


Fig. 2. Superhydrophobic coatings completely removed MPs after repeating the removal process three times: (a) 30 ± 4 MPs/mL were removed the first time, (b) 18 ± 2 MPs/mL were removed the second time and finally (c) 5 ± 1 MPs/mL were removed the third time. Reprinted with permission from [66].

influence of a magnetic field, the MPs were immobilized and the aqueous phase decanted (Fig. 3).

2.3. Meshes

The surface of a 304 stainless steel mesh was modified to confer superhydrophobicity/ superoleophilicity combining chemical etching and surface modification with dodecanoic acid (WCA = 169° and OCA = 0°) [70] and PDMS (WCA = 159° and OCA = 0°) [71]. The separation of MPs (HDPE and PP) in water was carried out in a laboratory-made device where the mesh was found at the value of the SA = 5° (Fig. 4a and b). The separation device led to the complete separation of water from the oil (100%) and MPs (99%) mixture (Fig. 4c). Additionally, the size of the microplastics during the separation process did not reveal changes (Fig. 4d and e).

In all the examined cases, the MPs were found in the aqueous phase. In fact, because of their intrinsic hydrophobic properties, the solid pollutants are located at the water–air interface. Once the minimum quantity of oil is added and an external force to bring together the solid pollutants is applied (movement or stirring/centrifugation), the MPs migrate from the aqueous phase to the organic one. Three different types of superhydrophobic materials (coatings, powdered materials and meshes) that also present superoleophilicity have been used to remove MPs from water, adsorbing the organic phase containing the MPs and completely removing all the MPs and oil from the aqueous phase at extremely high efficiencies (>99%) (Table 1).

As seen, the described materials present efficiencies of 99 % in all cases, which clearly reveals that all of them could be used to remove oils and microplastics from water without significant issues regarding their

efficiency and the ability to remove pollutants. In fact, these experiments allowed to show for the first time that superhydrophobic materials can effectively remove solid pollutants such as microplastics. Moreover, considering the ability to scale up these materials, it is important to take into account that a wastewater treatment plant operates continuously. Therefore, the materials used to remove oils and microplastics cannot be added and removed constantly. Because of this, the described materials (coatings, powder and meshes) should be used under continuous conditions, which makes meshes the most suitable material to use. In fact, superhydrophobic meshes can be easily prepared, and the experimental procedure is easy to reproduce on large surfaces. Additionally, using these meshes as a filter would be useful for implementing them in a continuous system, as they are easy to remove and replace. In terms of cost-effectiveness, the difference is marked by the price of the reagent. In fact, PDMS is more expensive than lauric acid, and since the etching process is exactly the same, the use of a cheaper reagent would be important. Additionally, the modified mesh with lauric acid also exhibits a higher WCA (169°) than in the case of modified meshes with PDMS (159°), which leads to low adherence of solids and avoids (bio)fouling of the surface due to its self-cleaning properties. In summary, for large quantities of wastewater containing microplastics or oils, it would be useful to consider using a superhydrophobic mesh modified with lauric acid to continuously remove microplastics. The use of previously described superhydrophobic surfaces cannot be considered only because the ability to remove microplastic, what is the most innovative part, but also because the ability to remove oils of different densities, viscosities as well as stabilized emulsions. This ability to completely remove two types of pollutants would be useful for wastewater treatment plants. Moreover, these

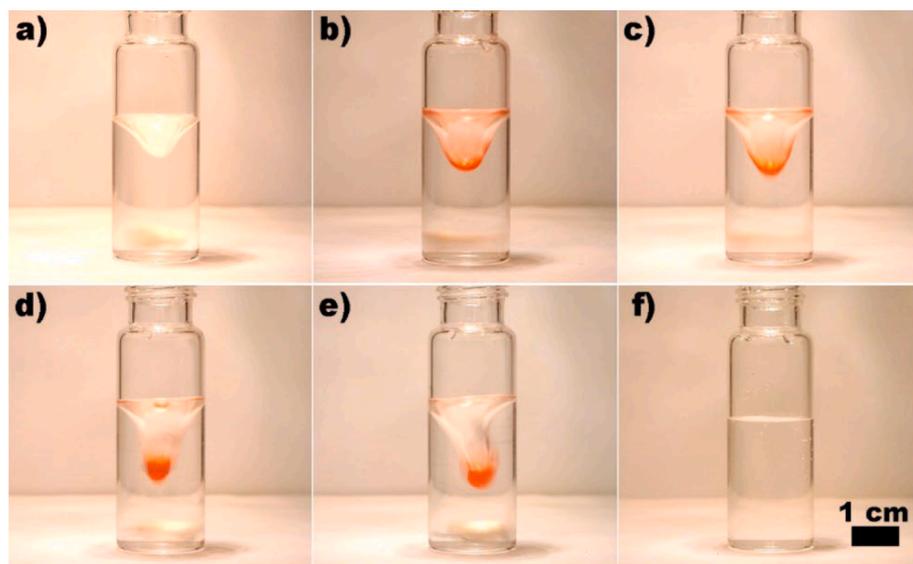


Fig. 3. The use of powdered materials such as powdered iron or a CuFeCo alloy can be divided into different stages (the water phase and the organic phase (red) can be seen): (a) under constant stirring, MPs are displaced to the stirring vortex; (b) oil was added to the system; (c–e) superhydrophobic powdered material was added to the vortex, which increases in length; and (f) water without the presence of MPs or oil. Reprinted with permission from [68]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

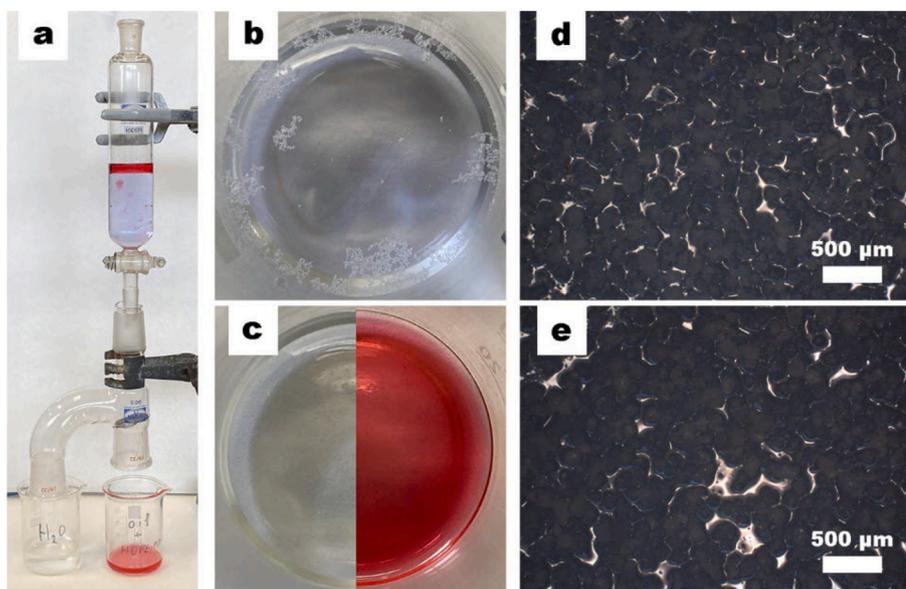


Fig. 4. The separation of MPs using meshes (modified with dodecanoic acid and PDMS) was carried out as follows: (a) a laboratory-made device containing water (blue) and hexane (red) was used for the removal of HDPE-MPs; (b) the aqueous phase with HDPE-MPs; (c) the aqueous phase (left) without the presence of HDPE-MPs and the organic phase (right) containing HDPE-MPs and hexane; HDPE-MPs (d) before the separation process and (e) after the process, with the size of the MP not affected by the organic solvent. Reprinted with permission from [70]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Summary of the three superhydrophobic materials used to remove MPs.

	Material	WCA	MP	Size	Efficiency	Reference
Coating	Al/dodecanoate	154°	PP	262 μm	99%	[66]
	Al/TiO ₂ /dodecanoate	153°	HDPE	133 μm	99%	[67]
Powder	Fe/dodecanoate	154°	HDPE	273–1250 μm	99%	[68]
	CuFeCo/dodecanoate	162°	HDPE	270–1240 μm	99%	[69]
Mesh	304SS/dodecanoate	169°	HDPE, PP	133–200 μm	99%	[70]
	304SS/PDMS	159°	HDPE	133 μm	99%	[71]

materials can be used to remove emerging pollutants that the current wastewater treatment plants may not be able to remove due to their small size or low concentration. Additionally, the ability of superhydrophobic surfaces to repel water can also reduce (bio)fouling and clogging of filtration systems, improving their efficiency. While the scalability of these materials makes them a promising option for large-scale wastewater treatment, it is important to address various limitations before implementing them. One such limitation is their cost, which should be reasonable and justifiable relative to their performance and benefits. In addition, these materials should be environmentally sustainable to avoid any negative impact on the environment, and the materials used in wastewater treatment plants must comply with relevant regulatory standards and requirements. As mentioned earlier, the use of superhydrophobic materials did not result in any change in the size of the microplastics used, suggesting that neither the superhydrophobic materials nor the organic phase had any effect on the solid pollutant. Additionally, in all the cases studied, the solid pollutants remained unchanged in terms of their shape. The only notable difference in morphology was observed in the case of powdered materials, where the stirring process caused the microplastics to reorganize into a more rounded shape. In the earlier studies, various oils (such as hexane, petroleum ether, and xylene) and types of microplastics (PP and HDPE) were used to investigate any notable differences between the use of oils and solid pollutants. However, as discussed in each respective article, no significant differences in terms of efficiency or selectivity were observed, since each type of oil was able to eliminate PP and HDPE microplastics with efficiencies exceeding 99%. As different types of chemical compounds there is an associated risk for health or environment if they are not well treated. Fortunately, PDMS as well as lauric acid (dodecanoic acid) are commonly used in various industrial applications, including medical devices, food packaging, and personal care products for PDMS or production of cosmetics, detergents, and

lubricants in case of lauric acid. In contrast, both compounds could be harmful if ingested or inhaled in large amounts according to the substance infocards from the European Chemical Agency (ECHA). Regarding this issue, in the revised published articles, the amount of PDMS or lauric acid were low as well as controlled in order to reduce the quantity of reactants or to ensure to produce large quantities of superhydrophobic materials in order to reduce residues. In summary, while PDMS and dodecanoic acid have many beneficial applications, their potential environmental and health impacts should be carefully considered and mitigated to ensure their safe and responsible use.

3. Superhydrophobic cotton fabrics

As previously described, during MPs removal, the presence of an organic phase is a key factor for promoting the migration of solid pollutants from water to the organic phase. Therefore, in the following section, a superhydrophobic cotton fabrics (WCA = $159 \pm 1^\circ$) surface will be used to remove HDPE and PP. The experimental results that will be obtained on the removal ability of superhydrophobic cotton fabric will confirm its potential for microplastics removal and demonstrate the possibility of studying the removal process from both surface and colloidal perspectives.

3.1. Experimental procedure

The surface modification of cotton woven fabric (2 cm × 2 cm in size, a surface weight of $112 \pm 5 \text{ g/m}^2$, a thickness of 0.25 mm and purchased from the local market) was carried out coating the substrate with polydimethylsiloxane (PDMS) (Sylgard 184 Silicone Elastomer) purchased from Dow Chemicals. Initially, cotton fabric was cleaned with ethanol and dried in the oven at 80 °C for 30 min. Then, the two-part kit containing the pre-polymer and curing agent were mixed in a 10:1

stoichiometry. Immediately after that, a 1% w/w PDMS in tetrahydrofuran (THF) solution was prepared. Finally, the cotton fabric was dip-coated in the PDMS solution for 1 h and rested for 24 h at room temperature to cause the crosslinking process of the elastomer. This procedure was repeated twice.

3.2. Characterization techniques

Electron microscopic characterization of the cotton surface was carried out with a JEOL J-7100 field emission scanning electron microscope (FESEM). Semi-quantitative elemental analysis was performed by Energy-Dispersive X-ray spectroscopy (EDS). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Fourier Bomem ABB FTLA system in the range of $4000\text{--}525\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . Additionally, High-Resolution X-Ray Photoelectron Spectroscopy (HR-XPS) was used on a PHI ESCA-5500 using a monochromatic X-ray source ($K\alpha(\text{Al}) = 1486,6\text{ eV}$ and 350 W) and Multipak (9.8) was used for the deconvolution analysis. To measure the contact angles, $3,5\text{ }\mu\text{L}$ droplets of deionized water (WCA) or hexane (OCA) were put into the surface of the samples and by using a Levenhuk digital microscope 3 photographs in different parts of the surface where taken. The reported values are the average of these

measurements of droplets. In case of HDPE-MPs and PP-MPs the WCA and OCA measurements were performed as follows: the solid pollutants were sprinkled over a glass slide containing an adhesive; then the samples were flattened by another glass slide to prevent roughness effects [72], the reported values are the average of three measurements at different parts of the microplastics surface. Finally, the particle-size distribution of microplastics was assessed by measuring the size of 200 MPs in FESEM micrographies and determining particle size with ImageJ.

3.3. Microplastics removal

To remove microplastics from water (deionized water) a solution was prepared with a concentration of $60 \pm 5\text{ MPs/mL}$ of HDPE ($260 \pm 5\text{ }\mu\text{m}$) and PP ($250 \pm 10\text{ }\mu\text{m}$) microplastics, both microplastics showed spherical shape and were purchased from Abifor. Then, hexane (purchased from Scharlab) was carefully added until the microplastics migrated to the organic phase. After that, the superhydrophobic cotton fabric surface was moved towards the hexane droplets containing the HDPE and PP MPs, respectively. This process was repeated until the microplastics were completely removed. To quantify the amount of microplastics removed, a Levenhuk digital microscope was used to

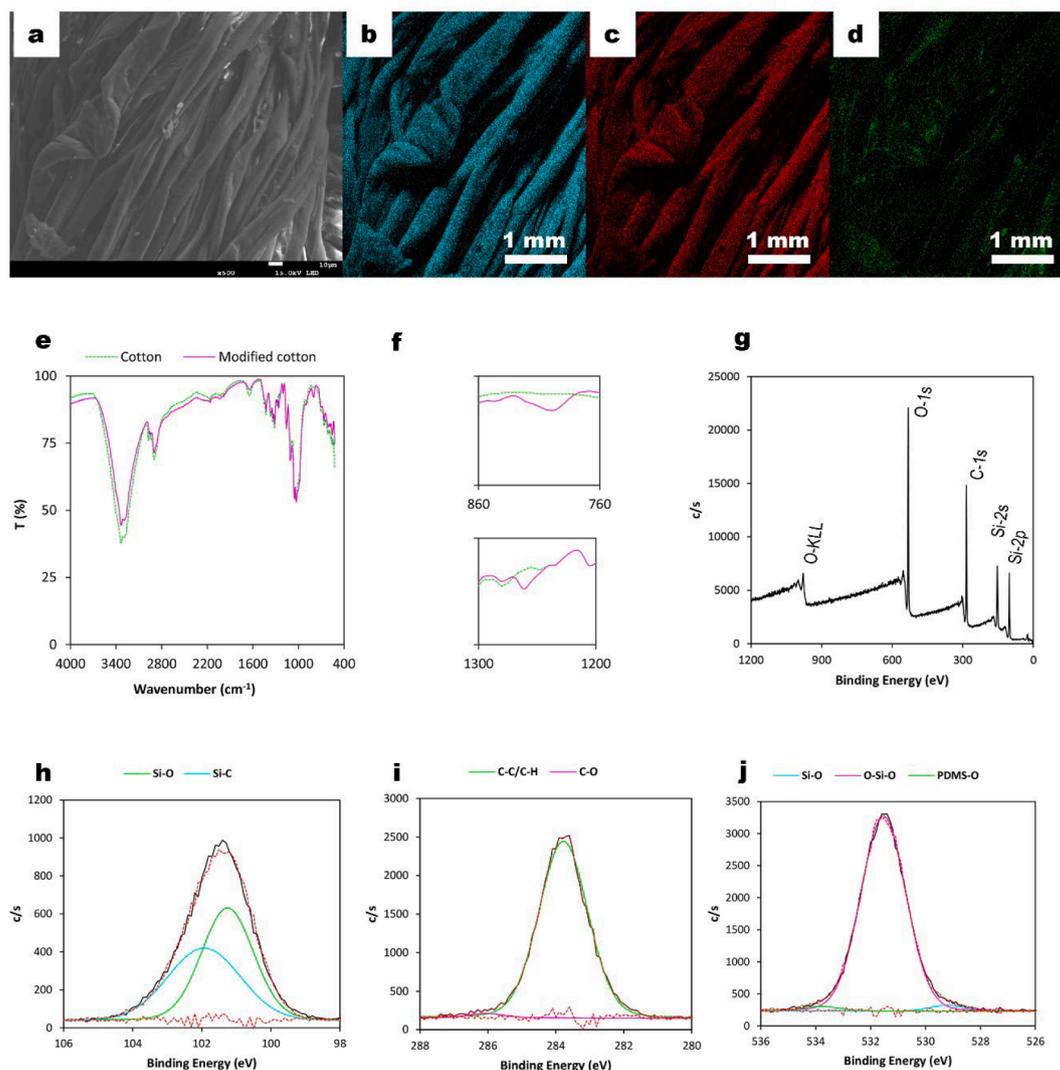


Fig. 5. FESEM micrographs of the cotton fabric coated with PDMS: a) morphology of the modified cotton and corresponding EDS maps: b) carbon c) oxygen and d) silicon. Surface chemical composition: e) ATR-FTIR of the superhydrophobic cotton fabric revealing the presence of PDMS and f) magnification that shows two characteristics bands of PDMS. HR-XPS analysis corresponding to g) general spectrum, h) Si-2p, i) C-1 s and j) O-1 s.

capture images, which were then analysed with the ImageJ software to count the number of microplastics captured by the superhydrophobic surface; the reported MPs counts are the average of three capture experiments and counting the number of MPs in the immersed surface. To evaluate the reusability of the superhydrophobic cotton fabric for removing microplastics, the fabric surface was subjected to a thorough washing process using ethanol to remove both the oil and microplastics. The surface was then dried at 50 °C, making it available for reuse.

4. Results and discussion

The FESEM microscope analysis was used to show the surface morphology as well as the semiquantitative elemental composition (EDS). The FESEM and EDS characterization of the cotton fabrics before surface modification is shown in [Supplementary materials \(Fig. 1 SM\)](#). FESEM micrograph shows the cotton structure that presents threads woven across the fabric ([Fig. 5 a](#)) with a thread width of $19 \pm 2 \mu\text{m}$ caused by the PDMS deposition on the cotton surface ($14 \pm 1 \mu\text{m}$ before surface modification). The semiquantitative EDS (wt %) showed the presence of 57.40 % O ($K\alpha = 0.5 \text{ eV}$), 40.47 % C ($K\alpha = 0.277 \text{ eV}$) and 2.12 % Si ($K\alpha = 1.379 \text{ eV}$) revealing the presence of silicon because the surface modifications with PDMS. At the same time, the EDS map ([Fig. 5 b - d](#)) showed the presence of carbon, oxygen as well as silicon that can be assigned to the presence of PDMS at the cotton fabric surface. ATR-FTIR spectroscopy was performed to establish the presence of chemical bonds at the surface level of the untreated cotton fabrics as well as the modified surface with PDMS ([Fig. 5 e](#)). Untreated cotton and PDMS modified cotton showed peaks regarding the cotton chemical structure. A wide band *ca.* 3320 cm^{-1} was assigned to $\nu\text{O-H}$ and a narrow peak at *ca.* 2900 cm^{-1} to $\nu\text{C-H}$ [73–75]. Asymmetric and symmetric νCH_2 from the alkyl chains on the cotton structure appeared at *ca.* 2971 cm^{-1} and *ca.* 2902 cm^{-1} , respectively [75]. A wide and low intense band at *ca.* 1622 cm^{-1} was assigned to $\nu\text{C=O}$ [75]. A group of intense and narrow peaks *ca.* 1000 cm^{-1} were assigned to C–H bending at *ca.* 1369 cm^{-1} , C–O bending at *ca.* 1314 cm^{-1} and the most intense peak at *ca.* 1030 cm^{-1} was assigned to C–O stretching [74,75]. On the other hand, the ATR-FTIR spectrum of the cotton sample modified with PDMS presented in addition to the previously mentioned peaks, a band at *ca.* 1264 cm^{-1} assigned to Si–C bending ([Fig. 5 f](#) at the bottom) and a less intense band assigned to $\nu\text{Si-C}$ at *ca.* 809 cm^{-1} that corresponds to the presence of PDMS at the surface of the cotton fabrics ([Fig. 5 f](#) at the top) [73,76]. HR-XPS was used to confirm the presence of PDMS found in the ATR-FTIR characterization. In case of XPS general spectrum ([Fig. 5 g](#)), different elements can be detected according to the surface treatment with PDMS. These elements were Si-2p (102 eV), Si-2s (152 eV), C-1s (284 eV), O-1s (532 eV) and O-KLL (977 eV). In the case of Si-2p ([Fig. 5 h](#)) two deconvolutions were found at 101 eV relative to Si–O bond and 102 eV related to Si–C [77–80]. In the C-1s ([Fig. 5 i](#)) the signal was deconvoluted into two peaks at 284 eV and 286 eV assigned to C–C/C–H and C–O bonds respectively [81,82]. Finally, in the case of O-1s ([Fig. 5 j](#)) there were three different deconvolutions at 529 eV assigned to Si–O at 531 eV assigned to PDMS–O and 534 eV from O–Si–O bonds in PDMS [83,84].

The interlacing of the cotton fabric fibers as well as the microstructure observed for each fiber after coating with PDMS generate a new hierarchical structure which, combined with the low surface energy of the PDMS will change the wetting properties. Moreover, through a combination of spectroscopic techniques including EDS, ATR-FTIR, and HR-XPS, we were able to confirm that the surface of the cotton fabrics was coated with PDMS. Specifically, we observed a strong Si signal in EDS and its corresponding map that showed that the cotton fabrics was coated with Si, the presence of Si–O and Si–C bonds in the ATR-FTIR spectra that are characteristic bands of PDMS, and characteristic PDMS signals of Si, C, and O in the HR-XPS spectra. Having confirmed that the cotton fabric was coated with PDMS, it should be noted that this compound exhibits low surface free energy (19.8 mN/m). When combined with the surface structure, it changes the wetting properties of the

substrate, promoting superhydrophobicity.

To determine the wetting properties the WCA as well as the OCA were measured for the prepared cotton fabric and the microplastics as well. The WCA as well as OCA for unmodified cotton fabrics showed total water and oil sorption as shown in [Supplementary material \(Fig. 2 SM\)](#). The WCA of the modified cotton fabric with PDMS was $159 \pm 1^\circ$ clearly indicating superhydrophobicity ([Fig. 6 a](#)). With regard to the microplastics, the measurements were $WCA = 140 \pm 1^\circ$ for HDPE-MPs and $WCA = 141 \pm 4^\circ$ in case of PP ([Fig. 6 b and c](#)). The OCA was 0° in case of PDMS modified cotton fabrics showing superoleophilic properties ([Fig. 6 d](#)) while both MP (HDPE and PP) also exhibited $OCA = 0^\circ$ with instant absorption ([Fig. 6 e and f](#)). Then, both solid pollutants showed hydrophobicity and superoleophilicity. The sliding angle of the cotton fabrics was measured and found to be $7 \pm 2^\circ$, indicating that the surface is superhydrophobic and shows self-cleaning properties. When the cotton fabric surface is covered with microplastics ([Fig. 6 g](#)), they can be easily removed from the surface ([Fig. 6 h](#)). This is a crucial feature as it enables effortless removal of accumulated microplastics from the surface. The durability of the superhydrophobic cotton fabrics against organic solvents was also investigated, and it was found to exhibit high resistance against hexane and xylene, without any significant changes in both the contact angle and sliding angle. As a result, due to their self-cleaning properties and solvent resistance, the superhydrophobic surface can be used repeatedly (up to 20 times) without any significant modification of its wetting properties. Additionally, the oil/water separation mechanism containing microplastics can be explained by the well-known Young-Laplace equation [57–59] (Eq. (3)):

$$\Delta p = -4\gamma_{ow}(\cos\theta_w)/d \quad (3)$$

where Δp is the intrusion pressure, γ is the surface free energy, θ_w the WCA of the modified membrane and d the diameter of the pore. After analyzing the results of the contact angle measurements, it can be inferred that the Laplace pressure exhibits a positive value at a contact angle of 159° for water, while it displays a negative value at a contact angle of 0° for oil. These outcomes serve as an indication that the superhydrophobic cotton fabric was impermeable to water, but oil can permeate the solid. Consequently, the oil and water separate, leading to o/w separation containing MPs.

The combination of the surface morphology of the coated cotton fabrics with the presence of PDMS leads to superhydrophobic properties that were assigned to the heterogeneous regime of Cassie-Baxter. In this wetting regime, where the cavities of the substrate were filled with air instead of water which makes it difficult for the liquid to wet the surface. This phenomenon causes an increase of the WCA ($159 \pm 1^\circ$). The presence of the air pockets also increases the surface area of the coated cotton-water (solid-liquid) interface, which reduces the contact area between the liquid and the surface. In contrast, the superoleophilicity was caused because the cavities were filled with hexane leading to instant oil adsorption and increase the contact area between the solid-liquid interface, in this case the coated cotton-hexane. Additionally, the WCA and the OCA measurements of HDPE and PP microplastics showed hydrophobicity and superoleophilicity due to the low surface free energy of these polymeric materials caused by the presence of long chains of C–H bonds [85] as well as their morphology and roughness. As will be discussed later, the presence of the organic phase as well as the superoleophilicity of the solids (modified cotton fabrics and microplastics) allows both phases (solid and oil) to quickly come into contact and improving the removal efficiency.

The PDMS coated cotton fabrics were used to remove microplastics ($60 \pm 7 \text{ MPs/mL}$) from an aqueous solution and hexane was used as organic phase. In order to determine the ability to remove MPs, the concentration (C_{MPs}) of HDPE and PP microplastics were measured, and the removal efficiency was determined as follows (Eq. (4)):

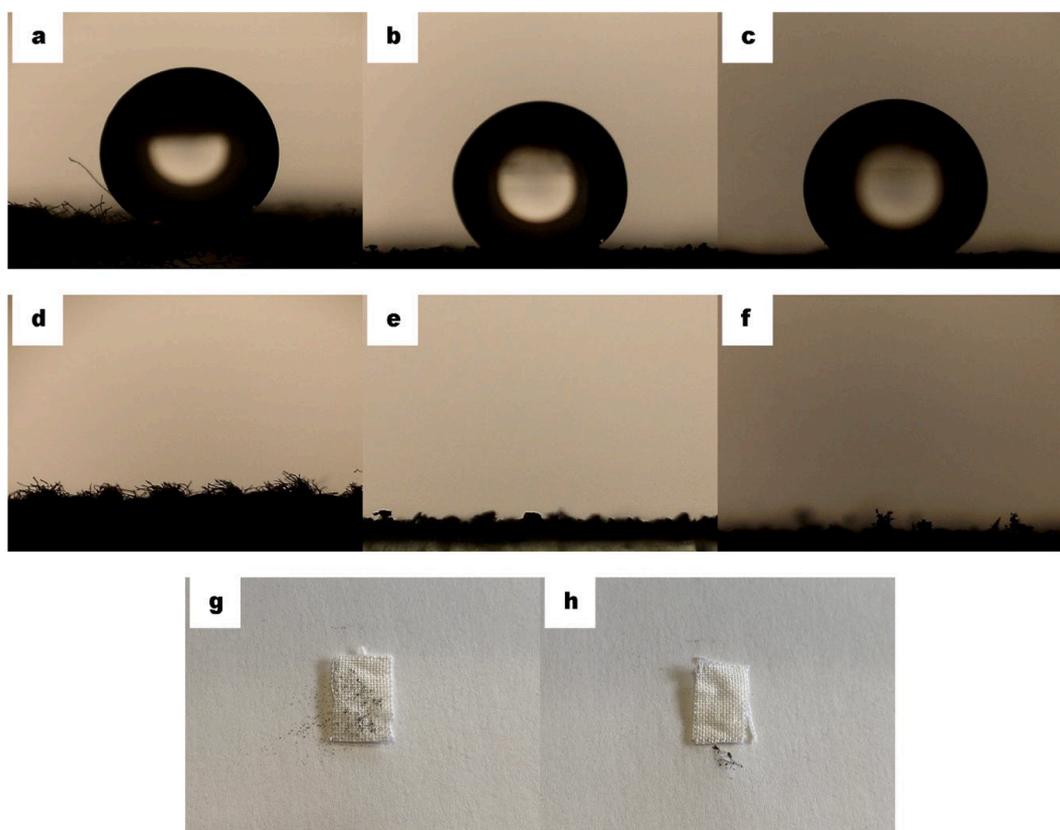


Fig. 6. Contact angle measurements: (a) water contact angle of superhydrophobic cotton fabric ($159 \pm 1^\circ$), (b) WCA of HDPE-MPs ($140 \pm 1^\circ$) revealing hydrophobicity, (c) WCA of PP-MPs showing hydrophobicity ($141 \pm 4^\circ$), (d) OCA of the modified cotton fabric showing oleophilicity (0°), (e) HDPE-MPs showing an OCA of 0° as well as in case of (f) PP-MPs (OCA = 0°). Both types of microplastics showed instant adsorption leading to oleophilicity, (g) superhydrophobic cotton fabric covered with colored microplastics and (h) because of self-cleaning properties the microplastics were completely removed.

$$\xi(\%) = \frac{C_{MPs}}{C_{0,MPs}} \cdot 100 \quad (4)$$

where $C_{0,MPs}$ and C_{MPs} are the concentrations of the microplastics (MPs/mL) before and after each removal process, respectively. In case of microplastics concentration (Fig. 7), the modified cotton fabrics surface was able to remove 52 ± 1 HDPE-MPs/mL and 54 ± 1 PP-MPs/mL from

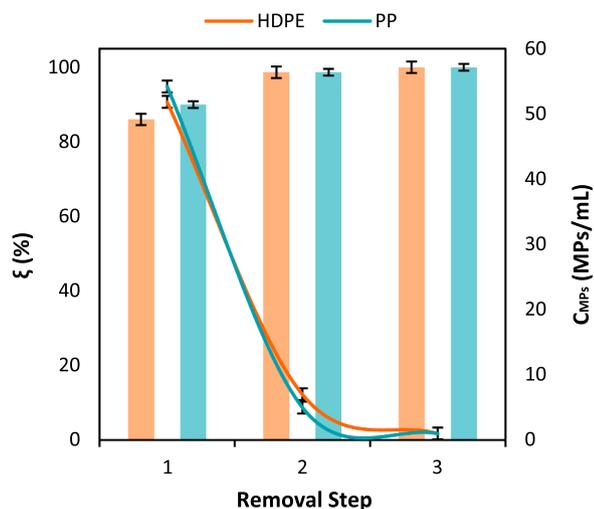


Fig. 7. The removal efficiency (ξ) for each step (left) and the microplastics concentration (C_{MPs}) for each solid pollutant (HDPE and PP). The removal efficiency increased up to 99 % while the microplastics concentration decreased after each step.

the oil droplet and required 5 s in both cases. After the first step, there were still present HDPE-MPs in the organic phase so the superhydrophobic cotton fabric was reused to repeat the process. In this second step, 7 ± 2 HDPE-MPs/mL and 5 ± 1 PPMs/mL were removed, and it was necessary 3 s. Finally, the process was repeated for a third time and 1 ± 1 MPs/mL were removed for HDPE and PP solid pollutants and required nearly a second. Regarding the removal efficiency, the values increased until the microplastics were completely removed. Then, the overall removal efficiency was higher than 99 %.

As it can be seen, HDPE-MPs as well as PP-MPs concentration decreased after each removal stage, while the removal efficiency increased. In the first removal step, after placing the superhydrophobic cotton fabrics into contact with the hexane droplet containing the microplastics, it rapidly adsorbed the oil with the microplastics because the superoleophilic properties of the modified cotton fabrics. At this point, the superhydrophobic surface was saturated with hexane and microplastics, covering a cotton surface of 1.2 cm^2 for HDPE-MPs and 1.1 cm^2 for PP-MPs, and it was no longer able to remove more pollutants. Then, in the second step and third step, as the remaining quantity of microplastics at the aqueous phase decreased, the hexane phase was completely adsorbed to the superhydrophobic surface. In these two steps, the total cotton fabric covered with microplastics was 2 cm^2 for HDPE-MPs and 2.2 cm^2 for PP-MPs in case of second step and 3.3 cm^2 for each type of microplastics in case of the third step.

During the removal process, MPs are transported to the oil–water interface and then penetrate the interface before being adsorbed in the organic phase. In the case of hexane, microplastics are found at the top of an oil/water mixture due to their lower density ($\rho_o = 0.655 \text{ g/mL}$) compared to water density ($\rho_w = 0.997 \text{ g/mL}$). A mechanic external force promotes the transport of MPs from the aqueous phase to the

organic one, which improves the gravity-driven transport from one phase to the other. Meanwhile, the MPs remain at the oil/water interface without penetrating any fluid. In fact, the effects of gravity are produced by the large mismatch in densities between that of the MPs and that of the solvent as well as a decrease in the dynamic viscosity from that of water (1.00 cP) to those of the organic solvents like hexane (0.31 cP). In the case of the binding energy (ΔE) of the MPs at the interface, the presence of an organic phase can be considered in the removal of MPs. Therefore, Eq. (1) can be modified as follows (Eq. (5)):

$$\Delta E = \pi R_p^2 \gamma_{ao} (1 \pm \cos \theta_o)^2 \quad (5)$$

where γ_{ao} is the surface free energy of the air–oil interface, θ_o the OCA on the MP surface and R_p the radius of the MPs. Therefore, ΔE can be calculated for the aqueous phase and the organic one to explain the behavior of MPs in each phase. As an example, if water ($\gamma_{aw} = 72.0$ mN/m) and hexane ($\gamma_{ao} = 18.3$ mN/m) are considered the aqueous and the organic phase, respectively. Moreover, HDPE-MPs ($R_p = 130$ μm) and PP-MPs ($R_p = 125$ μm) are the solid pollutants, with each fluid presenting their respective contact angle measurements HDPE-MPS ($\theta_w = 140^\circ$ and $\theta_o \sim 0^\circ$) and PP-MPs ($\theta_w = 141^\circ$ and $\theta_o \sim 0^\circ$). Then, in case of HDPE-MPs, the binding energies for water and oil will be -5.091×10^{10} $k_B T$ and -0.553 $k_B T$, respectively while in case of PP-MPs, the binding energies will be -4.271×10^{10} $k_B T$ for water and -0.511 $k_B T$ for hexane. Taking into account these results and Eq. (5), it can be concluded that at higher values of ΔE , MPs tend to aggregate rather than disperse, therefore making it easier to remove them from oil than from water.

Once MPs move from water to the organic phase, water molecules are no longer present and cannot ionize the surface functional groups of the MPs. Therefore, the Coulombic interactions between the surfaces of the MPs and the electrostatic cloud are no longer present, decreasing the repellency between the solid pollutants. In the case of van der Waals interactions, the Hamaker constant, which describes molecular interactions, should be considered [86–88]. This parameter can be considered in both phases (water and oil) to explain the behavior of MPs in both fluids during their removal. Usually, the Hamaker constant (A) is described as the relationship between two objects of different materials (A_{33} and A_{22}) in a common fluid (A_{11}) (Eq. (6)).

$$A_{312} = (\sqrt{A_{33}} - \sqrt{A_{11}})(\sqrt{A_{22}} - \sqrt{A_{11}}) \quad (6)$$

However, in our particular case, using the same type of MPs (where the objects are $A_{33} \sim A_{22}$), the equation can be modified as shown in Eq. (7):

$$A_{212} = (\sqrt{A_{22}} - \sqrt{A_{11}})(\sqrt{A_{22}} - \sqrt{A_{11}}) \quad (7)$$

Therefore, if we consider, that the MPs are composed of PP and HDPE ($A_{22-PP} \sim 6.06 \times 10^{-20}$ J and $A_{22-HDPE} \sim 6.34 \times 10^{-20}$ J) and are in water ($A_{11} \sim 3.7 \times 10^{-20}$ J) or in hexane ($A_{11} \sim 6.0 \times 10^{-22}$ J), the results from Eq. (7) for the Hamaker constant of the MPs in each fluid (A_{212}) will be: 2.90×10^{-21} J for water and 4.91×10^{-20} J for hexane in case of PP-MPs and 3.53×10^{-21} J for water and 5.17×10^{-20} J for hexane in case of HDPE-MPs. As can be observed, these results are positive, indicating a van der Waals attractive interaction between the MPs and, therefore, their aggregation. As the value for hexane is higher than that for water, the aggregation of MPs will be more prominent in the organic phase than in water.

After confirming the presence of van der Waals interactions in the organic phase, the change in the global DLVO interaction (the sum of the electrostatic double layer and the van der Waals interactions) in both fluids should be considered. For the MPs found in the organic phase, it can be assumed that their surface functional groups cannot completely dissociate and, therefore, the contribution of the electrostatic double layer is negligible ($U_{EDL} \sim 0$), while the van der Waals forces are still present because of the intrinsic properties of the MPs as well as their chemical composition ($U_{vdW} \neq 0$). Therefore, the MPs in the organic phase tend to aggregate rather than disperse due to the presence of the

van der Waals interactions and the lack of electrostatic interactions between the surfaces of the MPs and the oil.

In addition to van der Waals interactions, hydrogen bond interactions should be considered. In the particular case of a superhydrophobic surface obtained using PDSM to decrease the surface free energy of the material, in addition to the previously described colloid properties (transport, wetting, electrostatic and van der Waals interactions), the presence of hydrogen bond interactions could also play a role in the removal of the pollutants. In fact, we propose that the interaction between the hydrogen atom of the HDPE molecule and the oxygen atom of the PDMS forms these hydrogen bond interactions. This phenomenon may improve the separation of MPs containing hydrogen atoms when using a superhydrophobic material containing oxygen atoms or even electronegative atoms that can generate hydrogen bonds between the solid pollutants and the material.

5. Conclusions and future perspectives

Herein, we show that, after modifying the cotton fabrics surface with PDMS, it showed superhydrophobicity (WCA = $159 \pm 1^\circ$) and superoleophilicity (OCA = 0°). Additionally, the wetting properties of microplastics were measured, which showed hydrophobicity ($140 \pm 1^\circ$ for HDPE and $141 \pm 4^\circ$ for PP) and superoleophilicity in both types of microplastics (0°). Then, the ability of the superhydrophobic cotton fabrics to remove microplastics (HDPE and PP) was evaluated where the solid pollutants migrated from the aqueous phase to the organic phase (hexane). Moreover, the microplastics concentration decreased after each removal step leading to a removal efficiency after three steps of 99%. Furthermore, the removal behavior was explained by DLVO theory, the binding energy (ΔE) of the microplastics in water and oil as well as by the Hamaker constant. Combining these three theories, allowed us to show that due to the higher affinity of microplastics for the hexane (OCA = 0°), the solid pollutants aggregate better in oil than in the aqueous phase where microplastics tend to disperse. Superhydrophobic/superoleophilic surfaces produced as coatings, powdered materials or meshes or as we have reproduced here as a cotton fabric, these surfaces can easily remove microplastics from water. The behavior and properties of MPs during the removal process can be explained by considering the solid pollutants as colloids. The transport of microplastics to the interface, the wetting properties of the solid pollutants as well as their interactions at the interface are the driving forces that allow their separation. By establishing a relationship between the theoretical concepts of considering MPs as colloids and the results of the experimental removal methods and by adapting the equations used for the presence of MPs in water, the behavior of MPs in oil and their migration from water to the organic phase can be explained. Once superhydrophobic materials had been shown to remove solid pollutants like MPs, their performance was compared to that of current technologies. The removal of MPs with superhydrophobic materials avoids the breakdown [89,90] of MPs and allows for them to be collected easily and quickly. Additionally, as the surfaces present low adhesion, the solid pollutants remaining on the surface can be removed through the self-cleaning properties of the superhydrophobic materials, which prevent (bio)fouling. Moreover, the reported removal efficiencies are extremely high (>99%) when compared to more traditional methods such as the use of effluents (73%) [91] and coagulation (85%) [92], being comparable to those of highly efficient systems such as membrane bioreactors (99%) [93]. Despite the fact that the use of superhydrophobic materials show high efficiencies, the capacity to be used in large-scale waste-water treatment plans is still a challenge because some issues have to be addressed such as a balance between the cost and their performance, avoid any negative impact on the environment and consequently use sustainable materials as well as comply with regulatory standards and requirements. Regarding the removal efficiency of microplastics, future studies should consider controlling the relationship between the surface morphology and the surface free energy to enhance the removal efficiency. In fact, by

manipulating the surface morphology, the Cassie-Baxter could be optimized and create surfaces with enhanced superhydrophobic properties. In case of controlling the surface free energy, the adhesion forces between the surface and the microplastics may be adjusted and then enhancing the removal efficiency. After demonstrating these innovative applications of superhydrophobic materials, other issues associated with MPs should be considered in future studies. To fully explain the removal of microplastics and consider these persistent solid pollutants as colloids, future studies should take into account various parameters that could affect the removal efficiency, such as the radius of the MPs (R_p) or the surface free energy of the air–oil interface (γ_{ao}) described in the binding energy equation (Eq. (11)), the electrostatic interaction between particles from the DLVO equation (Eq. (9)) as well as the van der Waals interactions described by the Hamaker constant (Eq. (12)). In wastewater treatments, industrial events or even in the environment, MPs can undergo changes in their morphology and size due to the presence of abrasive materials like sand or erosion. These factors lead to the formation of NPs, which are within a size ranging from 1 to 1000 nm [94]. The interactions between nanoparticulate microplastics and their surroundings remain unclear, and the potential problems they may cause are also unknown [95]. These characteristics should be carefully studied when using superhydrophobic materials and it should be determined if the wetting and colloidal properties are still the driving forces in their removal. Although polyethylene and polypropylene are the most commonly found types of microplastics in water [96,97], it is important to consider other types such as polystyrene or copolymers in future research. Investigating the wetting properties of these microplastics and determining their ability to be removed with superhydrophobic materials, which have previously exhibited efficiencies of 99%, would be valuable. Furthermore, the studies published to date have used untreated MPs. However, in natural waters and wastewater treatment plants, the situation is much more complex, as MPs usually have a very thin layer at the surface that is composed of substances derived from microorganisms such as biomolecules and natural organic matter, the so-called eco-corona. In fact, the modified surface affects the colloidal interactions of the solid pollutants and different methods have been used to study and model the eco-corona [98,99] or reproduce a protein corona on PS-MPs [100]. It is not yet known how this layer could interfere with the removal of MPs and should be considered in future research by using microplastics from natural waters or mimicking the eco-corona with methods such as ultraviolet C lamps [101] or sonication in alkali media [11]. Ultimately, a new research field on superhydrophobic materials has been shown and could be used to keep studying not only the removal of MPs, but also other environmental applications that will be useful in the near future such as oil/water separation, desalination, removal of heavy-metals, dyes elimination among others [102–104].

CRedit authorship contribution statement

O. Rius-Ayra: Investigation, Conceptualization, Visualization, Methodology, Data curation, Writing – original draft. **M. Carmona-Ruiz:** Investigation, Conceptualization, Visualization, Methodology, Data curation, Writing – original draft. **N. Llorca-Isern:** Resources, Supervision, Validation, Writing – review & editing.

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 will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2023.05.127>.

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