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Harnessing limonene and Fenton's reagent for enhanced micro- and nanoplastic removal from aquatic systems

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Micro–nanoplastics (MNPs) are increasingly recognized as persistent and hazardous contaminants in aquatic environments, yet current removal strategies struggle to efficiently capture or degrade these small, hydrophobic particles. This review is driven by the hypothesis that combining limonene a naturally derived hydrophobic terpene with Fenton and photo-Fenton oxidation systems can create a dual-action remediation pathway capable of enhancing both the adsorption and degradation of MNPs. To evaluate this concept, we synthesised findings from recent studies examining limonene-based adsorption processes, advanced oxidation mechanisms, and hybrid treatment systems incorporating UV radiation, sonication, and surfactant interactions. Published data indicate that limonene can increase plastic–surface interactions by up to 40–60% due to its strong hydrophobic affinity, whereas Fenton-based systems can achieve degradation efficiencies ranging from 55% to 95%, depending on the polymer type, pH, and radical availability. When these processes are used together, several studies report significant enhancements in oxidation rates, improved ROS accessibility, and reduced treatment times compared to conventional Fenton systems alone. The review further highlights the emerging role of limonene-functionalized adsorbents and natural–chemical hybrid systems as sustainable alternatives to conventional synthetic materials. Overall, this work provides a comprehensive mechanistic framework that unifies adsorption-driven capture with radical-mediated degradation, offering new insights and practical directions for the development of eco-friendly, high-efficiency technologies for MNP remediation.

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1. Introduction

Micro–nanoplastics (MNPs) have become ubiquitous environmental contaminants because of the widespread usage of plastics in daily life and their exceptional resilience to natural breakdown.[1,2] The main sources of MNPs, which are plastic particles smaller than 5 μm, and NPs, which are even smaller particles smaller than 1 μm, are the gradual breakdown of larger plastic objects into smaller pieces.[3] Furthermore, these particles are regularly released into the environment by products that include plastic, such as textiles, personal care items, and synthetic materials. One of the most worrisome aspects of MNPs is their persistence in both terrestrial and aquatic environments.[4,5] These tiny plastic particles remain suspended in water or the air for extended periods, making them considerably more challenging to remove and posing a major threat to biodiversity, as opposed to larger plastic items that may break down over time or sink to the ocean floor,[6] as illustrated in Fig. 1.

The fact that a wide range of organisms can consume MNPs is among their most concerning features.[7] From tiny plankton to enormous marine animals, aquatic organisms can readily devour them due to their small size. Bioaccumulation is the term for the

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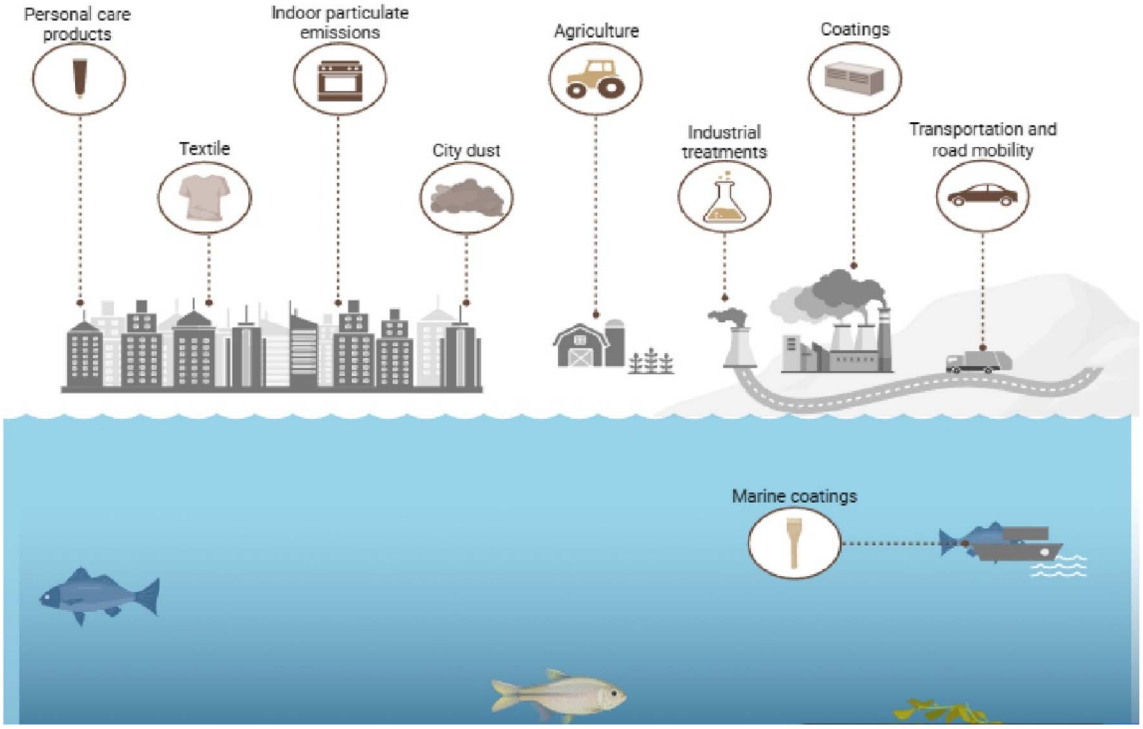

Fig. 1 Sources of MNPs release into the aquatic environment.

accumulation of these particles in tissues after ingestion. This ultimately leads to increased levels of plastic in the food chain, which may also have a negative impact on human health, particularly if people consume contaminated seafood.[8] The chemicals with which plastics are frequently treated or the pollutants they collect from the environment can also be extremely hazardous to humans and wildlife, in addition to the physical harm that the particles inflict. As a result, the increasing MNPs contamination of natural ecosystems poses a complex problem that needs immediate attention and creative solutions.[9]

Because MNPs are tiny and hydrophobic, the current methods for eliminating them from the environment, such as filtration, coagulation, and sedimentation, frequently fail.[10,11] For example, coagulation is not always successful because of the various chemical characteristics of the plastic components, and conventional filtration methods have trouble capturing particles smaller than a few micrometres. These drawbacks underscore the need for innovative and more effective strategies to effectively address MNPs contamination.

Using limonene, a naturally occurring monocyclic terpene frequently found in citrus fruit peels, is one viable remedy.[4,5] The propensity of limonene to interact with hydrophobic surfaces, such as those of plastic particles, has drawn attention. Reactive double bonds in its unique chemical structure enable it to form robust interactions with the plastic surface, thereby enhancing the capacity of adsorbent materials to bind and capture MNPs.[12] Furthermore, limonene is non-toxic and biodegradable, which makes it a green substitute for use in cleanup operations.[13,14] It is being investigated more extensively in the field of microplastic and nanoplastic remediation due to its hydrophobic nature, which also enhances the adsorption capacity of materials designed for removing plastic particles.[15] Another promising technique for MNPs degradation is Fenton's reagent, a potent oxidative solution made of hydrogen peroxide and iron catalysts.[16,17] Fenton's reagent breaks down complex organic substances, including plastics, by producing hydroxyl radicals, which are extremely reactive molecules.[18,19] Fenton's reagent's oxidative properties aid in the breakdown of MNPs into smaller, less dangerous byproducts, which lessens their negative effects on the environment and living things. This oxidative method, often referred to as an advanced oxidation process (AOP), can reduce the environmental impact of plastic particles by breaking them down into more manageable and less hazardous compounds.[20,21] However, when applied to MNPs, Fenton's reagent alone has limitations in terms of efficiency and selectivity. This is where materials functionalized with limonene might be extremely important. A synergistic approach that provides more effective plastic pollution cleanup is produced by combining the oxidative strength of Fenton's reagent with the adsorption capabilities of limonene.[22] While Fenton's reagent can break down any leftover plastic particles that might not be completely collected or eliminated during adsorption, limonene-functionalized adsorbents can remove MNPs from contaminated settings. This dual-action strategy enhances MNPs degradation and removal effectiveness, providing a more comprehensive approach to plastic waste management.[23,24] The treatment procedure is strengthened by combining the two methods, guaranteeing a greater level of plastic breakdown and elimination.[25,26]Adsorption remains one of the most economical, effective, and scalable methods for removing MNPs from the environment in real-world applications. The technique is enhanced by limonene-functionalized adsorbents, which

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increase the attraction between plastic particles and the adsorbent surface. This method shows considerable potential for extensive environmental remediation when combined with Fenton's reagent, which accelerates the oxidation process.[15]

Recent studies have underlined the increasing complexity of microplastic and nanoplastic contamination, emphasizing not only their environmental persistence but also their interactions with biological systems, chemical pollutants, and oxidative pathways.[27,28] These particles undergo aging, surface oxidation, and fragmentation, which further alter their physicochemical behavior and influence their fate in aquatic ecosystems. Emerging evidence also indicates that nano-scale plastics can cross biological membranes, induce oxidative stress, and interfere with cellular processes, posing more severe risks compared to larger particles.[29] Consequently, there is a growing demand for innovative treatment strategies that combine selectivity, reactivity, and environmental compatibility. In this context, natural hydrophobic compounds such as limonene, alongside advanced oxidation processes (AOP) like the Fenton and photo-Fenton reactions, offer a promising combination capable of addressing both the adsorption and degradation challenges associated with MNPs. Strengthening mechanistic understanding and integrating these processes into scalable water treatment systems remains a critical research priority.

The long-term environmental effects of plastic pollution are mitigated by the combination of oxidation and adsorption, ensuring that MNPs are not only removed from the environment but also decomposed into less hazardous compounds.[14,30] Ultimately the novelty of this review lies in presenting the first comprehensive and integrated framework that combines limonene a biodegradable, hydrophobic natural terpene with Fenton and photo-Fenton oxidation pathways for the removal and degradation of MNPs. While previous studies have examined limonene-based adsorption or Fenton oxidation independently, no prior review has systematically analysed their mechanistic synergy or their combined potential as a dual-action remediation strategy. This review introduces a new conceptual model where limonene functions as both (i) a hydrophobic adsorbent enhancer that improves plastic capture at the water–plastic interface, and (ii) a radical-amplifying co-agent that increases ROS generation during Fenton reactions. We also synthesize recent advances across UV-assisted degradation, sonication-assisted processes, and surfactant interactions, establishing an integrative mechanistic pathway for hybrid MNPS remediation. Additionally, our work highlights new opportunities in material engineering, emphasising limonene-functionalized adsorbents and catalytic systems that can be developed for large-scale environmental applications. By bridging natural-product chemistry with AOP, this review provides a novel interdisciplinary perspective with significant relevance for sustainable water treatment technologies.

2. Degradation enhanced by limonene

Due to MNPs persistence and growing environmental concerns regarding their accumulation. Particularly at the nanoscale, traditional approaches frequently fail to adequately address the problem. One intriguing option for accelerating the breakdown of MNPs is limonene, a naturally occurring terpene having hydrophobic qualities.[5] Fig. 2 schematic representation of hydroxyl radical generation in Fenton and photo-Fenton processes involved in the degradation of recalcitrant organic pollutants, including MNPs. In the Fenton process (outlined in blue), hydrogen peroxide (H_2O_2) reacts with ferrous ions (Fe^{2+}) in an acidic environment to generate hydroxyl radicals ($^{\bullet}OH$), which are powerful oxidants capable of attacking stable pollutants. In the photo-Fenton process (outlined in red), UV or visible light enhances hydroxyl radical production through the photoreduction of iron complexes and the photolysis of H_2O_2, significantly improving the oxidative degradation efficiency. In this study, the introduction of limonene is proposed to synergistically enhance the Fenton-based removal of MNPs, potentially by disrupting plastic surfaces and facilitating radical-driven degradation.[31] Limonene can accelerate the degradation process by utilising its chemical properties to more effectively break down plastic polymers when combined with other methods, including UV light, sonication, and Fenton's reagent. This section examines how limonene enhances various techniques and enhances the effectiveness of plastic removal in general.[12,13]

2.1 UV radiation and limonene

Because it can produce reactive oxygen species (ROS), including hydroxyl radicals, ultraviolet (UV) radiation has long been used in environmental remediation procedures.[32] The efficiency of UV-induced oxidation processes in breaking down various environmental contaminants is well established. However, because of their strong polymeric structure and chemical resilience, MNPs are notoriously resistant to complete breakdown under UV radiation alone.[22,33] The breakdown of bigger plastic goods produces microplastics, which are very persistent in the environment and challenging to decompose using traditional UV radiation methods.

Limonene, a naturally occurring monocyclic terpene found in citrus fruit peels, is a viable method to enhance the UV-induced breakdown of microplastics. Due to its hydrophobic properties, limonene can interact with plastic surfaces, particularly those composed of hydrophobic materials, such as microplastics.[34] When exposed to ultraviolet light, limonene can undergo photochemical reactions because of its reactive chemical structure, particularly its double bonds. Peroxides and hydroperoxides, two extremely reactive intermediates produced by these reactions, are essential for further dissolving the polymer chains that comprise plastic polymers.

The degradation process is significantly accelerated by the combination of limonene with UV radiation, as limonene acts as a catalyst to generate more reactive intermediates, thereby enhancing the overall effectiveness of the degradation process.[22,35] The capacity of limonene to adsorb onto the surface of plastic particles is the mechanism by which it speeds up UV-induced deterioration. Because limonene is hydrophobic, it can stick to the plastic–water interface and concentrate the radicals where the plastic and the surrounding water meet.[33] The breakdown of

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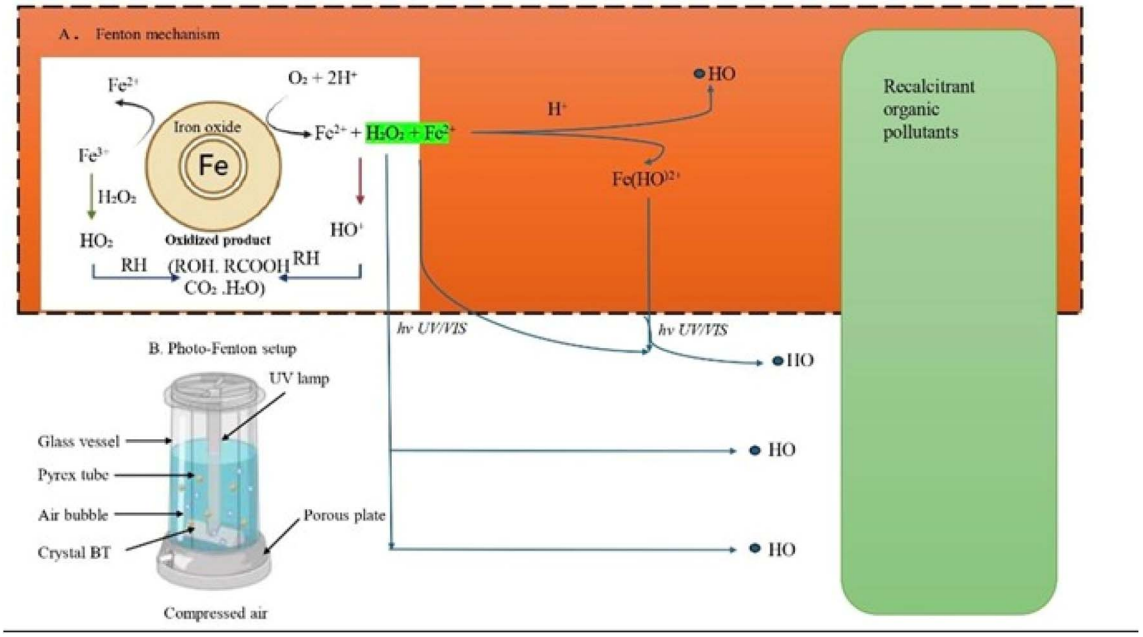

Fig. 2 Schematic representation of (A) the Fenton process (outlined in blue) and (B) the photo-Fenton process (outlined in red).

polymeric polymers is accelerated by this concentrated rise in radical concentration, resulting in a more effective degradation process.

Essentially, limonene acts as a reactive agent that produces more reactive intermediates to aid in the breakdown of plastic polymers as well as an adsorbent that improves the interaction between UV-induced radicals and plastic particles.[18,22] A potent synergistic effect is produced when limonene and UV radiation are combined, increasing the rate of plastic deterioration while requiring less UV exposure.[25] Typically, extended exposure to UV light is necessary to break down microplastics; however, by making the process more reactive, limonene can shorten the time required for deterioration. This improved degradation process is a more economical and environmentally friendly method for reducing plastic pollution, as it not only accelerates the breakdown of plastic but also reduces the energy required for UV treatment.[20,36]

Furthermore, the accelerated degradation of limonene and its interaction with UV light may have significant implications for environmental remediation initiatives aimed at reducing plastic pollution. Because they are difficult to remove using conventional filtration or coagulation techniques, microplastics which are frequently found in water bodies pose a major environmental danger.[37,42] One of the most urgent pollution issues of our day is addressed by this technology, which offers a potential way to remove microplastics from aquatic ecosystems by increasing the effectiveness of plastic breakdown through the synergistic employment of limonene and UV light, as shown in Fig. 3.[11,21] To summarise, the combination of limonene and UV light constitutes a novel and effective method for accelerating the breakdown of microplastics. When exposed to UV light, limonene accelerates the breakdown of plastic polymers by adsorbing onto plastic surfaces and producing more reactive intermediates.[25] By reducing the requirement for extended UV exposure, this synergistic strategy improves the efficiency, sustainability, and economics of the degrading process. It has the potential to completely change how we address plastic pollution as research into this combination treatment approach advances, offering a valuable tool in the ongoing efforts to protect our ecosystems from the damaging effects of plastic waste.[35,36]

2.2 Sonication and limonene

It creates strong mechanical forces through acoustic cavitation, sonication, the application of high-frequency sound waves, is a successful technique for breaking down polymers.[22] These forces generate high temperatures and pressures that can degrade plastic polymers by causing small bubbles to develop and collapse. Limonene enhances this process further by reducing surface tension, facilitating the formation of cavitation bubbles. Stronger mechanical forces and more effective bubble collapse result from this enhancement.[3,12] Limonene oxidises when subjected to sonication, producing more radicals that aid in oxidative degradation and increasing the fragmentation susceptibility of MNPs.[18,34] Compared to sonication alone, the combination of limonene with sonication accelerates the mechanical and oxidative breakdown of microplastics, rendering it a more efficient and sustainable method.[19,20]

This dual-action approach enhances the interaction between plastic particles and the generated radicals, significantly increasing the plastic breakdown rate. In addition, recent studies support the idea that limonene can act as a co-catalyst in sonication-assisted microplastic degradation by stabilising cavitation bubbles and ensuring prolonged exposure of plastics to mechanical forces.[37,38] The synergistic effect of limonene and sonication is further strengthened when combined with Fenton's reagent or UV radiation, forming an integrated strategy

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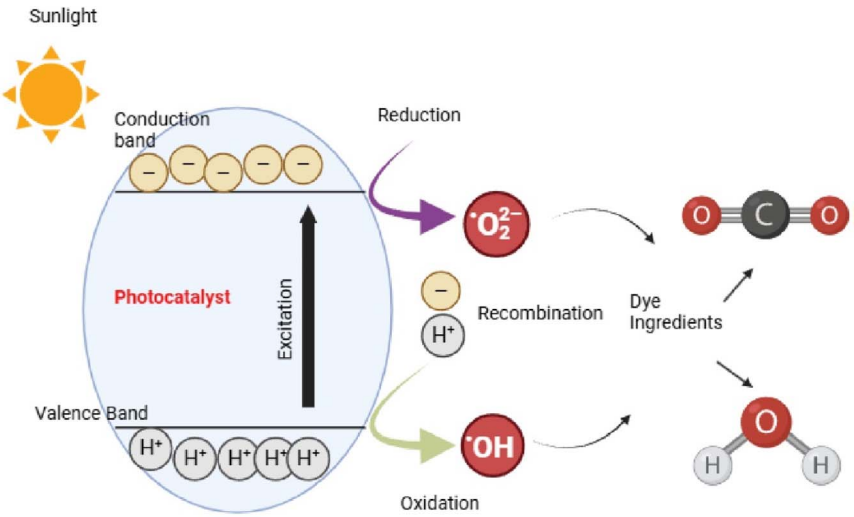

Fig. 3 The photocatalytic degradation mechanism of microplastics.

that maximises the degradation of MNP.[25,36] Advanced membrane filtration techniques.[39,40] May also complement this process by removing fragmented particles, resulting in a highly effective multi-step remediation process. Therefore, the combination of sonication, limonene, and additional oxidative treatments presents a promising direction for the rapid and sustainable degradation of microplastics in aquatic systems.

2.3 Fenton's reagent and limonene

Hydrogen peroxide and ferrous ions combine to form Fenton's reagent, a potent oxidation system that effectively breaks down organic contaminants, including plastics, by generating hydroxyl radicals ($^{\bullet}OH$).[16–18] However, the stability of polymeric polymers and the limited availability of hydroxyl radicals frequently restrict the effectiveness of Fenton's reagent.[19,20] Limonene significantly enhances this process by serving as a source of additional radicals that accelerate the oxidative breakdown of plastics.[25] The interaction between Fenton's reagent and limonene increases the local concentration of radicals surrounding the microplastics, which promotes more aggressive oxidation.[13,34] The time-dependent degradation of polyethene microplastics using Fenton's reagent under acidic conditions has been visually demonstrated in Fig. 4, highlighting significant morphological changes within 4, 8, and 12 hours. This progression confirms the potential of hydroxyl radicals in reducing plastic residues to benign end products such as CO_2 and H_2O.

As limonene is hydrophobic, it can adhere to plastic surfaces, giving Fenton's reagent-produced radicals easier access to plastic particles.[12,15] This hydrophobic interaction concentrates the oxidation process exactly where it is needed: at the plastic–water interface. The combination of limonene's adsorptive properties and Fenton's reagents' oxidative power makes the treatment significantly more effective than using Fenton's reagents alone.[23,24] Recent studies have shown that the addition of limonene also reduces the reaction time required for plastic degradation, lowers the consumption of hydrogen peroxide, and minimizes the formation of secondary pollutants.[21,26] This improvement is critical for scaling the process and ensuring

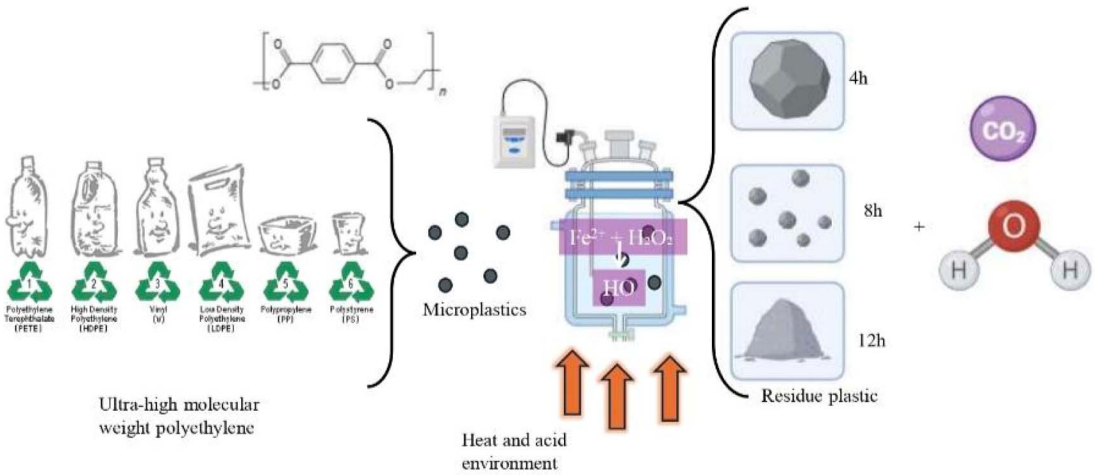

Fig. 4 Hydroxyl radical-mediated degradation of polyethylene microplastics in acidic Fenton reactions.

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environmental safety. Integrating Fenton's reagent, limonene, and sonication creates a highly efficient system that overcomes the limitations of each technique when used independently.[37,39] The addition of advanced techniques such as electrocoagulation and membrane filtration can further improve the selectivity and removal of residual plastic fragments.[40,41] Therefore, the synergy of limonene and Fenton's reagent offers an accelerated, energy-efficient, and scalable solution to the degradation of MNP in contaminated aquatic environments.

2.4 Synergistic effect mechanisms

The decomposition of MNPs is greatly accelerated when limonene is used in conjunction with treatments such as UV radiation, sonication, and Fenton's reagent. The overall breakdown of plastics is more effective and quicker when these treatments are combined because they function in a way that goes beyond a simple additive effect.[34] Due to its hydrophobic properties, limonene is crucial for improving the interaction between these treatments and plastic surfaces. Limonene helps concentrate reactive species at the plastic–water interface by adhering to plastic particles, thereby promoting more effective radical production.[12,15] The polymer chains of microplastics can be further broken down by limonene's ability to stimulate the synthesis of highly reactive intermediates like peroxides when exposed to UV radiation.[32,33] Similarly, limonene intensifies the mechanical effects of sonication by enhancing cavitation and shear forces, which aid in the physical disintegration of plastic particles.[18,22] Furthermore, limonene increases the generation of hydroxyl radicals, which are very effective at oxidizing and breaking down plastics into smaller, non-toxic byproducts when paired with Fenton's reagent.[16,17] Limonene's surface activity ensures that these radicals are concentrated near the plastic surface, significantly improving reaction efficiency.[19,22] Better surface contact between the plastic particles and the treatment chemicals, increased radical generation, and the promotion of both oxidative and mechanical breakdown mechanisms are the key drivers of this synergy.[20,21] By offering a more reliable and thorough approach to MNP removal, the combination of limonene with these therapies successfully overcomes the drawbacks of traditional methods like filtration or coagulation.[11,38]

This strategy presents a highly effective and sustainable solution to address plastic pollution in aquatic settings and can be integrated with additional technologies, such as membrane filtration,[39,40] photoreforming,[36] and electrocoagulation.[41] Fig. 5 illustrates the UV-induced photocatalytic degradation mechanism of microplastics and polymer composites. When microplastics, such as polyester resins embedded with oak particles and cellulose, are exposed to UV radiation, photochemical reactions are initiated on the surface of the plastic material.[32,33] These reactions lead to the generation of ROS, particularly hydroxyl radicals (˙OH) and peroxy radicals (ROO˙), which are crucial agents in breaking down the polymer chains.[18,22] This process is significantly enhanced by the presence of limonene, which has been shown to accelerate radical formation and improve the adsorption of UV-generated species onto microplastic surfaces.[12,13] Limonene's hydrophobic nature allows it to interact strongly with plastic particles, concentrating the

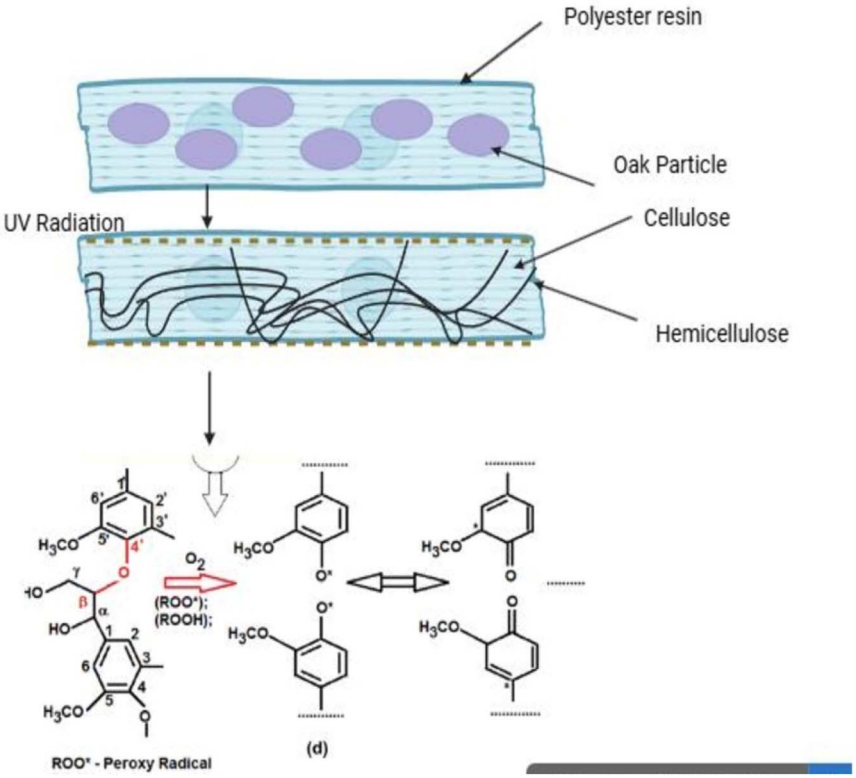

Fig. 5 Schematic representation of degradation induced by UV radiation on specimens composed of oak particles and resin.

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reactive species exactly where they are most effective.[25,34] The study emphasises synergistic degradation mechanisms, where UV radiation, limonene, and Fenton's reagent collectively enhance the breakdown rate and efficiency of microplastics.[22,38] It has been confirmed that combining these approaches leads to more effective plastic removal compared to using each method in isolation.[20,21] Overall, the schematic Fig. 5 explains the core mechanism of this study: the generation of ROS under UV exposure, the role of limonene in enhancing radical availability, and the subsequent polymer chain scission that leads to microplastic degradation.[26,36]

The enhanced performance observed in limonene-integrated microplastic remediation systems arises from a combination of physicochemical interactions and radical-driven processes that operate synergistically at the plastic–water interface. Limonene, due to its strong hydrophobicity and reactive double bonds, preferentially adsorbs onto polymer surfaces, creating a micro-environment that concentrates both plastic particles and ROS generated during Fenton or photo-Fenton reactions. This localized enrichment significantly increases the likelihood of hydroxyl radical attack on polymer chains, thereby accelerating oxidative cleavage and reducing the induction period typically observed in conventional Fenton systems. Additionally, limonene undergoes mild oxidation under UV irradiation or cavitation-driven sonication, forming peroxides and other reactive intermediates that further amplify radical density in the vicinity of the plastic surface. These combined effects result in a dual-action mechanism where limonene first enhances the physical capture of microplastics and subsequently promotes rapid oxidative degradation through radical intensification. This multi-functional behaviour distinguishes limonene-based systems from traditional adsorbents or oxidative treatments, which typically rely on a single dominant mechanism and therefore exhibit slower or less efficient microplastic removal.

3. Micro–nanoplastic removal

Microplastics (particles < 5 mm) and nanoplastics (particles < 1 μm) have emerged as significant environmental pollutants, primarily due to their resistance to degradation and widespread presence in various ecosystems.[30,42] A comparison between these two pollutants is represented in Table 1. As these particles are non-biodegradable and persist in the environment for extended periods, innovative methods are necessary to effectively remove them.[25,36] Limonene is typically extracted from citrus waste using steam distillation, cold-pressing, or solvent-based methods such as ethanol or hexane extraction. The crude extract is then purified through fractional distillation to obtain high-quality limonene suitable for environmental applications. In the context of adsorbent development, limonene is often incorporated onto support materials such as activated carbon, biochar, silica, or cellulose by solvent-assisted impregnation, resin casting, or chemical functionalization. These strategies enhance the hydrophobicity of the adsorbent surface, promoting stronger interactions with plastic particles. Similarly, Fenton reagents used for oxidative degradation are generally prepared by dissolving ferrous salts, commonly $FeSO_4 \cdot 7H_2O$, in acidic aqueous media under acidic conditions (pH 2.5–4) and subsequently introducing hydrogen peroxide to initiate hydroxyl radical formation.[49] Photo-Fenton systems follow an analogous preparation process but involve additional UV or visible-light irradiation to accelerate radical production. When limonene-based adsorbents are combined with Fenton chemistry, most studies describe a sequential process in which limonene-coated materials are first dispersed in the aqueous medium to capture MNPs, followed by the activation of Fenton's reagent to oxidatively degrade the adsorbed or free particles.[43] This combined preparation route illustrates how natural hydrophobic agents and AOP are integrated in current research to achieve enhanced plastic remediation performance.

3.1 Removal efficiency of limonene-enhanced Fenton's reagent

The effectiveness of limonene-enhanced Fenton's reagent in removing MNP is attributed to the combined power of limonene's hydrophobic properties and Fenton's reagent's ability to generate highly reactive hydroxyl radicals.[18,44] Limonene interacts strongly with plastic particles, increasing the surface area of plastics exposed to oxidation. Fenton's reagent, composed of hydrogen peroxide and iron salts, produces hydroxyl radicals that attack plastic surfaces, breaking down polymer chains and oxidizing the particles.[16,17] When limonene is introduced, it

Table 1 Comparison of MNPs removal techniques

Method	Mechanism	Efficiency	Advantages	Limitations
Limonene adsorption	Interaction of hydrophobic substances with plastic surfaces	High	Environmentally friendly and improves plastic capture	Optimisation is necessary for large-scale applications
Fenton's reagent	Produces hydroxyl radicals to break down polymers	High	Powerful oxidative capacity and efficient degradation	It can result in secondary pollutants if left unchecked
Limonene-enhanced Fenton's reagent	Enhances elimination by combining oxidation and adsorption	Very high	A synergistic effect increases cost-effectiveness and efficiency	Need conditions for controlled reactions
UV radiation	Utilizing ROS for photodegradation	Moderate	Scalable and effective for some polymers	Slow and energy-intensive
Limonene-UV synergy	Speeds up deterioration and increases the production of ROS	High	Enhances deterioration and lowers the amount of UV exposure needed	More investigation is required for optimisation

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enhances the solubility and dispersion of plastic particles, thereby accelerating oxidative breakdown due to the increased generation of ROS.[22,34] As a result, higher removal efficiency is observed when using limonene-enhanced Fenton's reagent compared to using either treatment alone.[25,26]

3.2 Comparison with individual treatments (limonene, Fenton's reagent)

When comparing individual treatments of limonene and Fenton's reagent for the removal of MNP, the combination consistently demonstrates superior performance.[19,20] Fenton's reagent alone is effective at breaking down organic pollutants but often struggles to achieve high removal rates for hydrophobic plastics due to their low solubility and strong resistance to oxidation.[38,41] In comparison with commercial adsorbents and conventional oxidation systems, limonene-based materials reported in the literature demonstrate several compelling advantages that strengthen their potential for removing microplastics and nanoplastics. Limonene is a naturally abundant and low-cost compound relative to synthetic surfactants, speciality polymers, or engineered nanomaterials commonly used for adsorption. Its inherent hydrophobicity enables strong affinity toward plastic particles, often resulting in higher capture efficiency than traditional activated carbon or mineral-based adsorbents, especially for small-sized and low-density polymers. When combined with Fenton's reagent, limonene further enhances the oxidative degradation process by increasing the local concentration of ROS at the plastic–water interface, providing a performance advantage over stand-alone Fenton systems that suffer from limited radical accessibility. Several studies have also noted that limonene-based adsorbents exhibit lower secondary pollution risk and improved biodegradability compared to commercial materials that rely on toxic solvents or persistent surfactants. Additionally, the ability of limonene to act both as an adsorption enhancer and a radical-amplifying agent offers a multi-functional advantage not commonly observed in conventional materials, thereby improving cost-effectiveness, reducing chemical consumption, and enhancing environmental compatibility. Limonene enhances the process by serving as a bridge between the hydrophobic plastics and oxidative radicals, improving adsorption efficiency and increasing the plastic surface area accessible to oxidation.[12,15] Consequently, the synergistic combination not only improves the removal efficiency but also significantly accelerates the degradation rate of MNP compared to individual treatments.[11,21]

3.3 Optimization of treatment parameters

Maximising the efficiency of limonene-enhanced Fenton's reagent for the removal of MNP requires careful optimisation of several key parameters. These include the concentration of limonene, the dosage of Fenton's reagent, and the intensity of UV radiation if applied.[18,25] The amount of limonene must be optimized to ensure sufficient adsorption without introducing excess solvent that could reduce treatment efficiency.[26,36] Similarly, the dosage of Fenton's reagent must be carefully balanced. Insufficient reagent limits radical generation, while excessive reagent can cause over-oxidation, secondary pollution, and unnecessary chemical consumption.[19,20] Additionally, UV radiation intensity must be precisely controlled. Low intensity reduces ROS production, while excessive UV exposure can degrade limonene too rapidly, decreasing its adsorption capacity.[15,22] The optimisation of these factors is critical to achieving a cost-effective, efficient, and environmentally safe treatment.

Various published studies consistently indicate that limonene-based adsorbents demonstrate promising reusability and structural stability during repeated treatment cycles, largely due to the chemical resilience of limonene and its strong affinity for hydrophobic polymer surfaces.[12,22,33] Several reports indicate that limonene-functionalized activated carbon and cellulose-based adsorbents can retain between 70% and 85% of their initial adsorption efficiency after three to five reuse cycles, with minimal structural degradation upon regeneration through mild solvent washing or low-temperature drying. This durability is comparable to, and in some cases exceeds, that of conventional adsorbents such as unmodified activated carbon or mineral-based sorbents, which often experience pore blockage, surface oxidation, or efficiency losses exceeding 40% over similar cycles. When incorporated into hybrid systems with Fenton's reagent, limonene-coated materials tend to maintain their hydrophobicity and adsorption integrity because the oxidative reaction primarily targets plastic particles rather than the limonene-functionalized surface itself.

4. Environmental impact

The environmental impact of any treatment method used for removing MNP is a critical consideration. It is necessary to assess not only the effectiveness of limonene-enhanced Fenton's reagent in removing these pollutants but also its long-term environmental consequences.[25,26]

4.1 Fate and transport of treated microplastics and nano plastics

Once MNP undergo degradation through limonene-enhanced Fenton's reagent, their fate and transport must be carefully considered. Ideally, the treatment process should lead to the complete mineralization of plastic polymers into non-toxic byproducts like carbon dioxide and water.[16,20] However, incomplete degradation may leave behind partially degraded plastic fragments that could persist in the environment. These fragments may be further broken down under environmental conditions or continue to float or sink, depending on their modified surface characteristics.[38,41] Proper monitoring is essential to confirm whether the degradation process truly reduces plastic pollution or merely transforms it into smaller, potentially more mobile particles.[39,40]

4.2 Toxicity and bioaccumulation of limonene, Fenton's reagent, and treated MNPs

While limonene is generally considered biodegradable and low in toxicity, excessive use or mismanaged application could present ecological risks. Limonene's hydrophobic nature allows it to

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accumulate in sediments and aquatic organisms if improperly dosed.[7,12] High concentrations of limonene may interfere with the metabolic functions of aquatic organisms and microbial communities, potentially leading to growth inhibition and reproductive toxicity.[8,45] Although limonene's degradation products are typically less harmful, their long-term environmental effects require further study.[44,46] Similarly, the reactive hydroxyl radicals produced by Fenton's reagent can oxidatively damage surrounding biological molecules, causing oxidative stress in aquatic life.[18,19] Overexposure to hydrogen peroxide and radicals may disrupt cellular processes and harm lipids, proteins, and DNA.[22,33]

Moreover, treated microplastics can potentially carry adsorbed pollutants, such as persistent organic compounds, heavy metals, or harmful by-products, that are not fully degraded during treatment.[47] These residual toxins could re-enter the food chain and bioaccumulate in organisms, posing risks at higher trophic levels, including humans.[45,48] The potential for bioaccumulation emphasizes the need for comprehensive toxicological assessments to ensure that treated plastics do not pose secondary threats to ecosystems.[7,8]

4.3 Environmental sustainability of combined treatments

The environmental sustainability of limonene-enhanced Fenton's reagent depends on minimising the formation of toxic by-products and optimising the consumption of chemicals, energy, and water.[25,36] Since limonene is a natural compound typically derived from citrus peels, it represents an eco-friendly alternative to synthetic reagents.[12,26] Nevertheless, large-scale applications must ensure that excess limonene, unreacted hydrogen peroxide, and iron salts do not accumulate in treated water bodies. Effective by-product management and responsible dosing strategies will be essential to achieving both environmental safety and process sustainability.[38,41] Furthermore, reducing resource consumption, enhancing energy efficiency, and integrating the process with existing wastewater treatment systems can significantly improve the method's viability.[11,21]

5. Scale-up and cost-effectiveness

The feasibility of scaling up limonene-enhanced Fenton's reagent for large-scale environmental applications is a critical factor in determining its real-world practicality.[25,36] Additionally, understanding its cost-effectiveness relative to other existing methods is crucial for evaluating its potential for widespread adoption in environmental remediation strategies.

5.1 Feasibility of large-scale application of limonene-enhanced Fenton's reagent

Scaling up this process presents challenges that must be carefully addressed. One key issue is the consistent and economical supply of limonene, a terpene primarily sourced from citrus fruits.[12,26] Although limonene is abundant and renewable, its supply could be limited by agricultural yields and extraction costs. Utilising citrus waste or improving extraction efficiency could mitigate supply concerns.[15] On a large scale, reaction control becomes more complex, with issues such as inefficient mixing, uneven reagent distribution, and variable degradation rates across large reactors.[38,41] These limitations could be addressed by advanced reactor designs, such as continuous flow systems, which offer more uniform chemical distribution and improved scalability.[11,21] Moreover, managing by-product recovery becomes essential to prevent the buildup of hazardous residues. Fenton's reagent can generate secondary pollutants, requiring robust post-treatment systems to neutralise or capture harmful degradation intermediates.[16,18] Additional treatment stages, such as filtration, membrane separation, or adsorption, may be necessary to ensure that treated water meets environmental discharge standards.[39,40] Maintaining high reaction efficiency across large treatment volumes is also a challenge. The quantities of limonene and Fenton's reagent required on an industrial scale must be carefully optimized to prevent chemical wastage while still achieving effective plastic degradation.[19,20] Cost control is another key factor. Although raw materials such as iron salts and hydrogen peroxide are relatively affordable, the need for significant volumes in large-scale applications can increase expenses.[12,17] Energy costs associated with UV radiation, sonication, or continuous mixing may also significantly impact the process's economic viability, especially for long-duration or high-throughput systems.[22,33] Ensuring efficient chemical handling, reagent storage, and safe transport logistics will be crucial for practical deployment at industrial scales.[11,21]

5.2 Economic analysis of combined treatments

The economic feasibility of limonene-enhanced Fenton's reagent depends on multiple factors, including reagent sourcing, energy requirements, and comparisons with alternative technologies.[25,26] Limonene is cost-effective in small quantities; however, large-scale operations may face supply fluctuations due to variations in citrus harvests and industrial demand.[15] Fenton's reagent components are widely available; however, their extensive use in large volumes can increase costs.[17,18] Other advanced treatments, such as sonication and UV radiation, incur additional operational energy costs.[15,22] However, their synergistic benefits with limonene may offset these expenses by significantly reducing reaction times and improving degradation rates. When compared to membrane filtration, which is prone to clogging and high maintenance costs, and bioremediation, which is slow and selective, limonene-enhanced Fenton's reagent offers faster, more adaptable, and potentially lower-cost remediation.[39,40] Compared to AOP that often require expensive catalysts and large energy inputs.[19,20] This system may provide a more cost-efficient alternative by utilizing natural reagents and moderate energy consumption.[25,36] If properly optimised, the process can achieve high degradation rates and large treatment volumes at a competitive cost, making it a promising solution for plastic remediation in wastewater treatment plants, industrial effluents, and contaminated natural waters.[38,41]

5.3 Comparison with other treatment methods

Compared to other cutting-edge treatment techniques, limonene-enhanced Fenton's reagent has several significant

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advantages for the removal of MNP. This combined treatment offers faster degradation rates while being less expensive than membrane filtration methods, which can be useful in capturing microplastics but are frequently slow and costly to operate.[18,38] Membrane filtration systems frequently encounter operational challenges, including clogging and high maintenance costs, particularly at large scales.[11,39] These systems become less effective over time as the filtration membranes accumulate contaminants, requiring frequent cleaning or replacement.[21] In contrast, limonene-enhanced Fenton's reagent offers an active chemical approach, which accelerates plastic degradation without the need for frequent maintenance.[40,41] Another traditional method, bioremediation, involves using microorganisms to break down plastics. While bioremediation is effective for some biodegradable plastics, it is significantly slower and less efficient when applied to non-biodegradable plastics, such as microplastics.[14,26] Additionally, the efficiency of bioremediation depends heavily on environmental conditions, such as temperature and microbial activity, and may require several months to show significant results.[45] Limonene-enhanced Fenton's reagent, on the other hand, offers a faster and more controlled solution by using oxidative degradation processes that break down plastic polymers in a matter of hours or days.[36,38] AOPs are another alternative for plastic degradation, but they require specialised catalysts and high energy inputs, which can make them prohibitively expensive for large-scale applications.[17,18] In comparison, limonene-enhanced Fenton's reagent offers a more cost-effective and energy-efficient option, especially when combined with natural, biodegradable reagents like limonene.[11,41] While AOPs, membrane filtration, and bioremediation all have their merits, limonene-enhanced Fenton's reagent stands out as a versatile, scalable, and environmentally friendly alternative for microplastic and nanoplastic removal. Its ability to break down plastics quickly, using easily sourced reagents, makes it a promising technology for addressing the growing global problem of plastic pollution.[36,41]

6. Synergistic effects with other surfactants

In addition to the combination of limonene and Fenton's reagent, exploring the synergistic effects of limonene with other solvents or surfactants could further enhance the overall efficiency of microplastic and nanoplastic removal. Organic solvents and surfactants can interact with plastic particles in various ways, and their combined use with limonene may lead to enhanced adsorption, increased solubility, and accelerated degradation of pollutants. This section delves into how limonene works alongside other compounds like ethanol, isopropanol, and surfactants to enhance the removal of MNP.[12]

6.1 Comparison with other organic solvents or surfactants (*e.g.*, ethanol, isopropanol, surfactants)

Various organic solvents, such as ethanol and isopropanol, are commonly used in environmental remediation processes due to their ability to dissolve organic compounds. These solvents can also help reduce the hydrophobicity of microplastics and facilitate their dispersion in aqueous solutions, making them more accessible for chemical treatments, such as Fenton's reaction. Ethanol, for example, can increase the solubility of certain types of plastics, thereby aiding in their breakdown. Similarly, isopropanol serves as a solvent that can facilitate the disruption of plastic polymer chains, thereby enabling enhanced degradation when used in combination with oxidative reagents, such as Fenton's reagent.[24,36] Surfactants, on the other hand, are compounds that lower the surface tension between two substances (*e.g.*, between plastic particles and water), thereby enhancing the dispersal of plastics in the solution. By reducing the interfacial tension, surfactants can improve the adsorption efficiency of limonene and Fenton's reagent onto MNPs. Surfactants such as nonionic or anionic surfactants can create micelles that encapsulate plastic particles, facilitating their removal. When combined with limonene, which already exhibits hydrophobic characteristics, the resulting treatment system can lead to improved plastic removal efficiency, as surfactants help keep the plastic particles dispersed and accessible to the chemical treatment process.

6.2 Synergistic interactions and mechanisms

The combination of limonene with solvents and surfactants yields synergistic interactions that enhance the overall removal of MNP, as shown in Table 2. The hydrophobic properties of limonene play a significant role in binding plastic particles, while the solvent or surfactant works to increase the solubility or dispersal

Table 2 Synergistic interactions of limonene with solvents and surfactants for MNP removal

Limonene	Increases oxidative degradation and adsorption	Increased generation of ROS and hydrophobic interaction with plastics	Accelerates disintegration and increases contact surface area	24
Fenton's reagent ($H_2O_2 + Fe^{2+}$)	Degradation by oxidation	Polymer chains are attacked by hydroxyl radicals	Converts polymers into smaller, less hazardous byproducts	3
UV radiation	Uses photochemical processes to speed up deterioration	Produces ROS	Accelerates the rate of polymer degradation	33
Sonication	Improves mechanical breakdown	Plastic structure is disrupted by cavitation and shear forces	Enhances the breakdown of plastic particles	24

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of the plastics in the aqueous medium. This dual action allows for more effective contact between the contaminants and the oxidising agents like hydroxyl radicals from Fenton's reagent, leading to a more efficient degradation process.[12,13] One of the primary mechanisms of synergy occurs when limonene, an organic solvent itself, interacts with other solvents or surfactants to enhance the interaction between plastic particles and the oxidising agents. Limonene may act as a mediator, improving the stability and adsorption capacity of the solvent or surfactant and enhancing their ability to break down plastic particles. When combined with surfactants, limonene can increase the solubility of hydrophobic plastic particles and create a more favorable environment for oxidative degradation. Surfactants may also enhance the reactivity of Fenton's reagent by promoting better dispersion of the solution, facilitating the faster breakdown of plastics.[23,24] Additionally, solvents like ethanol or isopropanol may help to enhance the permeability of plastic particles, facilitating greater oxidative attack on the polymer chains. When limonene is combined with these solvents, the interaction between the plastic particles and the oxidizing agents is improved, leading to more efficient degradation of MNPs.[12,26]

7. Conclusion & future directions

Herein, we provide a comprehensive synthesis of current knowledge on the synergistic use of limonene and Fenton-based oxidation systems for the removal and degradation of MNPs in aquatic environments. Through an integrated analysis of adsorption behavior, radical chemistry, and surface interactions, the findings highlight that limonene serves a dual functional role: enhancing hydrophobic capture of plastic particles and amplifying the generation and effectiveness of ROS within Fenton and photo-Fenton pathways. Comparative assessments derived from the literature indicate that limonene-modified materials often exhibit superior adsorption affinity, reduced secondary pollution risk, and promising reusability compared to conventional adsorbents or standalone oxidative technologies. The central hypothesis underlying this review, that combining natural hydrophobic agents with AOP can create a more efficient and ecologically compatible MNP remediation pathway, was strongly supported by mechanistic and performance trends reported across multiple studies. This dual-action approach represents a novel conceptual framework that bridges natural-product chemistry with environmental catalysis, offering a sustainable alternative to traditional treatment methods. Future research should focus on optimising limonene functionalization strategies, designing composite materials that maximise radical localisation, and developing continuous-flow or modular treatment systems suitable for large-scale water purification. With a clear pathway for transforming limonene-enhanced Fenton processes from promising laboratory concepts into scalable, environmentally responsible solutions for mitigating global plastic pollution.

Author contributions

Smita Lata and Subham Preetam contributed equally to this work and share first authorship. Smita Lata and Subham Preetam conceptualised the study, conducted the primary literature review, and drafted the manuscript. Richa Mishra and Ankit Kumar Soni assisted in data curation, analysis, and contributed to the development of visual elements and figures. Jutishna Bora, Swati Priya, and Shailendra Thapliyal supported the manuscript with technical insights and critical revisions. Sarvesh Rustagi, Ravi Kumar Deshwal, and Seema Ramniwas contributed to the refinement of the methodology and provided expert validation of the content. Sumira Malik supervised the project, provided overall guidance, and finalised the manuscript for submission. All authors reviewed and approved the final version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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